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QUENCHING AND SENSITIZATION PROCESSES OF COORDINATION COMPOUNDS

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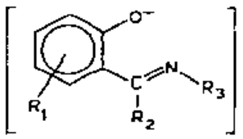
ABBREVIATIONS

AC	2-acetylcyclohexanonate
acac	acetylacetonate
atp	antipyrine
BA	benzoylacetonate
BTC	di-*n*-butyldithiocarbamate
BTFA	benzoyltrifluoroacetonate
CT	charge transfer
CTTL	charge transfer to ligand
CTTM	charge transfer to metal
CTTS	charge transfer to solvent
DBM	dibenzoylmethane anion
DDQ	4,4′-dimethyl-3,3′-dimethylene-2,2′-biquinoline
dipy	2,2′-dipyridyl
DMF	dimethylformamide
dmp	dimethylphenanthroline
DMSO	dimethylsulphoxide
DPM	dipivaloylmethane anion
DPT	1,5-diphenyl-1,3,5-pentanetrione
EDTA	ethylenediaminetetraacetate
en	ethylenediamine
EP	etioporphyrin
fba	1,1,1-trifluoro-5,5-dimethylhexane-2,4-dithionate
gly	glycinate
HDAC	(2,4-hexadienyl)trimethylammonium chloride
HFA	hexafluoroacetylacetonate
imid	imidazolone
isc	intersystem crossing
L-1	2,2′-thio-bis(4-(1,1,3,3-tetramethylbutyl)phenolate)
L-2	*O*-butoxy-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-phosphonate
L-3	butyl-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-phosphonate
MAA	3-methylacetylacetonate
mal	malonate
MC	metal-centred
Me	methyl
MF	methylformamide
MP	mesoporphyrin
p-MVP	*p*-methoxyvalerophenone
NSNa$_2$	2,5-naphthalenedisulphonic acid disodium salt
ox	oxalate
phen	1,10-phenanthroline
pn	propylenediamine
py	pyridine
pyO	pyridine-*N*-oxide
8-quinO	8-oxyquinolinate
sal	salicylate



	R_1	R_2	R_3
S-1	S-1: CH_3 (*para* to oxine group)	CH_3	OH
S-2	S-2: CH_3 (*para* to oxine group)	$C_{11}H_{23}$	OH
S-3	S-3: CH_3 (*para* to oxine group)	CH_3	C_4H_9O
S-4	S-4: CH_3 (*para* to oxine group)	$C_{11}H_{23}$	H
S-5	S-5: CH_3 (*para* to oxine group)	CH_3	$(CH_2)_2O$
S-6	S-6: H (*para* to oxine group)	H	t-C_4H_9
S-7	S-7: CH_3O (*para* to OH group)	H	n-C_4H_9
S-8	S-8: t-C_4H_9 (*para* to OH group)	$C_{17}H_{35}$	OH

TAA	dithioacetylacetonate
THF	tetrahydrofuran
THMF	tetrahydromethylfuran
tn	trimethylenediamine
TPP	tetraphenylporphyrin
TTA	thenoyltrifluoroacetonate
UP	uroporphyrin

A. INTRODUCTION

In the last 15 years there has been an extraordinary expansion in the field of photochemistry. The tremendous surge of interest and activity in this area has led to some progress in the knowledge of the *chemistry of the excited states.* This may be considered as a new dimension of chemistry [1], and its systematic exploration is very promising from both theoretical and practical points of view. In the field of organic chemistry it has already been shown that sensitization and quenching techniques constitute a powerful tool for obtaining information on the chemistry of the excited states [2, 3]. These techniques have recently been introduced with success in the field of transition metal complexes which exhibit an extremely varied and very interesting photochemical behaviour upon direct excitation [4]. The dual aim of this review is that of (i) collecting the data so far obtained in the quenching and sensitization processes involving coordination compounds and (ii) emphasizing the great potential utility of these techniques for directing the course of photochemical reactions, for elucidating mechanisms of photochemical reactions, and for obtaining information about the photophysical behaviour of the electronically excited states. A systematic discussion of the kinetic aspects of quenching and sensitization is also given. Because of the authors' interest, emphasis is placed on the complexes of the transition metals and on fluid solution systems, although the most important results concerning rare earth compounds and solid state systems are also reported.

B. RESULTS

This section presents a survey of the most important papers which have appeared up to date. Emphasis has been given to those systems where the photoreaction or emission of a coordination compound is sensitized or quenched (Sects. B(i) to B(iv)). The results obtained with other systems are briefly summarized in Sect. B(v). Finally, Tables 2 and 3 schematically collect all the available results (including those that have not been discussed in Sects. B(i) to (v)) for the systems in which a coordination compound acts as sensitizer or quencher.

(i) Sensitization of coordination compound photoreactions

(a) Chromium(III) complexes

Introduction. One of the crucial points in the recent development of coordination compound photochemistry has been the debate concerning the identity of the excited state(s) responsible for the photoreactions which are obtained by irradiating Cr^{III} complexes in their ligand field bands [4, 5]. The results of direct photolysis experiments [4] showed that the most likely candidates are the lowest spin-forbidden and spin-allowed excited states (^2E and $^4T_{2g}$, respectively, in octahedral symmetry, see Fig. 4, Sect. E(v)). Such experiments, however, did not allow any definite conclusion concerning the actual role played by each one of these two states.

Several groups have tried to solve this problem by means of sensitization or quenching techniques. As far as the sensitization is concerned, however, there is an important limitation to be considered. Since the ground state of these complexes is a quartet, energy transfer from triplet donors to both doublet and quartet excited states is spin-allowed (see Sect. D(ii)(a)). Owing to this loss of selectivity of the spin selection rules, discrimination between the two excited states involved can only be obtained on energy grounds. This, however, is very difficult because in most cases the two states are very close in energy. Quenching experiments have been more successful in this regard (Sect. B(iii)).

$Cr(NH_3)_6^{3+}$. The photoaquation reaction of this complex was sensitized by naphthalene triplets (E_T = 21.3 kK) in 50% water—ethanol solutions at 18°C [6]. The limiting sensitization yield was 0.18 (assuming $\varphi_{isc} = 0.72$ for naphthalene). The Stern—Volmer constant for the sensitized reaction depends on the oxygen concentration and the nature of the counter ion (NO_3^- or ClO_4^-). The possibility of a chemical quenching was discarded since no decrease in naphthalene concentration was observed.

$Cr(NH_3)_5Cl^{2+}$. The main photoaquation reaction of the complex, NH_3 aquation, was found to be sensitized by the lowest naphthalene triplet [6]. A chemical sensitization process was excluded because of the lack of sensitizer consumption. The limiting sensitization yield in 50% water—ethanol at 18°C was 0.35, assuming $\varphi_{isc} = 0.72$ for the donor. Spectrophotometric measurements unambiguously indicated that at least 90% of the product was *cis*-$Cr(NH_3)_4(H_2O)Cl^{2+}$. The lack of sensitized Cl^- production allowed the

authors to claim that the NH_3 to Cl^- ratio in the sensitized photoaquation was not lower than that found for the direct photoaquation (ca. 50:1).

When riboflavin was used as sensitizer [7] the limiting sensitization yield for NH_3 photoaquation (aqueous solution, $pH = 3.2$, 25°C) was 0.18, i.e. lower than that reported above. Since the riboflavin fluorescence was quenched by the complex, an energy transfer process from the lowest excited singlet of the donor ($E_S = 20.0$ kK) to the lowest excited quartet of the complex was suggested to occur. It is to be noted, however, that in some runs detectable decomposition of riboflavin occurred. In order to interpret the low value of the limiting sensitization yield with respect to the quantum yield of the direct reaction (≈ 0.4 [4]), it was assumed that two independent and equally important quenching processes take place, only one of which produces excited quartet $Cr(NH_3)_5Cl^{2+}$. In our terminology (Sect. C(iv)(a)) this means that $\eta_s = 1/2$. Although this hypothesis is not unreasonable it cannot be related, as the author does [7], to the fact that the "sensitization" constant was found to be half the "quenching" constant. In fact, these constants are simply the "overall bimolecular quenching rate constant" of the emitting state obtained from the sensitization and quenching Stern—Volmer plots, respectively (Sects. C(i) and C(iv)). Thus, they *must* be the same whenever only one excited state of the donor is involved. It follows that either the proposed mechanism is wrong, or the results obtained from the sensitization and quenching experiments are not comparable because they refer to different experimental conditions. The same criticisms are valid for the results reported in the same paper for the riboflavin—$Cr(NH_3)_5(NCS)^{2+}$ system (see below). In the riboflavin—$Cr(NH_3)_5Cl^{2+}$ system, sensitization of Cl^- aquation also seems to occur [7]. The quantum yield of this reaction decreased in the presence of O_2, while the sensitized NH_3 photoaquation was not affected by degassing.

$Cr(NH_3)_5(NCS)^{2+}$. Sensitization experiments were carried out on this complex in 0.1 N H_2SO_4, using biacetyl or acridinium ion as sensitizers [8]. With biacetyl ($E_T = 19.6$ kK), sensitization of only the NH_3 aquation (which is the main photoreaction mode upon direct excitation [4]) was observed, concomitant with quenching of donor phosphorescence. The limiting sensitization yield was 0.21, in deoxygenated solutions at 25°C. NH_3 photoaquation was the main sensitized reaction even when acridinium ion was used as a donor. In this case, a concomitant donor fluorescence ($E_S = 21.8$ kK) quenching was observed, and both phenomena were O_2 independent. The limiting sensitization yield was again 0.21 at 25°C. For both donors, experimental evidence ruled out the possibility of a chemical reaction between excited donor and the complex.

Acridinium ion also sensitized the NCS^- photoaquation reaction of $Cr(NH_3)_5(NCS)^{2+}$ [8] in a tenfold to twentyfold smaller yield than NH_3 aquation. This yield decreased when O_2 concentration increased. For a more detailed discussion of the $Cr(NH_3)_5(NCS)^{2+}$ sensitization, see below.

Qualitatively similar results were obtained with the same donors in acidic water—acetone mixtures [9]. Using Michler's ketone as a donor, no sensitization occurs in aqueous solution [8], while some sensitized NH_3 aquation can be observed in water—acetone [9].

In the riboflavin—$Cr(NH_3)_5(NCS)^{2+}$ system (aqueous solution, $pH = 3.2$, 25°C), both donor fluorescence quenching and sensitized NH_3 aquation of the complex occurred, but no NCS^- aquation was found [7, 10]. The limiting quantum yield for the sensitized reaction was 0.24 [7]. A quantitative discussion of the sensitized reaction was also given, but it is subject to the criticisms mentioned before for the riboflavin—$Cr(NH_3)_5Cl^{2+}$ system.

$Cr(en)_3^{3+}$. The biacetyl-sensitized photoaquation reaction of $Cr(en)_3^{3+}$ and the concomitant quenching of donor phosphorescence were investigated in acidic aqueous solution at 15°C [11]. The limiting sensitization yield for the sensitized reaction (0.8) is about twice the quantum yield of direct photolysis. For a comparison with the sensitized emission, see Sect. B(ii)(b). For quenching results, see Sect. B(iii)(b).

$Cr(CN)_6^{3-}$. The sensitized photosolvation reaction of this complex was studied by Sabbatini et al. [12, 13], using eight different donors in H_2O, H_2O—ethanol mixtures or DMF. Naphthalene, pyrazine, xanthone and acridine were able to sensitize the photoreaction of the complex; for the last three donors, the limiting quantum yields were 0.1, 0.003 and 0.01 respectively. O_2 was found to affect the sensitized reaction in the case of pyrazine and xanthone but not in the case of acridine. Naphthalene fluorescence was quenched by $Cr(CN)_6^{3-}$ while those of pyrazine and acridine were not. Michler's ketone, 2-acetonaphthone, $Ru(dipy)_3^{2+}$ and erythrosin did not sensitize the reaction of $Cr(CN)_6^{3-}$, although the $Ru(dipy)_3^{2+}$ phosphorescence was quenched. These results will be discussed in Sect. E(i).

The quenching of the zinc-uroporphyrin triplet by $Cr(CN)_6^{3-}$ (in 0.1 M KCN, at 25°C) has been suggested to occur via an electron transfer from zinc-uroporphyrin [14] (see also Sect. D(iii)).

$Cr(ox)_3^{3-}$. The photoracemization reaction of *d*-$Cr(ox)_3^{3-}$ is sensitized by $Ru(dipy)_3^{2+}$ ($E_T = 17.8$ kK) in aqueous solution [15]. A limiting quantum yield of 0.033 (at 20°C) was calculated from a single quantum yield determination and the Stern—Volmer plot of the $Ru(dipy)_3^{2+}$ phosphorescence quenching. This value is about 1/3 the quantum yield obtained for the direct photoracemization in the region of the spin-allowed metal-centred bands. Three different hypotheses were advanced in order to explain this result [15].

Other complexes. Scattered, qualitative observations concern the photosensitization of $Cr(NH_3)_2(NCS)_4^-$ (NCS^- release) by biacetyl and methylene blue [9], of $Cr(NCS)_6^{3-}$ by biacetyl [9] and of 1,1,1-trifluoro-5,5-dimethylhexane-2,4-dionato-chromium(III) (*cis—trans* isomerization) by methyl-*o*-benzyl-oxyphenylglyoxylate [16].

General remarks. As mentioned in the introduction, the sensitization technique has been applied to the photochemistry of Cr^{III} complexes with the principal aim of contributing to the identification of the reactive excited state of these complexes. Except in the case of $Cr(CN)_6^{3-}$, this goal has not been achieved because it is practically impossible to populate the various excited states of these complexes in a selective way (see also Sect. E(i)).

The sensitized photoreactions of Cr^{III} complexes are always the same as those which occur upon direct irradiation. It has been generally assumed that the sensitization occurs via energy transfer from singlet or triplet excited states of the donor, and in many cases experimental evidence in favour of this hypothesis has been reported. A chemical mechanism, such as for example electron transfer or hydrogen abstraction, seems rather improbable, because of the heterolytic nature of the observed reaction. The limiting sensitization yields are in many cases lower than the quantum yield of the corresponding direct photoreactions. This may be due to the quenching of the donor by the complex without electronic excitation of the latter [7, 8] or with excitation to an electronic state less reactive or lower in energy than the excited state responsible for the direct photoreaction [15].

Another explanation may be that direct excitation and sensitization lead to different vibrational levels of the reactive excited state of the complex [11], so that deactivation and/or reaction efficiency may be different in the two cases.

In the case of mixed ligand complexes, either one or two sensitized photoreactions have been found, depending on the sensitizer used. The different effect of O_2 on the sensitized reactions seems to indicate that two donor excited states are involved, but further experiments are needed for clarifying the sensitization mechanism. Let us consider, for example, the case of $Cr(NH_3)_5(NCS)^{2+}$, which seems to be the best studied. Biacetyl was found to cause only NH_3 aquation, while acridinium ion also caused NCS^- aquation [8]. In this last case, the ϕ_{NH_3} to ϕ_{NCS^-} ratio was 33, whereas this ratio is 22.2 or 8.2 in direct photolysis experiments, depending on whether the irradiation is carried out in the lowest quartet or doublet region [4]. In order to be consistent with the interpretation given for the direct irradiation results (i.e. NH_3 aquation originates from the lowest excited quartet and NCS^- aquation from the lowest excited doublet), it was assumed [8] that triplet biacetyl (E_T = 19.6 kK) was only able to populate the lowest quartet excited state of the complex, whereas, when acridinium ion was used as a donor, both singlet (E_S = 21.8 kK)—quartet and triplet($E_T \sim$ 17 kK)—doublet transfers could take place. No explanation was given for the lack of triplet—doublet transfer when biacetyl was used, although this process is spin as well as energy allowed. The authors [8] have also neglected the effects of the splitting of the lowest-energy "octahedral" quartet state in complexes of lower symmetry, while recent studies [17] have shown that the different photoreactions observed in mixed ligand complexes most probably originate from different quartet excited states.

(b) Cobalt(III) complexes

$Co(NH_3)_6^{3+}$. Several donors sensitize the photoredox decomposition of this complex in various solvents. The lowest singlet excited state of the donor (E_S ~ 31 kK) is involved in the sensitization by naphthalene [18], as is shown by the quenching of the donor fluorescence and the lack of O_2 effects on the sensitization. The limiting sensitization yield is 0.6 in 50% water—ethanol at 25°C. Triplet excited states of the donors seem to be involved in the sensitization by benzophenone (E_T = 24.0 kK; ϕ(lim) ~ 1, in 50% water—ethanol) [19] or biphenyl (E_T = 23.0 kK; ϕ(lim) = 0.63, limiting sensitization yield about 0.82, in 70% water—ethanol at 25°C) [20]. Sensitization by quinoline [21] shows a strong dependence on pH, ethanol concentration (in water—ethanol mixtures) and O_2. This last result seems to indicate that the triplet excited state of the donor (E_T = 22.0 kK) is involved in the sensitization, although some fluorescence quenching was observed at relatively high $Co(NH_3)_6^{3+}$ concentrations in acidic conditions [21]. The pH dependence is probably due to the ground-state equilibrium between quinoline and quinolinium ion. The limiting quantum yield is 0.055 for quinoline and about 20 times lower for its ion: such a difference could be due to either a change in φ_{isc} of the donor or a change in η_s, the limiting sensitization efficiency (Sect. C(iv)(a)).

The first results obtained using biacetyl as sensitizer were contradictory. A sensitized photoredox decomposition and a concomitant quenching of donor phosphorescence were observed by Vogler and Adamson [19] in 50% water—ethanol, while only the donor emission quenching was found by Scandola and Scandola [20] in aqueous acidic solution. A subsequent investigation [18] showed that the quantum yield of the sensitized reaction depended on ethanol, H^+, and complex concentration. This behaviour was explained on the basis of two competing processes: (i) reaction of triplet state biacetyl with ethanol to produce a radical capable of reducing the complex, and (ii) energy transfer from triplet state biacetyl to the complex. A chemical process can also be responsible for part of the sensitized photoreaction which is obtained with benzophenone [19] and naphthalene [18] while experimental evidence in favour of an almost complete energy transfer process was obtained in the case of biphenyl [20] and quinoline [21]. The effect of ethanol on the sensitized reaction, however, was also observed when quinoline was used. It is to be noted that ethanol increases the quantum yield of the direct photoreaction when $Co(NH_3)_6^{3+}$—Cl^- ion pairs are present [18]. The photoderox decomposition of $Co(NH_3)_6^{3+}$ is also sensitized by *trans*-stilbene-4-carboxylic acid [19], but no quantitative results were obtained for this system.

For the sensitization by triplet donors, it was generally assumed that a reactive charge transfer triplet excited state of the complex was populated by energy transfer; such a state should be located about 20 kK above the ground state [21]. When biphenyl (a triplet donor) or naphthalene (a singlet donor) were used as sensitizers, the limiting sensitization yield was higher than the quantum yield of the direct photoreaction upon excitation in the singlet charge transfer bands of the complex (0.16—0.37, depending on the medium [18]). In the former case, the difference may reflect the low efficiency of the intersystem crossing between singlet and triplet charge transfer excited states of the complex (Sects. E(i) and E(ii)). This explanation, however, cannot be applied to naphthalene sensitization. In this case it was suggested that different vibrational levels of the singlet excited state of the complex may have a different deactivation efficiency to non-reactive states [18].

Co(NH$_3$)$_5$X^{n+}. The Ru(dipy)$_3^{2+}$—Co(NH$_3$)$_5$Br^{2+} system has been extensively investigated in the last few years because of a dispute about the nature of the sensitization process. In aqueous solutions of low acidity, the sensitized redox decomposition of the Co complex [22, 24] and the quenching of the Ru(dipy)$_3^{2+}$ phosphorescence [22] were observed. Moreover, Ru(dipy)$_3^{3+}$ was formed in 1 N H_2SO_4 solution [22, 24] (note that this species is not stable in solutions of lower acidity [22]). This last result led Gafney and Adamson [22] to suggest an electron transfer from Ru(dipy)$_3^{2+}$ triplet as the most probable sensitization mechanism. Natarajan and Endicott [23], however, pointed out that a product analysis is not sufficient to establish a mechanistic hypothesis in this system. By means of flash photolysis and scavenger techniques [23, 24] they were able to show that (i) radicals are produced in the sensitized redox decomposition of Co(NH$_3$)$_5$Br^{2+}, (ii) the primary radicals oxidize Ru(dipy)$_3^{2+}$ at a nearly diffusion controlled rate and (iii) the production of Co^{2+} is increased and that of Ru(dipy)$_3^{3+}$ decreased when radical scavengers are present. On the basis of these results, Natarajan and Endicott [23, 24] concluded that the dominant reaction mode is an energy transfer from the lowest Ru(dipy)$_3^{2+}$ triplet (E_T = 17.8 kK)*.

Sensitization studies have also been carried out on Co(NH$_3$)$_5$(NO$_2$)$^{2+}$ [26]. Using acetone, benzaldehyde or biphenyl as sensitizers, both the redox decomposition and the linkage isomerization were observed, the two processes occurring in essentially the same ratio as in the direct photolysis [27]. The limiting quantum yields for Co^{2+} production were close to the quantum yields obtained by direct excitation with radiations corresponding to the triplet energy of the sensitizers used (E_T = 27.6, 25.2 and 23.0 kK, for acetone, benzaldehyde and biphenyl, respectively). From a comparison of these results with those obtained by direct excitation, it was suggested that the sensitizers transfer energy to a reactive triplet charge transfer excited state of the complex, and that this state has a dissociative potential energy surface, like the corresponding singlet excited state. The vertical energy separation between these two states is estimated to be only 3 kK. When biacetyl was used as sensitizer, efficient quenching of donor triplets but no reaction of the complex was observed. An energy transfer to an unreactive triplet ligand field excited state of the complex was postulated [26].

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* A recent investigation has shown, however, that electron transfer is important for quenching by Co(NH$_3$)$_5$X^{n+} complexes [25] (see Sects. B(iv)(b) and D(iii)(d)).

The redox decomposition of $Co(NH_3)_5Cl^{2+}$ is sensitized by $Ru(dipy)_3^{2+}$ [22]. $Co(NH_3)_5(H_2O)^{3+}$ and $Co(NH_3)_5(OCHO)^{2+}$ undergo a redox photodecomposition when sensitized by benzophenone in DMSO, probably through H abstraction by the excited triplet donor [28]. The photoreaction of the former complex is also sensitized by benzil and *trans*-stilbene-4-carboxylic acid (in 80% ethanol—water), and by benzophenone in dimethylacetamide [19].

EDTA complexes. Natarajan and Endicott have thoroughly investigated the $Ru(dipy)_3^{2+}$-sensitized redox decomposition of $Co(EDTA)^-$ [29, 30] and $Co(HEDTA)X^-$ (X = Cl, Br, NO_2) [29, 31]. Particular care was paid to establish the identities and stoichiometries of the products using flash photolysis and scavenger techniques [24]. The results obtained suggested that the sensitized redox decomposition is due to triplet—triplet energy transfer, and that there is no evidence for the electron transfer process which had previously been proposed by Gafney and Adamson [22] for $Co(HEDTA)Cl^-$. The limiting sensitization yields were found to be higher than the quantum yields obtained upon direct excitation in the spin-allowed CTTM bands, except for $Co(HEDTA)Cl^-$ [29, 31]. For the $Co(HEDTA)X^-$ complexes, sensitized X^- aquation (and/or linkage isomerization for $X = NO_2$) was also obtained [29, 31], as happens upon direct excitation. It was suggested that a triplet CTTM excited state is responsible for the sensitized redox decomposition, and a triplet ligand field excited state for the other sensitized reaction. Both these excited states are assumed to be reached by energy transfer from $Ru(dipy)_3^{2+}$ triplets (E_T = 17.8 kK). The efficiency of the radiationless transitions between the various excited states of the Co complexes was also discussed [30, 31].

Cyanide complexes. The photoaquation reaction of $Co(CN)_6^{3-}$ is sensitized by biacetyl (E_T = 19.6 kK), whose phosphorescence is quenched in parallel [32,34]. Triplet—triplet energy transfer is the most likely mechanism for this photoreaction. A competition between the complex and its aquation product, $Co(CN)_5(H_2O)^{2-}$, for the triplet excited state of biacetyl was observed [34], the latter complex being a more efficient quencher (k_q = 3.7×10^8 M^{-1} s^{-1} in H_2O) than $Co(CN)_6^{3-}$ ($k_q = 6.5 \times 10^5$ M^{-1} s^{-1}). A limiting quantum yield of 0.8 was obtained for the sensitized reaction. The lower value (0.23) previously reported by Porter [32] is most probably due to the failure of the last author to appreciate the competitive quenching by $Co(CN)_5(H_2O)^{2-}$, which led the author to overestimate the extent of energy transfer to the $Co(CN)_6^{3-}$ ion. The quantum yield for the direct photoreaction upon excitation into the singlet ligand field bands of the complex is 0.31 [4], i.e. much lower than the limiting sensitization yield. This indicates that the singlet—triplet intersystem crossing efficiency of $Co(CN)_6^{3-}$ is about 0.4 [34].

The photoreaction of $Co(CN)_6^{3-}$ can also be sensitized by uranyl ion in 1 M aqueous phosphoric acid [35]. Since the UO_2^{2+} phosphorescence was simultaneously quenched, a triplet—triplet energy transfer mechanism was assumed.

It has also been reported that the photoaquation of $Co(CN)_6^{3-}$ can be sensitized by acetone [33].

The quenching of benzohydroquinone fluorescence by $Co(CN)_6^{3-}$ was assumed to occur via an electron transfer mechanism ($k_q = 1.4 \times 10^{10}$ M^{-1} s^{-1}, in H_2O) [36]. This assumption is supported by the fact that the production of the semiquinone upon flash photolysis of benzohydroquinone increases when the complex is present. However, no reduction product of the complex has been observed. The quenching of zinc-uroporphyrin triplet by $Co(CN)_6^{3-}$ also occurs most probably via an electron transfer process [14].

The photoaquation of $Co(CN)_5(NCS)^{3-}$ and $Co(CN)_5(N_3)^{3-}$ is sensitized by biacetyl, with a concomitant quenching of the donor phosphorescence [33]. The limiting sensitization yields in water are practically equal to the quantum yields of the direct photoreactions (0.23 and 0.20, respectively). Thus for both complexes the intersystem crossing efficiency should be practically unity.

$Co(ox)_3^{3-}$. The $Ru(dipy)_3^{2+}$-sensitized photoredox decomposition of $Co(ox)_3^{3-}$ has been recently investigated by Demas and Adamson [15]. The limiting quantum yield for Co^{2+} production, in 0.1 N H_2SO_4 at 20°C, is 0.86, which is to be compared with the quantum yield (0.10) obtained upon direct excitation in the 450 nm region. The bimolecular quenching rate constant for the donor phosphorescence, k_q, is 7×10^9 M^{-1} s^{-1}, and is practically equal to that obtained from the sensitization Stern—Volmer plot. In solutions of high acidity, the reduction of $Co(ox)_3^{3-}$ is accompanied by the formation of $Ru(dipy)_3^{3+}$. The authors report some results indicating that the radical formed in the direct redox decomposition of $Co(ox)_3^{3-}$ does not oxidize $Ru(dipy)_3^{2+}$, but is able to reduce $Ru(dipy)_3^{3+}$. Therefore they suggest that the sensitization of $Co(ox)_3^{3-}$ decomposition by $Ru(dipy)_3^{2+}$ triplet occurs via electron transfer rather than energy transfer.

$Co(phen)_3^{3+}$. The photoredox decomposition of $Co(phen)_3^{3+}$ is sensitized by phenanthroline [37]. Since a concomitant quenching of donor fluorescence was also observed, the sensitization is assumed to occur through a singlet—singlet energy transfer. The limiting quantum yield of the sensitized reaction (aqueous solution at pH = 5.5; 25°C) is 0.10, i.e. much higher than that obtained upon direct excitation in the spin-allowed CTTL band (0.004). It is therefore suggested that the reactive state of the complex (i) is CTTM in nature, (ii) lies below 29.5 kK and (iii) is very inefficiently populated from the CTTL state.

General remarks. The main problem concerning the photosensitized reactions of Co^{III} complexes regards the nature of the sensitization mechanism. The dilemma "energy transfer" or "chemical sensitization" is not completely resolved so far, but it seems that each of the two mechanisms may predominate, depending on the specific Co^{III} complex involved. In any case, the energy transfer mechanism can be confidently accepted for the sensitization of the photosubstitution reactions of Co(HEDTA)X^- and cyanide complexes. Since triplet donors are involved in these processes, spin-forbidden reactive excited states of the complexes have been individualized and their upper limit energy has been established. Since the limiting quantum yields were usually higher than the quantum yields obtained upon direct excitation in the spin-allowed bands, a low efficiency for the intersystem crossing processes between metal-centred excited states of these complexes is indicated.

(c) Other complexes

$Cr(CO)_6$. The lowest excited triplet state of $Cr(CO)_6$, populated by energy transfer from benzophenone triplet (E_T = 24.0 kK), undergoes ligand detachment [38]. In benzene solutions, the limiting quantum yield is equal to unity and the bimolecular quenching rate constant, k_q, is 4.7×10^7 M^{-1} s^{-1}. Since the same quantum yield value was obtained upon direct excitation in the singlet bands [4], the singlet—triplet intersystem crossing process for $Cr(CO)_6$ must have unit efficiency [38].

$Mn(CN)_6^{3-}$. This complex quenches the triplet state of Zn-uroporphyrin in 0.1 M KCN solution, probably via an electron transfer process from the uroporphyrin to the cyanide complex [14].

Iron complexes. The photooxidation of ferrocene in 50% chloroform—ethanol is sensitized by naphthalene [39]. Experimental evidence was given in favour of an energy transfer process from singlet excited donor ($E_S \sim 31$ kK) directly to a singlet CTTS excited state of the ferrocene—halocarbon solvent complex. Unit quantum yields were obtained for both the direct and sensitized reaction, under experimental conditions in which secondary reactions are unimportant. This result suggests that energy transfer from singlet naphthalene to unreactive intramolecular excited states of ferrocene is relatively inefficient, probably because of steric factors [39].

The *cis—trans* isomerization of styrylferrocene can be sensitized by benzophenone, presumably through a triplet—triplet energy transfer process [40].

The photooxidation of Fe^{2+} is induced by light absorbed by riboflavin [10], but this process was not investigated in detail. In the eosine—O_2—Fe^{2+} system, the autooxidation of ferrous ion was suggested to procede via eosine excitation and energy transfer to a singlet excited state of O_2, which then reacts with Fe^{2+} [41] (see also Sect. D(iii)(c)).

Zinc-uroporphyrin triplets are quenched by $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ at about the same rate in water at *p*H 7, although the possibilities for the suggested quenching mechanism (charge transfer) are different in the two cases [14].

Both *cis*- and *trans*-$Fe(CNCH_3)_4(CN)_2$ undergo $CNCH_3$ aquation when irradiated in the singlet charge transfer or ligand field bands [42]. The same reaction with the same quantum yield (0.15 for both isomers, in aqueous solution) can also be obtained by means of biacetyl sensitization [42a]. Since a concomitant quenching of biacetyl phosphorescence is observed (E_T = 19.6 kK), it has been argued that the reactive excited state of the complexes is a triplet ligand field excited state [42a].

The $Ru(dipy)_3^{2+}$ phosphorescence is quenched by $Fe(ox)_2^-$ [15], but the quenching is not accompanied by any appreciable sensitized reaction of the iron complex [15] (this result seems to be in contrast with a previous report [22]). A completely reversible electron transfer process or an energy transfer to a low-lying but inactive excited state of $Fe(ox)_2^-$ has been suggested in order to account for the observed behaviour [15].

Similarly, $Fe(HEDTA)(H_2O)$ quenches the phosphorescence emission of $Ru(dipy)_3^{2+}$, but no sensitized reaction of the iron complex takes place [30].

Copper(II). The biacetyl-sensitized photoredox decomposition of bis(4,4'-dimethyl-3,3'-dimethylene-2,2'-biquinolyn)copper(II) was investigated in O_2-free alcoholic solutions [43]. Quenching of biacetyl phosphorescence also occurred. The authors suggested a triplet—triplet energy transfer from biacetyl to the complex and proposed a mechanism for the photoredox decomposition.

$Mo(CN)_8^{4-}$. The sensitized photoaquation reaction of $Mo(CN)_8^{4-}$ in ethanol—water basic solutions was studied using benzophenone, phenanthrene, anthraquinone or naphthalene as sensitizers [44]. The quantum yields of the sensitized reactions, although obtained in non-limiting conditions, were significantly higher than that found by the same authors for the direct reaction, $\phi = 0.15$, at 25°C. It is to be noted, however, that this last value is much lower than that ($\phi = 0.8$) recently obtained in neutral aqueous solution by other authors [4]. The effectiveness of the above mentioned organic triplet donors in sensitizing the solvolysis of $Mo(CN)_8^{4-}$ was assumed to imply a triplet—triplet energy transfer. In neutral solution the phosphorescence of biacetyl (E_T = 19.6 kK) was quenched by $Mo(CN)_8^{4-}$, while no sensitized reaction was observed [44]. It was suggested that the energy transfer from biacetyl leads to the lowest $^3A_2$ excited state of the complex, which is unreactive, whereas the energy transfer from the other sensitizers ($E_T \geqslant 21.3$ kK) populates the higher-energy $^3B_1$ state (absorption maximum at 19.7 kK) which is responsible for the photoreaction. When naphthalene was used as sensitizer, the quantum yield of the sensitized reaction increased with decreasing wavelength of irradiation (for example, with $[Mo(CN)_8^{4-}] = 2 \times 10^{-3}$, $\phi = 0.42$ at 286 nm and 0.26 at 311 nm) [44]. This fact was related to the possibility that the electron emission, which is observed upon direct UV excitation [4], may also take place upon sensitization.

Ruthenium(II) complexes. $Ru(dipy)_2(\textit{trans}\text{-}4\text{-stilbazole})_2^{2+}$ and $Ru(dipy)_2(\textit{cis}\text{-}4\text{-stilbazole})_2^{2+}$ undergo ligand isomerization both on direct excitation and by Michler's ketone (E_T = 21.4 kK), zinc-ethioporphyrin I (E_T = 14.4 kK) or ethioporphyrin I (E_T = 14.0 kK) sensitization [45, 46]. Note that the two last donors have triplet energy lower than the "spectroscopic" energy of the emitting triplet state of the *trans* complex (~ 18 kK). In butyronitrile solution at 25°C, the *trans—cis* ratio at the photostationary state depends on the irradiation wavelength in the direct photoreaction and on the sensitizer used. The quantum yields of the direct photoisomerizations are much higher than the limiting quantum yields of the sensitized reactions, even using Michler's ketone, whose triplet is energetic enough to form "spectroscopic" triplet states of the complexes. Since the donors used have nearly unit intersystem crossing efficiency, this result may be due to the low isomerization efficiency of the triplet states of the complexes, and thus it may indicate that the direct photoisomerization originates from some singlet excited state(s) [46].

Rhodium(III) ammine complexes. Recent investigations on the direct photochemistry of $Rh(NH_3)_6^{3+}$ [47], $Rh(NH_3)_5X^{2+}$ (X = Cl, Br, I) [48] and $Rh(NH_3)_4I_2^+$ [48] have been complemented by sensitization studies. The $Rh(NH_3)_6^{3+}$ photoaquation occurs upon both direct excitation in the singlet ligand field bands and pyrazine sensitization [47]. Since the donor fluorescence is not quenched, a triplet ligand field excited state of $Rh(NH_3)_6^{3+}$, populated by energy transfer from pyrazine triplet (E_T = 26.2 kK), should be responsible for the sensitized reaction. For the other complexes, when biacetyl is used as a sensitizer a photoaquation reaction and a concomitant quenching of donor phosphorescence (E_T = 19.6 kK) are observed [48]. The sensitized reaction is the same as that observed upon direct excitation in the singlet ligand field bands, except for $Rh(NH_3)_5I^{2+}$ which only undergoes NH_3 aquation upon sensitization, while its direct excitation also leads to minor amounts of I^- aquation. For the $Rh(NH_3)_5X^{2+}$ complexes in 2×10^{-3} N $HClO_4$ at 25°C, the limiting quantum yields are practically equal to the quantum yields of the direct photoreactions. This suggests that the photochemically reactive states are ligand field excited states of triplet spin multiplicity, and the intersystem crossing from the singlet to the triplet ligand field manifolds occurs with nearly unit efficiency. For $Rh(NH_3)_4I_2^+$ the limiting quantum yield is about 20% higher than ϕ(dir), suggesting that spin—orbit coupling effects may provide an efficient mechanism for deactivation of the singlet excited states to the ground state [48]. It is interesting to note that biacetyl does not sensitize the photoreaction of $Rh(NH_3)_6^{3+}$, probably because of energy reasons [47].

Platinum(II) complexes. Contradictory results were obtained on the sensitized photoaquation reaction of $PtCl_4^{2-}$. Using biacetyl as a donor, Sastri and Langford [49] found a quantum yield higher than 0.26 for the sensitized reaction, whereas Demas and Adamson [50] obtained a limiting quantum yield 0.07 using $Ru(dipy)_3^{2+}$ (note that the quantum yield for the direct photoreaction at 472 nm is 0.17 [4]). In both cases quenching of the donor phosphorescence was also observed. In each one of these papers, ad hoc interpretations of the results were given. In reality it is very difficult if not impossible to reconcile these results, at least in terms of an energy transfer mechanism, since biacetyl and $Ru(dipy)_3^{2+}$ have similar triplet energy (19.6 and 17.8 kK, respectively) and their singlet—triplet intersystem crossing efficiencies are both practically unity. A chemical sensitization could account for the observed discrepancy, but it seems rather improbable for a sensitized photoaquation reaction.

The photochemical isomerization of *cis*-$Pt(gly)_2$ can be sensitized by triplet donors having $E_T \geqslant 26.0$ kK (pyrazine, xanthone) but not by donors having $E_T \leqslant 22.9$ kK (thioxanthone, quinoline, naphthalene, biacetyl) [51]. These results will be discussed in Sect. B(iii)(c) together with those obtained by quenching experiments. Biacetyl does not act as sensitizer although its phosphorescence is quenched by the complex [51]. The authors attributed this particular behaviour to either an intramolecular deactivation of the biacetyl triplets catalyzed by the complex or an energy transfer process from biacetyl triplets to a *cis*-$Pt(gly)_2$ excited state which cannot be a precursor to the isomerization.

Acetone and acetophenone triplets can sensitize the ethylene photoaquation of Zeise's salt, $Pt(C_2H_4)Cl_3^-$ [52]. With acetone, a nearly unit limiting quantum yield was obtained in 0.5 M HCl at 25°C. This indicates that both η_s and η_r (Sect. C(iv)(a)) are practically unity. The other photoreaction which occurs upon direct irradiation of $Pt(C_2H_4)Cl_3^-$ in the 305—385 nm region, *cis*-Cl^- photoaquation, does not take place in the sensitization experiments. Biacetyl does not sensitize any photoaquation of the complex, although its phosphorescence is quenched. These results as well as the wavelength dependence of the direct photoreactions were discussed in terms of reactivity of the various excited states of the complex. The authors suggested that energy transfer from triplet acetone or acetophenone (E_T = 27.6 and 25.8 kK, respectively) leads to the thermally equilibrated, singlet ligand field excited state of lowest energy which can only cause C_2H_4 aquation: this transfer, however, would be subjected to strong Frank—Condon restrictions (the excited state was supposed to be very distorted with respect to the ground state) and thus would occur with a very low probability, in contrast with the rather high value which was reported for the bimolecular quenching rate constant ($k_q = 1.4 \times 10^9\ M^{-1}\ s^{-1}$ with acetone assuming $\tau^0 = 4 \times 10^{-7}$ s). Cl^- aquation was suggested to originate from hot ground-state molecules of the complex. The quenching of biacetyl is assumed to be due to an energy transfer to the lowest non-reactive triplet excited state of $Pt(C_2H_4)Cl_3^-$. In the acetone—$Pt(C_2H_4)Cl_3^-$ and acetophenone—$Pt(C_2H_4)Cl_3^-$ systems, Pt^{IV} species were also produced [52], probably through a secondary chemical process involving radicals formed in the direct photodecomposition of the donor.

(d) General remarks

The use of the sensitization technique for studying the photochemistry of coordination compounds began in 1969, and about 40 papers have appeared up to now on this subject. The results do not seem to answer the photochemists expectations in a completely satisfactory way. For the two families of coordination compounds which have mainly been investigated, chromium(III) and cobalt(III) complexes, the reasons for this partial disappointment have been discussed above. It should also be noted that this technique has often been used incorrectly, and that in several cases its use seems to have been dictated by the current fashion rather than by a real necessity.

The best results were obtained by systematic studies in which a number of sensitizers were used having different energies. In several cases sensitization was a useful method for establishing the photochemical reactivity of spin-forbidden non-spectroscopic excited states of the complexes (see also Sect. E(i)). Upper limits for the energy of these states and approximate values for the intersystem crossing efficiency from the corresponding spin-allowed states were also obtained (Sect. E(ii)).

The most common sensitizers were the usual organic donors and $Ru(dipy)_3^{2+}$. This last compound should be used with caution as an energy transfer donor, because its lowest energy triplet excited state is a strong reductant [53]. Quenching of the donor emission without any concomitant sensitized reaction was observed in systems containing biacetyl as donor and $Co(NH_3)_5(NO_2)^{2+}$ [26], $Mo(CN)_8^{4-}$ [44], $Pt(gly)_2$ [51], or $Pt(C_2H_4)Cl_3^-$ [52] as acceptor, and $Ru(dipy)_3^{2+}$ as donor and $Cr(CN)_6^{3-}$ [13], $Fe(ox)_2^-$ [15] or $Fe(HEDTA)(H_2O)$ [30] as acceptor. Energy transfer to a low-lying non-reactive excited state of the acceptor was generally assumed for explaining these results. The low value for the triplet energy of these sensitizers, with respect to the energy of the other donors which are able to sensitize the photoreaction of the same complexes, supports this hypothesis. It is to be noted, that a similar explanation was often advanced for interpreting the difference between the limiting quantum yield of the sensitized reaction and the quantum yield of the direct reaction.

For some of the systems reported above, bimolecular quenching rate constants were calculated from the Stern–Volmer plot of the emission quenching and/or of the sensitized reaction. In the majority of these cases the values obtained are lower than the diffusion rate constant in the medium used. However, in many cases these values either refer to processes which are O_2 dependent, or were calculated using lifetimes which were measured under different experimental conditions. When the bimolecular quenching rate constants (or the corresponding Stern—Volmer constants) were calculated in parallel for the sensitized and the quenching process, their values were practically equal, as is expected if only one excited state of the donor is involved (Sect. C(iv)(a)). Only for the riboflavin—$Cr(NH_3)_5Cl^{2+}$ and riboflavin—$Cr(NH_3)_5(NCS)^{2+}$ systems [7] was a difference between the two constants claimed to be real. The unreliability of this result and the inconsistency of its mechanistic interpretation has been fully discussed in Sect. B(i)(a).

(ii) Sensitized luminescence of coordination compounds

(a) Introduction

The two most important categories of photoluminescent coordination compounds are the rare earth ions and the Cr^{III} complexes [54—56]. Therefore it is not surprising that sensitized emission has been reported only for these two classes of compounds. Other photoluminescent coordination compounds which have been characterized recently (e.g. ruthenium(II) chelates) are not suitable for study as acceptors because of their very intense absorption spectra (see Sect. B(iv)).

Studies on sensitized emission have particularly developped in the last few years, especially as far as fluid solutions are concerned. Sensitized emission is a direct and unequivocal proof that electronic energy transfer has occurred from the donor to the acceptor and therefore the method is currently applied as a test for excited molecules. It can also be used for estimating donor properties such as lifetimes and intersystem crossing efficiencies (Sect. E). It should be noted that sensitized emission by itself does not prove that electronic energy transfer is the only type of donor—acceptor interaction in the system. This problem can be solved only by comparing the quantum yields of the direct and sensitized emissions, as will be discussed in Sects. C(iv) and D(ii)(a).

The sensitized emission of rare earth ions finds important applications in the analytical determination of these ions [54, 57] and in problems related to laser materials [56]. However, the extensive Russian literature on the sensitization of rare earth ion luminescence seems to have been ignored by most Western authors.

Because of the authors' interest, fluid solutions will be treated in more detail than solid state systems and for the same reason solid state systems involving rare earth ions (phosphors, etc.) will be neglected.

(b) Cr(III) complexes in fluid solutions

The first example of sensitized emission of Cr(III) complexes in fluid solution was reported by Binet et al. [58] in 1968. They found using mixed solvents (methanol—water or ethanol—ethylene glycol) at —113°C, that the phosphorescence emission of $Cr(CN)_6^{3-}$, $Cr(NCS)_6^{3-}$, $Cr(acac)_3$ and $Cr(en)_3^{3+}$ was sensitized by benzil (E_T = 18.8 kK) or anthracene (E_T = 14.9 kK) triplets. Since the sensitized emission was almost completely quenched when the solution was frozen to give a rigid glass, a collisional process was involved. For the benzil—$Cr(CN)_6^{3-}$ system, the Stern—Volmer constant obtained from the sensitization experiments was in agreement with the k_{SV}'s obtained from the quenching of the donor phosphorescence emission and lifetime (Sect. C). For benzil—$Cr(NCS)_6^{3-}$, the results indicated that some contribution from a long-range transfer mechanism was present. As far as the collisional mechanism is concerned it should be recalled that the spin selection rules allow energy transfer from triplets to both doublets and quartets (Sect. D(ii)(a)). Except in the case of $Cr(CN)_6^{3-}$, both the lowest doublet and the lowest excited quartet of the acceptor complexes were in the energy range of the triplet donors. Therefore, energy transfer generally populated the emitting state of the donor, ^2E_g, either directly or through the excited quartet, $^4T_{2g}$ (the Jablonski diagram of Cr^{III} complexes is shown in Fig. 4, Sect. E).

For the benzil—$Cr(CN)_6^{3-}$ system, comparison of the direct and sensitized phosphorescence quantum yields showed that the η_{isc}^{Cr}/η_s ratio (η_{isc}^{Cr} = efficiency of the $^4T_{2g} \rightarrow {}^2E_g$ intersystem crossing of the complex: η_s = limiting energy transfer efficiency, Sect. C(iv)(a)) was about 0.5. The meaning of this result will be discussed in Sects. D(ii) and E(ii). Benzil (E_T = 18.8 kK) and erythrosin (E_T = 16.4 kK) were found to cause sensitized phosphorescence of $Cr(NCS)_6^{3-}$, $Cr(NCS)_4(NH_3)_2^-$ and $Cr(NCS)_4(aniline)_2^-$ in fluid solutions (90% ethanol—water) at —72°C [59]. For more details of these results, see Sect. D(ii)).

Chen and Porter [60] found that the phosphorescence emission of $Cr(CN)_6^{3-}$ was sensitized by *trans*-$Cr(NCS)_4(NH_3)_2^-$ in deoxygenated fluid solutions (methanol—water—ethylene glycol) at —65°C but when the fluid solution was transformed into a rigid glass (—130°C), no sensitization could be observed and the sensitization process must be due to a collisional mechanism. A linear Stern—Volmer plot for the sensitized emission was obtained and the Stern—Volmer constant was in agreement with those obtained from the quenching of the *trans*-$Cr(NCS)_4(NH_3)_2^-$ phosphorescence intensity and lifetime. Since the lowest quartet excited state of $Cr(CN)_6^{3-}$ is at much higher energy than the *trans*-$Cr(NCS)_4(NH_3)_2^-$ doublet, the electronic energy transfer was to the doublet state of the acceptor. The value ~ 7×10^5 M^{-1} s^{-1} for k_{et} obtained from either quenching or sensitization on the assumption that electronic energy transfer was the sole quenching process was somewhat lower than the diffusion rate constant (~ 4×10^6 M^{-1} s^{-1}) calculated for the experimental conditions used. Evidence for back energy transfer from $Cr(CN)_6^{3-}$ (^2E_g) to *trans*-$Cr(NCS)_4(NH_3)_2^-$ (^2E_g) was also obtained (k_{et} ~ 3×10^4 M^{-1} s^{-1}).

Sensitized phosphorescence from $Cr(CN)_6^{3-}$ was also observed using triplet $Ru(dipy)_3^{2+}$ (E_T = 17.8 kK) and erythrosin as donors in deoxygenated DMF solutions at 7°C [12, 13, 61]. Details concerning these systems will be given in Sect. E(i).

Sensitized phosphorescence from $Cr(en)_3^{3+}$ was obtained using biacetyl (E_T = 19.6 kK) as a donor in deoxygenated aqueous solutions at 20°C [11]. A parallel quenching of the biacetyl phosphorescence was observed, whereas the biacetyl fluorescence was not affected. An upper limit value ~ 0.6 was obtained for the limiting energy transfer efficiency from a comparison between the quantum yields of the direct and biacetyl-sensitized emissions.

(c) Cr(III) complexes in the solid state

Schläfer et al. [62,63] reported that electronic energy transfer can occur from the cation to the anion in a series of Cr^{III} double salts of the generic type

$[CrA_6][Cr(CN)_6]$ at 77 K (A = urea, atp, imid, NH_3, 1/2 en, 1/2 pn or 1/2 tn). The evidence for energy transfer was the anion emission upon cation photoexcitation (note that the ^2E_g state of $Cr(CN)_6^{3-}$ is the lowest excited state in the double salt whereas the lowest quartet excited state of $Cr(CN)_6^{3-}$ is higher in energy than the lowest quartet excited states of the donors). The quantum yield for the sensitized emission was some 10 to 20 times that obtained by direct irradiation of the anion in the potassium salt. The existence of such an "amplification factor" was attributed either to differences in the intersystem crossing efficiencies in the donor and acceptor ions or to changes in their luminescence properties when residing in different lattices [63]. Similar experiments were carried out by Candori and Furlani [64] on double salts of the type $[CrA_6][CrB_6]$, where A = urea or 1/2 en, and B = NCS^- or 1/2 mal. Sensitized emission from the anions was observed, but no "amplification" was found.

A thorough investigation carried out by Kirk and Schläfer [65] on the $[Cr(atp)_6][Cr(CN)_6]$ system led to the conclusion that electronic energy transfer is not the major mechanism of ^2E_g emission from the $Cr(CN)_6^{3-}$ ions in the double salt. The temperature dependence of the intensity showed that the observed phenomenon most probably arises from a marked change in the luminescence properties of $Cr(CN)_6^{3-}$ upon placing this ion in the lattice of the double salt. The authors [65] suggested that such an explanation may also be valid for all the previously investigated [62, 63] double salts (see also ref. 66).

Flint and Matthews [67] have recently reported unambiguous evidence for electronic energy transfer between complex ions in the same crystal. A homogeneous crystalline solid was prepared which contained less than 1% of $Cr(NH_3)_5Cl^{2+}$ in $[Cr(NH_3)_6](ClO_4)_3$. At 80 K, sensitized emission from $Cr(NH_3)_5Cl^{2+}$ was obtained and it was found that the risetime of the sensitized phosphorescence was two orders of magnitude longer than the risetime of the direct $[Cr(NH_3)_5Cl]Cl_2$ phosphorescence, which was less than 3 μs. Moreover, the rate constant of the hexammine decay was similar to the rate constant for the population of the $Cr(NH_3)_5Cl^{2+}$ phosphorescent state. Similar results were obtained for the $Cr(ND_3)_6^{3+}$—$Cr(ND_3)_5Cl^{2+}$ system. In a subsequent investigation [68], Flint et al. produced pentammine species of the type $Cr(NH_3)_5X^{2+}$ (X = Cl, Br, I, NO_3) by irradiation of $[Cr(NH_3)_6]ZnCl_4X$ (X = NO_3^- and Cl^-) or $[Cr(NH_3)_6]X_3$ (X = Cl^-, Br^-, I^- and NO_3^-). Risetime and decay curve measurements indicated that electronic energy transfer occurred from the reactant to the product in these photolyzed systems.

Energy transfer from $Ru(dipy)_3^{2+}$ to anionic Cr^{III} complexes in double salts at 77 K has also been reported [69, 70]. Excitation in the ^{1}CT band of $Ru(dipy)_3^{2+}$ was found to cause phosphorescence emission from $Cr(mal)_3^{3-}$, $Cr(ox)_3^{3-}$, $Cr(CN)_6^{3-}$ and $Cr(NCS)_6^{3-}$. A complete quenching of the $Ru(dipy)_3^{2+}$ phosphorescence was observed, except for $Cr(CN)_6^{3-}$. Since this last complex is the only one among the quenchers used which has its lowest excited quartet at higher energy than the ^{1}CT state of the donor, it was assumed that energy transfer mainly occurred from ^{1}CT to $^4T_{2g}$ of the Cr complexes. This interpretation is supported by the fact that in the Rh(dipy)$_3^{3+}$—Cr(CN)$_6^{3-}$ double salt, where the lowest spin-allowed excited state of the donor is higher than the $^4T_{2g}$ level of Cr(CN)$_6^{3-}$, the sensitized Cr^{III} phosphorescence is accompanied by a complete quenching of the donor phosphorescence [70].

Finally, sensitized emission from the chromium complex has been reported for the double salts [Cr(NH$_3$)$_6$] [Co(CN)$_6$] [71, 72] and [Cr(en)$_3$] [Co(CN)$_6$] [72]. The temperature dependence of this process from 20 to 293 K has also been investigated for the first salt [71]. Sensitized emission from the Cr centre has also been observed for Cr^{3+}: K$_3$Co(CN)$_6$ powders [73].

(d) Rare earth compounds in fluid solution

The first example of intermolecular energy transfer to rare earth ions in fluid solutions was reported in 1963 by Matovich and Suzuki [74], who observed luminescence emission upon solvent photoexcitation of solutions of Eu^{3+} or Tb^{3+} salts in aromatic ketones. Similar experiments using acetophenone as a solvent and Sm^{3+}, Dy^{3+}, Tb^{3+} and Eu^{3+} ions as acceptors were carried out by Ballard and Edwards [75]. Heller and Wasserman [76] found that a number of aromatic aldehydes and ketones were able to sensitize the Eu^{3+} and Tb^{3+} luminescence in glacial acetic acid at room temperature. Since oxygen was found to quench the sensitization process, the triplet state of the donor had to be involved. The viscosity effect and the decrease of sensitization in rigid glasses showed that the process was collisional in nature, with an effective radius of interaction of 5—10 Å. Similar experiments were carried out by Morina et al. [77] using aromatic ketones as donors and Eu^{3+} and Tb^{3+} as acceptors in acetone solutions. In particular, they found that the quenching constant of benzophenone triplets by Eu^{3+} was about 30 times lower than the diffusion constant. Subsequent studies by the same group showed that the quenching constant of n,π^* triplet states by rare earth ions is on average an order of magnitude larger than that of π,π^* triplets [78, 79]. This result was attributed to the different degree of overlap between the donor and acceptor orbitals in the two cases. They also found that the quenching constant decreased by more than two orders of magnitude when electron acceptor substituents were introduced into the phenyl rings of benzophenone [78]. For n,n'-dimethoxybenzophenone and n-dibenzoylbenzene, evidence was found for complex formation with the rare earth ions [78].

For ketones with the lowest triplet level of π,π^* character, the limiting quantum yield of the ketone-sensitized Eu^{3+} luminescence in acetone and acetonitrile was found to be close to the quantum yield obtained upon direct Eu^{3+} excitation. On the contrary, for ketones with the lowest triplet of n,π^* character, the limiting quantum yield was much lower [80]. These results were taken as an indication of a photochemical interaction between the ketones with lowest n,π^* triplets and the rare earth ions.

Sensitized Eu^{3+} luminescence can also be obtained using UO$_2^{2+}$ as a donor in several solvents [81]. The quenching rate constant for aqueous solutions at room temperature was found to be about 10^7 M^{-1} s^{-1}, i.e. of the same order of magnitude as the calculated diffusion constant assuming an interaction radius of 5 Å. However, the influence of the ionic strength on the calculated value (see Sect. C(ii)) was not considered.

Sensitized emission of Eu^{3+} chelates in fluid solution was first reported by El-Sayed and Bhaumik [82, 83]. Excitation of benzophenone [82] or other aromatic molecules [83] was found to cause metal-centred emission from $Eu(HFA)_3$. The assumed mechanism was as follows:

$$\text{benzophenone}\ (S_0) \xrightarrow{h\nu} \text{benzophenone}\ (S_1) \quad (1)$$
$$\text{benzophenone}\ (S_1) \rightarrow \text{benzophenone}\ (T_1) \quad (2)$$
$$\text{benzophenone}\ (T_1) + Eu(HFA)_3 \rightarrow \text{benzophenone}\ (S_0) + Eu(HFA)_3(T_L) \quad (3)$$
$$Eu(HFA)_3(T_L) \rightarrow Eu(HFA)_3(Q_M) \quad (4)$$
$$Eu(HFA)_3(Q_M) \rightarrow Eu(HFA)_3 + h\nu' \quad (5)$$

where T_L is the ligand-centred triplet excited state of the ligand and Q_M is the emitting metal-centred excited state, $^5D_0$. The intermolecular energy transfer step (3) is diffusion controlled [82, 83]. Similar investigations carried out by Ermolaev et al. [84, 85] confirmed that the energy transfer from organic donors to Eu^{3+} chelates takes place by means of triplet—triplet transfer.

Sensitization of Eu^{3+} luminescence in fluid solution has also been obtained by a two-step process where Tb^{3+} acts as an intermediate between the organic donor and the acceptor (Eu^{3+}) [86]. This mechanism was substantiated by measurements of luminescence and excitation spectra, luminescence lifetimes and time-resolved spectra. A two-step sensitization of the Eu^{3+} luminescence by Tb^{3+} ion via the triplet state of 2-acetylnaphthalene has also been reported [87].

Several authors have used the sensitized emission of rare earth ions or rare earth complexes as a probe for excited organic molecules in fluid solutions. The triplet lifetime of triphenylamine and benzophenone was indirectly measured by Ermolaev and Sveshnikova [85] using energy transfer to Eu^{III} chelates via naphthalene as an intermediate (Sect. E(iii)). Filipescu and Mushrush [88] carried out a systematic investigation on the rare earth ion sensitized luminescence by several types of organic donors. Aromatic hydrocarbons which are known to undergo efficient intersystem crossing did not cause any sensitization, whereas many aromatic ketones, aldehydes and carboxylic acids did. Even in these cases, however, the sensitization constant was found to be one order of magnitude lower than the diffusion controlled value. In a subsequent paper [89], the sensitized emission of Tb^{3+} was used as a means for obtaining information on the photoreduction of *p,p'*-dimethoxybenzophenone.

Lamola and Eisinger [90—92] used Eu^{3+} ions as "triplet counters" and emphasized the biological interest of this method in view of the possibility of using it under physiological conditions, i.e. in water near *p*H 7 and at room temperature. They also applied this method to estimate lifetimes of both excited singlet and triplet states as well as intersystem crossing efficiencies (see

Sects. E(ii) and E(iii)). The donors used were 3-benzophenone sulphonic acid sodium salt, acetophenone, orotic acid, tryptophan and some mononucleotides [91, 92]. In agreement with other authors [93], they found that energy transfer from triplet donors to Eu^{3+} occurred by means of a collisional mechanism with a rate constant which is at least two orders of magnitude lower than the diffusion constant. For several donors, it was observed that Eu^{3+} quenches the excited singlet states without becoming excited to an emission level. It was suggested that this mechanism involves induced internal conversion in the singlet donor due to formation of a complex with Eu^{3+} in which charge transfer may play an important role.

(iii) Quenching of coordination compound photoreactions

(a) Introduction

There are only a few examples of quenching of coordination compound photoreactions. This is due to the fact that the excited states responsible for the photochemical behaviour of coordination compounds have generally short lifetimes and low energies, so that their quenching meets with many experimental difficulties. Since the quenching approach to the characterization of the excited-state reactivity is in principle much more fruitful than the sensitization approach, it is easy to forecast that the number of studies dealing with photoreaction quenching will grow rapidly.

The results so far available are summarized in Table 1.

(b) Chromium(III) complexes

The fact that some Cr^{III} complexes exhibit phosphorescence under the experimental conditions in which photochemistry is studied has promoted investigations aiming at comparing the phosphorescence quenching with the

TABLE 1

Quenching of coordination compound photoreactions

Complex	Reaction	Quencher	Ref.
$Cr(NH_3)_6^{3+}$	NH_3 aquation	OH^-	94
$Cr(en)_3^{3+}$	en aquation	$CoCl_2$, $FeCl_2$	95
$Cr(phen)_3^{3+}$	racemization	I^-	96
$Cr(NH_3)_2(NCS)_4^-$	SCN^- aquation	$Cr(CN)_6^{3-}$	97
$Co(CN)_6^{3-}$	CN^- aquation	biacetyl	98
$Ir(phen)_2Cl_2^+$	Cl^- aquation	O_2, $Cr(CN)_6^{3-}$	99
$Ir(5,6\text{-dmp})_2Cl_2^+$	Cl^- aquation	O_2, $Cr(ox)_3^{3-}$	99
cis-$Pt(gly)_2$	isomerization	$NiSO_4$	51
UO_2^{2+}	reduction by lactic acid	Tl^+	100

photolysis quenching. Since the phosphorescence is known [55] to originate from the lowest doublet ^2E_g, Fig. 4, such a comparison can actually give important information on the relative importance of the ^2E_g and $^4T_{2g}$ states in determining the photochemical reaction (see Sects. B(i)(a) and E(i)).

The first investigation of this kind was carried out by Chen and Porter [97] in 1970. Working with deoxygenated fluid solutions (methanol—water—ethylene glycol in the ratio 2:1:1) at —65°C, they found that the quantum yield of NCS^- release from *trans*-$Cr(NH_3)_2(NCS)_4^-$ (reineckate ion) is reduced in the presence of $Cr(CN)_6^{3-}$, but not as much as is the reineckate phosphorescence emission. Their results indicated that only 50% of the photoreaction was quenched under conditions where phosphorescence quenching was complete. Therefore they concluded that half of the photoreaction must occur from excited molecules that have not been through the ^2E_g doublet state which is responsible for the phosphorescence emission. It should be noted that, while these data show that some state other than ^2E_g (presumably, the lowest excited quartet) is responsible for the non-quenchable part of the photoreaction, they do not prove that the remaining part of the photoreaction comes from the lowest doublet directly. As pointed out by Porter et al. [97, 101], the quenchable part of the photoreaction may originate from thermal repopulation of the quartet state via back intersystem crossing from the lowest doublet, followed by reaction in the quartet. This hypothesis, which is also supported by data on the temperature dependence of the phosphorescence lifetime [60], seems to be more reasonable than that of the doublet state reactivity, even on theoretical grounds [101].

The quenching of the reineckate phosphorescence and photolysis is most probably due to electronic energy transfer from the lowest doublet of the reineckate ion to the lowest doublet of $Cr(CN)_6^{3-}$, as shown by (i) the parallel intensity and lifetime quenching of the reineckate phosphorescence and (ii) the simultaneous sensitization of the $Cr(CN)_6^{3-}$ phosphorescence [60, 101]. A different quenching mechanism must be operative for the $Cr(NH_3)_6^{3+}$ and $Cr(phen)_3^{3+}$ complexes studied by Langford et al. [94, 96], although the same conclusions were reached on the roles of the doublet and quartet states. For $Cr(NH_3)_6^{3+}$ it was found that the phosphorescence was completely quenched in basic solution when no more than one-third of the photoreaction (NH_3 release) was quenched [94]. For optically active $Cr(phen)_3^{3+}$, iodide ions were found to quench both the phosphorescence and the racemization but 14% of the racemization was unquenchable [96]. For this system, the apparent activation energies of the nonquenchable (2.2 kcal mol^{-1}) and quenchable (10.1 kcal mol^{-1}) components of the quantum yield [96] and the apparent activation energy of the phosphorescence intensity (—1.6 kcal mol^{-1}) [102] were also measured. These data support the hypothesis that the quenchable part of the photoreaction occurs through thermal repopulation of the reactive quartet state via back intersystem crossing [96].

The quenching of the $Cr(en)_3^{3+}$ photolysis by some transition metal ions has very recently [94] been investigated in aqueous solution. As happens for the $Cr(en)_3^{3+}$ phosphorescence quenching [103] (see Sect. B(iv)(b)), $MnCl_2$ does not exhibit any quenching effect whereas $CoCl_2$ and $FeCl_2$ do quench the photoreaction, which consists in the detachment of one end of an ethylenediamine molecule. Once again the photoreaction is less quenched than the phosphorescence and the results show that 40% of the photoreaction directly originates from the lowest quartet excited state ($^4T_{2g}$) prior to intersystem crossing to the lowest doublet (^2E_g), whereas the remaining 60% is due to molecules which pass through ^2E_g and thus can be quenched. A quantitative analysis based on all the data which are available concerning the photochemical and photophysical behavior of $Cr(en)_3^{3+}$ shows that the quenchable part of the photoreaction probably also comes from $^4T_{2g}$ after back intersystem crossing from ^2E_g [103] (see also Sect. E(i)).

For $Cr(CN)_6^{3-}$ in DMF, the phosphorescence quenching by O_2 and H_2O is not accompanied by any quenching of the photosolvation reaction [104] (Sect. E(i)).

(c) Other complexes

Preliminary investigations have shown that the photoaquation of $Co(CN)_6^{3-}$ is quenched by biacetyl [98] and that the photoaquation reactions of $Ir(phen)_2Cl_2^+$ and $Ir(5,6\text{-dmp})_2Cl_2^+$ in 45% v/v DMF—water are partially quenched by oxygen and anionic complexes [99].

The *cis—trans* isomerization of $Pt(gly)_2$, which is known to take place via an intramolecular twisting mechanism [4], is quenched by Ni_{aq}^{2+} (8.9 kK) but not by Mn_{aq}^{2+} (18.9 kK) [51]. Both ions were added as sulphate salts. From the Stern—Volmer plot of the quenching by Ni_{aq}^{2+}, a value of about 2 M^{-1} was obtained for k_{SV}. The lack of sensitization by donors in the 22.9—19.2 kK energy range (Sect. B(i)(c)) and the lack of quenching by Mn_{aq}^{2+} (18.9 kK) were taken as an indication of the distortion of the excited state that is responsible for the *cis—trans* isomerization.

The photoreaction of uranyl ion with lactic acid is quenched by Tl^I which also quenches the uranyl fluorescence at a diffusion controlled rate. The quenching constants of Hg^I, Mn^{II}, Co^{II} and Cu^{II} for both the fluorescence and photolysis are one to two orders of magnitude smaller than that of Tl^I [100].

(iv) Quenching of coordination compound luminescence

(a) Introduction

As mentioned in Sect. B(ii), the most important categories of photoluminescent coordination compounds are rare earth ions and Cr^{III} complexes. However, very recently a new class of photoluminescent coordination compounds, namely the Ru^{II}, Ir^{III} and Rh^{III} chelates with phenanthroline, dipyridyl and their derivatives, has been characterized [105—107]. Some of these complexes and particularly $Ru(dipy)_3^{2+}$ exhibit strong luminescence in fluid solution and because of their intrinsic properties (solubility, absorption spectrum, etc.) are very suitable for luminescence quenching experiments. The characterization of these compounds has caused a rapid growth in sensitization and quenching studies in the field of transition metal complexes (see also Sects. B(i) and B(ii)).

(b) Fluid solutions

Cr(III) complexes. The quenching of the phosphorescence emission of $Cr(CN)_6^{3-}$ by molecular oxygen, water and naphthacene in DMF solutions has been studied by Wasgestian [104, 108]. The relevance of these studies for determining the photoreactive state of the hexacyanochromate ion will be discussed in Sect. E(i).

The intensity and lifetime quenching of the $Cr(en)_3^{3+}$ phosphorescence by some transition metal ions in water at room temperature has been investigated by Wasgestian et al. [103]. $MnCl_2$ exhibits no quenching effect but $FeCl_2$ and $CoCl_2$, which have low-lying excited states ($\leqslant$ 10 kK), quench the $Cr(en)_3^{3+}$ phosphorescence. In the case of the quenching by $CoCl_2$, the Stern—Volmer plots obtained from lifetime and intensity measurements showed a positive curvature. This result was quantitatively accounted for by considering the relative abundances and the different quenching abilities of the various Co^{II} species that are present in aqueous solutions containing Co^{2+} and Cl^- ions. The bimolecular quenching constants were 1.5×10^5 M^{-1} s^{-1}, 5×10^6 M^{-1} s^{-1}, 8×10^7 M^{-1} s^{-1} and $\sim 2 \times 10^8$ M^{-1} s^{-1} for $Co(H_2O)_6^{2+}$, $Co(H_2O)_5Cl^+$, $Co(H_2O)_2Cl_2$ and $Co(H_2O)Cl_3^-$, respectively.

The quenching of the phosphorescence intensity and lifetime of $Cr(NH_3)_2(NCS)_4^-$ by $Cr(CN)_6^{3-}$ has been studied by Chen and Porter [60, 97]. The experiments were carried out in deoxygenated methanol—water—ethylene glycol mixtures at —65°C. The intensity and lifetime quenching showed linear Stern—Volmer plots and the bimolecular quenching constant calculated from both steady state and transient measurements was lower than the diffusion rate constant (for more details, see Sect. B(ii)(b)).

The quenching of the phosphorescence lifetime of some Cr^{III} complexes (namely, $Cr(NCS)_6^{3-}$, $Cr(CN)_6^{3-}$, $Cr(en)_3^{3+}$, $Cr(tn)_3^{3+}$, $Cr(acac)_3$, $Cr(NH_3)_2(NCS)_4^-$) by molecular oxygen in fluid solutions was studied by Pfeil [109]. Large quenching constants (of the order of the diffusion rate constant) were obtained for complexes with ligands which possess extensive π electron systems ("conducting" ligands) whereas a very small quenching effect was observed for complexes containing ligands like ethylenediamine ("insulating" ligands). For complexes containing conducting ligands the quenching constant decreased with increasing charge of the complex. This effect was attributed to an insulating effect of the hydration sphere towards electronic energy transfer (see also Sect. D(ii)(d)). The activation energy of the quenching process was found to be equal to that for solvent fluidity.

The quenching of the emission intensity of $Cr(phen)_3^{3+}$ by I^- ions [96, 110] and of $Cr(NH_3)_6^{3+}$ by OH^- ions [94] has been reported by Langford et al. In the former case the quenching follows a linear Stern—Volmer relationship, with $k_{SV} = 4.2 \times 10^5$ M^{-1}.

Ru(II) complexes. The use of $Ru(dipy)_3^{2+}$ as a donor in the field of coordination compounds was suggested by Demas and Adamson [50] in 1971, and since then many studies have been carried out using this complex. The most important features which make this complex a very useful donor are the following [50]: (i) the prominent visible absorption that is due to a spin-allowed CTTL transition; (ii) the intense and long lived emission which originates from the lowest CTTL triplet state (E_T = 17.8 kK); (iii) its photochemical and thermal inertness [15, 31]; (iv) its solubility in water, where sensitization and quenching experiments involving coordination compounds are generally carried out. Demas and Adamson [50] also reported the first example of quenching of the $Ru(dipy)_3^{2+}$ phosphorescence intensity and lifetime by a coordination compound. The quencher used was $PtCl_4^{2-}$. The quenching process was diffusion controlled ($k_q = 6.5 \times 10^9$ M^{-1} s^{-1}) and a concomitant sensitized aquation of the acceptor complex occurred (Sect. B(i)).

The quenching of the $Ru(dipy)_3^{2+}$ phosphorescence intensity by some Cr^{III} complexes ($Cr(CN)_6^{3-}$, $Cr(en)_3^{3+}$, $Cr(mal)_3^{3-}$, $Cr(ox)_3^{3-}$) and by $Co(ox)_3^{3-}$ was studied by Fujita and Kobayashi [111] in aqueous solutions at 25°C. The kinetics of the quenching process were investigated as a function of the viscosity and ionic strength of the solution. The Stern—Volmer constant was found to be independent of solvent viscosity but decreased with increasing ionic strength. On this basis the authors assumed that the quenching was due to an intramolecular process occurring in preformed ion pairs (static quenching, see Sect. C(iii)) without any appreciable contribution from dynamic quenching processes.

The quenching of the $Ru(dipy)_3^{2+}$ phosphorescence by $Cr(CN)_6^{3-}$ in aqueous solution has been reinvestigated recently [112]. Lifetime and intensity measurements showed that the quenching is actually due to a dynamic collisional process. The bimolecular quenching constant was found to be affected by the ionic strength of the solution as would be expected for the interaction of charged species. Extrapolation to zero ionic strength yielded a value of 2.1×10^{10} M^{-1} s^{-1} for k_q at ~ 22°C, in good agreement with the calculated diffusion controlled value.

A diffusion controlled quenching of the $Ru(dipy)_3^{2+}$ phosphorescence by $Cr(CN)_6^{3-}$ in water and in DMF has also been found by Sabbatini et al. [12, 13, 61]. The importance of these studies for determining the photoreactive state [12, 13] and the efficiency of intersystem crossing [61] of the $Cr(CN)_6^{3-}$ will be discussed in Sects. E(i) and E(ii).

The lifetime and intensity quenching of the $Ru(dipy)_3^{2+}$ phosphorescence by some $Cr(en)_2XY^+$ (X, Y = F, Cl, Br or NCS) complexes in aqueous solutions has been studied recently [113]. The quenching occurred by means of a dynamic process whose k_q was always lower than the diffusion rate constant. The actual value of k_q was found to depend strongly on the nature of the ligands and on the geometry of the complex. The quenching ability of the ligands increased in the series F < Cl < NCS < Br. The *cis* isomers were better quenchers than the corresponding *trans* isomers (see Sect. D(ii)(b)).

The quenching of the $Ru(dipy)_3^{2+}$ phosphorescence by various Co^{III} complexes has been investigated as a complement of the photosensitized reactions which take place in these systems (Sect. B(i)). Gafney and Adamson [22] reported that $Co(NH_3)_5Br^{2+}$ quenches the intensity and the lifetime of the phosphorescence of $Ru(dipy)_3^{2+}$ in 1 N H_2SO_4. The quenching follows a linear Stern—Volmer plot with $k_{SV} = 255$ M^{-1}. Natarajan and Endicott [23, 24, 29—31] studied the quenching of the phosphorescence intensity of $Ru(dipy)_3^{2+}$ by $Co(EDTA)^-$, $Co(HEDTA)X^-$ ($X = Cl, Br, NO_2$), $Co(NH_3)_5Br^{2+}$ and $Fe(HEDTA)H_2O$. The bimolecular quenching constants were in the range 10^8—10^9 M^{-1} s^{-1}. The dispute concerning the actual mechanism of the quenching process (electron transfer [22] or energy transfer [23, 24]) in these cases has led to further studies of the quenching of the $Ru(dipy)_3^{2+}$ phosphorescence by $Co(NH_3)_5X^{3+}$ ($X = Br^-, Cl^-, H_2O, NH_3$) and by $Ru(NH_3)_5X^{3+}$ ($X = Cl^-, NH_3$) [25]. In 1 N H_2SO_4 linear Stern—Volmer plots were obtained, and for the Co^{III} complexes the quenching rate constants increased with changing ligand in the order $NH_3 < H_2O < Cl^- < Br^-$, with the values of the rate constants ranging from $\sim 10^7$ M^{-1} s^{-1} for $Co(NH_3)_6^{3+}$ to 2.5×10^9 M^{-1} s^{-1} for $Co(NH_3)_5Br^{2+}$. $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_5Cl^{2+}$ both quenched the phosphorescence much more effectively than the Co^{III} complexes, with quenching rate constants of 2.1×10^9 M^{-1} s^{-1} and 2.7×10^9 M^{-1} s^{-1} respectively. The mechanistic details of these quenching reactions are discussed in Sect. D(iii).

The lifetime and intensity quenching of the $Ru(dipy)_3^{2+}$ phosphorescence by some $M(ox)_3^{3-}$ complexes (M = Cr, Co, Fe) has been studied by Demas and Adamson [15]. For $Cr(ox)_3^{3-}$ and $Co(ox)_3^{3-}$ the quenching process was shown to proceed via a dynamic mechanism at a nearly diffusion controlled rate. The same was probably true for $Fe(ox)_2^-$, which is the principal species present in $Fe(ox)_3^{3-}$ solutions. Contrary to a previous report [111], no evidence for static quenching was found for the $Ru(dipy)_3^{2+}$—$Co(ox)_3^{3-}$ system. Electron transfer is suggested to be the most probable quenching mechanism for the $Ru(dipy)_3^{2+}$—$Co(ox)_3^{3-}$ system, but energy transfer is assumed to take place in the $Ru(dipy)_3^{2+}$—$Cr(ox)_3^{3-}$ system.

The quenching of the $Ru(dipy)_3^{2+}$ phosphorescence by aquometal ions supports the mechanism of quenching of $(^3CT)Ru(dipy)_3^{2+}$ by electron transfer at least in some cases. Fe_{aq}^{3+} and Fe_{aq}^{2+} quench the phosphorescence with quenching rate constants of 1.9×10^9 M^{-1} s^{-1} and 1.6×10^7 M^{-1} s^{-1} respectively [114] and an electron transfer process is involved in the case of the quenching by Fe_{aq}^{3+} [115]. The quenching of the $Ru(dipy)_3^{2+}$ phosphorescence by Tl^{3+} ions has been shown to be due to electron transfer from the $(^3CT)Ru(dipy)_3^{2+}$ [114]. The phosphorescence quenching is accompanied by photochemical reduction of the Tl^{3+} and the Stern—Volmer constants for the quenching and the photochemical reaction are the same. The production of the intermediate oxidation state, Tl^{2+}, by the electron transfer from $(^3CT)Ru(dipy)_3^{2+}$ resulted in a limiting quantum yield for the oxidation of $Ru(dipy)_3^{2+}$ of 2 (eqns. (6) and (7)). The quenching rate constant was 1.1 ×

10^8 M^{-1} s^{-1}, which is nine orders of magnitude faster than the rate of the

$$(^3CT)Ru(dipy)_3^{2+} + Tl^{3+} \rightarrow Ru(dipy)_3^{3+} + Tl^{2+} \qquad (6)$$

$$Tl^{2+} + Ru(dipy)_3^{2+} \rightarrow Ru(dipy)_3^{3+} + Tl^{+} \qquad (7)$$

thermal electron transfer reaction between ground-state $Ru(dipy)_3^{2+}$ and Tl^{3+}, emphasising the greatly increased ease of electron transfer from a triplet charge transfer state of this kind.

The quenching of the $Ru(phen)_2(CN)_2$ intensity and lifetime emission by Cu^{2+} ions in water at 22°C occurs via both a diffusional and a static process [116]. In deoxygenated solutions the Stern—Volmer quenching constant for the dynamic part is 335 M^{-1} and the first association constant for Cu^{2+} and $Ru(phen)_2(CN)_2$ is 270 M^{-1}, so that dynamic and static mechanisms contribute almost equally to the quenching. This is probably the first unambiguous example of static quenching in systems involving coordination compounds. The authors [116] emphasized that the quenching technique can provide a new and sensitive method for measuring association and ion-pairing constants (Sect. E(viii)).

The simultaneous occurrence of static and dynamic quenching between inert saturated coordination compounds has recently been reported [117]. The donor used was $Ru(dipy)_3^{2+}$ and the quenchers were $Mo(CN)_8^{4-}$, $IrCl_6^{3-}$ and $PtCl_4^{2-}$. The experiments were carried out in various solvents (water, MF, DMF) at 22°C. For most of the systems phosphorescence lifetime and intensity were quenched in parallel, showing that only dynamic quenching was operative. For two systems however (namely $Ru(dipy)_3^{2+}$—$Mo(CN)_8^{4-}$ in water and $Ru(dipy)_3^{2+}$—$PtCl_4^{2-}$ in DMF) the intensity quenching was greater than the lifetime quenching, in agreement with the presence of both static and dynamic quenching processes. The ion-pairing equilibrium constants obtained from the quenching results were in agreement with the calculated values. For all systems, the k_q values of the dynamic process were near the respective diffusion rate constants.

Oxygen quenching of charge transfer excited states of some Ru^{II} complexes and evidence for concomitant singlet oxygen formation has been reported by Demas et al. [118]. Lifetime and intensity measurements showed that only a dynamic mechanism was operating and that the process was practically diffusion controlled.

The quenching of $Ru(dipy)_3^{2+}$ phosphorescence intensity by anthracene, *trans*-2-styrylpyridine, *trans*-4-styrylpyridine and *trans*-stilbene in deoxygenated ethanol—benzene solutions at 25°C proceeds via triplet—triplet energy transfer [119]. As expected, the bimolecular quenching rate constant is near diffusion controlled when the energy transfer is clearly exothermic but decreases greatly when the donor and acceptor triplet levels are nearly isoenergetic.

Uranyl ion. The quenching of the UO_2^{2+} emission has been extensively investigated in connection with photochemical studies. A great variety of molecules (including aromatic molecules [120—123], aliphatic alcohols

[122—124], rare earth ions [81, 125] and coordination compounds [35] have been used as quenchers. Quite different quenching mechanisms seem to be involved but they are generally not well understood.

Matsushima et al. reported that the quenching of the UO_2^{2+} luminescence occurred with lower than diffusion rates when the quenchers used were aromatic molecules [121, 122] or aliphatic alcohols [122, 124] which have no excited states lying below the emitting state of uranyl ion. Mechanisms were proposed which involved a physical radiationless decay of an excited state π complex for aromatic molecules, and a chemical decay via a hydrogen abstraction of an exciplex or collision complex for the aliphatic alcohols.

The quenching of uranyl ion emission by aliphatic alcohols has recently been investigated [126] by using flash techniques. The authors suggested that the quenching occurs via an exciplex formation by means of "physical" and "chemical" deactivation. The rate constants for both the quenching processes were found. The quenching of UO_2^{2+} emission by stilbenes and the concomitant sensitized isomerization of the stilbenes has been reported to occur without reduction of UO_2^{2+} ions [127].

Tl^+ ion and lactic acid quench the uranyl fluorescence in 1 N sulphuric acid through a collisional mechanism [100]. The bimolecular quenching constants are 5×10^9 M^{-1} s^{-1} and 3.8×10^6 M^{-1} s^{-1} at 20°C for Tl^+ and lactic acid, respectively. In the presence of both the quenchers, the two quenching processes occur independently.

The quenching of UO_2^{2+} luminescence by Eu^{III} in water or acetic acid solutions was studied by Kropp [81]. The quenching follows a Stern—Volmer relation and is due to a collisional mechanism. The quenching of UO_2^{2+} luminescence by $Co(CN)_6^{3-}$ has been reported by Matsushima [35] and a collisional mechanism seems to be operating in this case also, with $k_{SV} = 38$ M^{-1}.

Other transition metal complexes. The quenching of the Zn-etioporphyrin I fluorescence by several organic molecules which form no ground-state complexes with porphyrin has been studied by Whitten et al. [128] in various solvents at 28°C. The quenching follows a Stern—Volmer relationship. The k_q values are a little lower than the diffusion controlled limit, and show a general increase with the solvent polarity. A mechanism involving exciplex formation was thought to be responsible for the quenching by nitrobenzene and other nitro compounds.

The triplet lifetime of Zn- and Pt-etioporphyrins and of Pd-mesoporphyrin in rigid, viscous and fluid solutions at various temperatures has been investigated by Callis et al. [129]. The triplet lifetime was found to depend on the complex concentration. This observation was interpreted in terms of a kinetic mechanism that postulates the formation of triplet excimers.

Solutions of *cis*-$W(CO)_4(py)_2$ in *cis*-1,3-pentadiene at 77 K do not show the characteristic luminescence of the complex [130].

The luminescence emission of $Ir(phen)_2Cl_2^+$ and $Ir(5,6\text{-dmp})_2Cl_2^+$ in 45% v/v DMF—water is quenched by oxygen and anionic complexes [99].

Rare earth. The quenching of the luminescence emission of rare earth complexes and ions has extensively been studied by several authors, especially those of the Russian school. Many potential acceptors (organic molecules, rare earth ions, etc.) have been used and several quenching mechanisms have been proposed in order to account for the great variety of the experimental results.

Generally the quenching of rare earth ion and rare earth chelate luminescence by organic molecules and rare earth ions is assumed to be induced by an exchange resonance mechanism [131—135]. Ermolaev et al. [134] found that the energy transfer rate constants also depend on covalent interactions (directly or through a bridge-bond structure) and on Coulombic interactions when both donor and acceptor are charged species. Non-radiative energy transfer from rare earth ions to stable cation radicals of aromatic hydrocarbons has recently shown to proceed via dipole—dipole energy transfer [136].

The rate constant for the quenching of Tb^{3+} by anionic and cationic dyes strongly depends on the addition of CH_3COO^- ions [137]. This effect was attributed to a Tb^{3+} charge neutralization, resulting in a change in the ionic Coulombic interaction. Similar effects of added salts on the quenching rate constant between rare earth ions have also been reported [138, 139].

The rate constant for the luminescence quenching between rare earth ions was found to depend on the nature of the solvent and specifically on its chemical properties [140, 141].

Quenching experiments involving energy transfer from Tb^{3+} to Eu^{3+} via the excited state of 2-acetylnaphthalene have been reported [87] and a two-step intermolecular energy transfer process from 4,4′-dimethoxybenzophenone to Eu^{3+} ions via excited Tb^{3+} ions has also been studied [86].

The quenching ability by some organic ligands of the Ce^{3+} ion fluorescence in water was found to parallel the complexing ability of these ligands towards Ce^{3+} ions [142].

(c) Solid state systems

Quenching experiments in double salts containing coordination compounds have been carried out for a variety of systems. The mechanism of these processes is not yet clearly understood. Experiments which had first been taken as a proof of non-radiative intermolecular energy transfer from the cation to the anion in $[Cr(atp)_6][Cr(CN)_6]$ and similar systems at 77 K [62, 63] have later been reinterpreted by Kirk and Schläfer [65] in terms of a lattice influence on the luminescence properties. No energy tranfer seems also to occur in $Cr_xCo_{1-x}(CN)_6^{3-}$ mixed crystals at room temperature [66]. Similar experiments were carried out on Cr^{III} double salts [64] and more recently, on Cr^{III}—Co^{III} double salts [72]. Clear evidence for the participation of intermolecular energy transfer in quenching processes between Cr^{III} double salts at 80 K has been reported by Flint et al. [67, 68]. Evidence for energy transfer from $Co(CN)_6^{3-}$ to $Cr(CN)_6^{3-}$ in powder samples has been reported recently [73].

The quenching of the $Ru(dipy)_3^{2+}$ [69, 70] and $Rh(dipy)_3^{3+}$ [70] emission by some Cr^{III} complexes at 77 K has been studied by Fujita and Kobayashi. An intermolecular energy transfer mechanism was proposed where an efficient path for energy transfer was that from the ^1CT state of $Ru(dipy)_3^{2+}$ to the $^4T_{2g}$ state of the Cr^{III} complexes [70].

For more details on the systems dealt with in this Section, see Sect. B(ii)(c).

(v) Other quenching processes involving coordination compounds

(a) Introduction

In this section we consider the quenching of donor states by coordination compounds in which the quenching is apparently not accompanied either by sensitized photoreaction of the coordination complex or by sensitized emission from the quenching complex, for donors which are not themselves coordination complexes. The donors are principally organic triplet states, or singlet oxygen, and the mechanism of the quenching is frequently obscure.

The very few systems for which coordination complexes have been shown to act as donors to non-transition metal compounds, without observable quenching of a photoreaction or luminescence of the donor coordination complex are also covered in this section.

(b) Vanadium complexes

Vanadium(III) quenches the excited singlet state of riboflavin (E_S = 20.0 kK) with a rate constant of 4.6×10^9 M^{-1} s^{-1} at 30°C in water (*p*H 2.6) [10]. At this *p*H ca. 6% of the V^{III} may be present as VOH^{2+} ions. Riboflavin is photochemically reduced from the singlet state by Fe^{II} and the quenching by V^{III} may also involve electron transfer.

(c) Chromium complexes

The quenching of excited states of organic molecules by chromium ions and complexes is rarely accompanied by emission from the chromium species at room temperature. Triplet naphthalene (E_T = 21.3 kK) is quenched in water at room temperature by Cr_{aq}^{3+} with k_q 6.9×10^7 M^{-1} s^{-1} [143], but triplet acridine (E_T = 15.8 kK) is scarcely quenched ($k_q < 10^6$ M^{-1} s^{-1}) although the $Cr(ox)_3^{3-}$ complex quenches triplet acridine with $k_q = 6.1 \times 10^8$ M^{-1} s^{-1} [144]. Both these studies were made by measuring the decay of the organic triplet—triplet absorption following flash excitation. In 95% ethanol—water glasses at −196°C the phosphorescent lifetime for triplet perdeuteronaphthalene is dependent on the concentration of the added transition metal quenching ions, including Cr_{aq}^{3+}, suggesting that the effective quenching efficiency is dependent on the separation distance, and that energy transfer in this case is taking place over large distances [145]. In THF and THF—H_2O mixtures $CrCl_3$ quenches triplet anthracene (E_T = 14.9 kK), k_q falling rapidly as the concentration of water increases [146].

The quenching of a number of organic triplet donors in H_2O—C_2H_5OH and H_2O—THMF mixtures by Cr^{III} complex ions, $Cr(CN)_6^{3-}$, $Cr(NH_3)_2(NCS)_4^-$,

$Cr(urea)_6^{3+}$, $Cr(en)_3^{3+}$, $Cr(en)_2Cl_2^+$ and $Cr(NH_3)_5Cl^{2+}$ takes place at less than diffusion controlled rates [147] despite the fact that energy transfer should be quite favourable in many cases: triplet naphthacene, with a triplet energy of 10.3 kK well below the lowest acceptor levels of Cr^{III}, on the other hand, is not quenched. Similarly, in benzene solution $Cr(acac)_3$ quenches a number of organic triplets with near diffusion controlled rate [148]. In a careful study of the quenching of the fluorescent intensity of triplet riboflavin in water at pH 2.6 at 30°C, k_q for Cr_{aq}^{3+} was found to be 3.6×10^9 M^{-1} s^{-1}, with an activation energy of 1.8 kcal mol^{-1}. The process appears to be one of straightforward energy transfer [10].

Chromium ions or complexes quench a number of photochemical reactions or photosensitized reactions of organic molecules, both as donors and as substrates. The diethyl ketone sensitized oxidation of cumene, which arises from sensitization of an excited state of diethyl ketone, is quenched by $Cr(L\text{-}1)_3$ [149]. Chromium chelate complexes quench both the singlet and triplet states of benzophenone. The relative rates of the triplet quenching and the sensitized photoreduction of benzhydrol are 380 for $Cr(acac)_3$ and 45 for $Cr(DPM)_3$ in benzene [150], and organic quenchers with relative efficiencies of ca. 600 have been considered to quench at a diffusion controlled rate. The quenching efficiency of $Cr(DBM)_3$ is very high, the relative rate being of the order of 1520, suggesting that in this case the quenching is partly of the precursor singlet state of benzophenone. The complex also quenches the triplet benzophenone sensitized *cis*—*trans* isomerization of stilbene, which is diffusion controlled, under conditions where the concentration of stilbene is very much higher than that of the chromium complex, and this supports the view that the complex is able to quench singlet benzophenone [151].

(d) Manganese complexes

Manganese(II) has an energy level 18.9 kK above the ground state and because of the height of this level and the d^5 configuration which makes all transitions spin-forbidden, is frequently only a poor quencher. The large E^0 for Mn^{3+}, +1.56 V, reduces the possibility of quenching by electron transfer. In those cases in which Mn^{II} does act as a quencher its quenching efficiency is usually lower than that of other first-row transition metal ions such as Fe^{II} and Co^{II}.

Triplet—triplet absorption measurements showed that triplet naphthalene is quenched with k_q 2.8×10^7 M^{-1} s^{-1} in water and 1.6×10^7 M^{-1} s^{-1} in ethylene glycol and, although the authors consider this to be an example of a paramagnetically catalyzed spin conservation quenching process [143], the energy levels of triplet naphthalene (E_T = 21.3 kK) and Mn^{2+} (18.9 kK) are such that an energy transfer process may occur. Triplet anthracene (E_T = 14.9 kK) is quenched in pyridine (k_q 4.3×10^6 M^{-1} s^{-1}) and in tetrahydrofuran (k_q 1.3×10^6 M^{-1} s^{-1}) but the efficiency is noticeably lower in 40% H_2O—THF mixtures, where k_q is only 3.7×10^4 M^{-1} s^{-1} [146]. The rate constant for quenching the triplet state of tetraphenylporphyrin in pyridine is $< 5 \times 10^5$ M^{-1} s^{-1}, and in water the triplet β-naphtholsulphonic acid emission is reduced by about 11% by 10^{-2} M Mn^{2+} [146].

Triplet benzophenone (E_T = 24.3 kK) is quenched by Mn^{II} with k_q 8.3×10^7 M^{-1} s^{-1} in water; this result obtained from measurements of the decay of the phosphorescence, is in agreement with the reduction in the quantum yield for benzophenone photolysis at 254 nm from 0.05 to 0.005 in the presence of 10^{-3} M Mn^{2+} [152].

Triplet acridine (E_T = 15.8 kK) in 50% H_2O—ethanol mixtures is not quenched ($k_q < 10^5$ M^{-1} s^{-1}) by Mn^{2+} [144]. As energy transfer is not possible it appears that spin-catalyzed conversion is the only possible quenching mode, but that the efficiency must be very low, if it occurs at all. Mn^{2+} is similarly inefficient in quenching singlet riboflavin (E_S = 20 kK, k_q $< 4 \times 10^7$ M^{-1} s^{-1} in water at *p*H 2.6) [10] and singlet oxygen in 2-butoxyethanol at 0°C (E_S = 7.9 kK, $k_q < 10^6$ M^{-1} s^{-1}) [153].

In contrast to the quenching of triplet benzophenone, where Mn^{2+} has an efficiency close to that of Fe^{2+} and Co^{2+}, $Mn(DPM)_3$ is very much less efficient than the Co^{II}, Ni^{II} and Cu(II)—DPM complexes in quenching triplet benzophenone in benzene. The quenching rate constant was not measured, but the ratio of the k_q to the rate of the reaction of triplet benzophenone with benzhydrol is > 32 [150].

(e) Iron complexes

As with the other first-row transition metals, the limited solubilities of many iron complexes have restricted the number of complexes which can be used in quenching experiments with organic donors, and in many cases only iron(III) complexes have been used. Triplet naphthalene (E_T = 21.3 kK) and singlet riboflavin (E_S = 20.0 kK) in aqueous solution have been quenched by Fe^{2+}_{aq} or Fe^{3+}_{aq} ions. Fe^{2+}_{aq} ions quench triplet naphthalene in ethylene glycol solution with $k_q = 3.8 \times 10^7$ M^{-1} s^{-1}, just faster than the rate of quenching of the same donor in water by Fe^{3+}_{aq} ions, $k_q = 2.9 \times 10^7$ M^{-1} s^{-1} [143]. The only other comparison of quenching by Fe^{2+}_{aq} and Fe^{3+}_{aq} ions is the quenching of singlet riboflavin, in water at 30°C. The quenching rate constants were 3.6×10^9 M^{-1} s^{-1} (Fe^{2+}_{aq}) and 7.7×10^9 M^{-1} s^{-1} (Fe^{3+}_{aq}), but as the *p*H of the solutions was 2.6 it is exceedingly doubtful that the latter constant applies to the Fe^{3+}_{aq} ion. As k_q is so close to the diffusion controlled rate, and as the concentration of $FeOH^{2+}$ at this *p*H is about equal to that of Fe^{3+}_{aq}, it seems probable that the hydroxy species may quench the singlet riboflavin state about as efficiently as the aquo ion. For quenching by Fe^{2+}_{aq} the activation energy was 3.0 kcal mol^{-1}, and the rate was sensitive to the addition of glycerol to the solutions. It is noteworthy that there was some sensitized photooxidation of Fe^{2+} by the singlet riboflavin, and in ethanol glasses at 77 K, 0.1 M Fe^{2+} gave significant quenching of the riboflavin emission [10]. 3×10^{-3} M Fe^{2+} reduces the quantum yield for the disappearance of benzophenone (E_T = 24.0 kK) in water effectively to zero, indicating that Fe^{2+} is a better quencher of triplet benzophenone than Mn^{2+}, for which k_q is

8.3×10^7 M^{-1} s^{-1} and which reduces the quantum yield by 90% in 10^{-3} M solution [152].

In non-aqueous solvents a number of iron complexes quench organic donors with near diffusion controlled efficiency. In benzene, triplet 1-naphthaldehyde (E_T = 19.7 kK) is quenched by Fe(acac)$_3$ ($k_q = 2.7 \times 10^9$ M^{-1} s^{-1}) while Fe(DPM)$_3$ quenches triplet 1-naphthaldehyde and triplet benzophenone ($k_q = 9 \times 10^8$ M^{-1} s^{-1}, for both donors) [154]. These measurements were made by direct observation of the decay of the triplet—triplet absorption. Quenching of triplet benzophenone has also been studied from the effect of the metal complexes on the quantum yields for the sensitized reduction of benzhydrol, the ratio of k_q/k_r being 540 (Fe(acac)$_3$), 100 (Fe(DPM)$_3$), 550 (Fe(MAA)$_3$), and 860 (Fe(AC)$_3$) [150]. The ratio of the quenching efficiencies of the Fe(acac)$_3$ and Fe(DPM)$_3$ derived in this way is somewhat greater than that obtained by the direct method [150, 154]. Benzophenone is quenched so efficiently by Fe(DBM)$_3$ (relative efficiency 3400) that the precursor singlet benzophenone state must be quenched also [151]. For a range of organic donors with excited state energies ranging from 23.3 kK (triphenylene) to 14.9 kK (anthracene) in benzene, ferrocene is about equally effective as an acceptor, but Fe(acac)$_3$ shows a variation in quenching efficiency of a factor of 5 from phenanthrene ($k_q = 3.3 \times 10^9$ M^{-1} s^{-1}) to anthracene (7×10^8 M^{-1} s^{-1}). The increased efficiency of ferrocene may perhaps be due to the stereochemistry and the π-orbital system of the cyclopentadienyl rings [148].

Singlet O_2 generated in benzene by triplet anthracene photosensitization is quenched much less efficiently by ferrocene ($k_q = 9 \times 10^6$ M^{-1} s^{-1}). In this system the singlet O_2 concentration was monitored by the rate of disappearance of 1,3-diphenylisobenzofuran by its reaction with singlet O_2 [155].

(f) Cobalt complexes

The number of donors quenched without sensitized reaction or light emission is similar for iron and cobalt, solubilities limiting the types of acceptor which can be used to quench many organic donors. In water ($k_q = 5 \times 10^7$ M^{-1} s^{-1}) and ethylene glycol ($k_q = 4.4 \times 10^7$ M^{-1} s^{-1}) Co^{2+}_{aq} quenches triplet naphthalene (E_T = 21.3 kK) with the same efficiency [143]. For these relatively slow quenching reactions the solvent viscosity is of only minor importance in determining the quenching rate constant. In ethanol glasses at 77 K, Co^{2+} ions quench the emission from deuteronaphthalene with an efficiency which is dependent on the encounter distance and therefore on the concentration of Co^{2+} [145]. While Co^{2+}_{aq} quenches triplet acridine (E_T = 15.8 kK) in water with $k_q = 1 \times 10^7$ M^{-1} s^{-1}, the hexammine complex $Co(NH_3)_6^{2+}$ is much more efficient ($k_q = 3.6 \times 10^8$ M^{-1} s^{-1}). Both ions have energy levels below that of the triplet acridine, and the difference in the efficiencies may be due to the nephelauxetic effect [144]. Singlet riboflavin (E_S = 20.0 kK) is quenched by Co^{2+}_{aq} in water with much the same efficiency as other first row transition metal ions (k_q = 3.2 × 10^9 M^{-1} s^{-1}) and with an activation energy of 1.4 kcal mol^{-1} [10]. In a study of the quenching of triplet anthracene (E_T = 14.9 kK) in mixed solvents by $CoCl_2$ the efficiency was found to be markedly dependent on the water content [146]. The quenching rate constant in pure THF (2.1 × 10^8 M^{-1} s^{-1}) was almost the same as in pyridine (6.2 × 10^7 M^{-1} s^{-1}) and the fall in k_q with increasing water concentration was equally effective. The changes in solvation of the Co^{2+} ions are paralleled by changes in the absorption spectra, and suggest that the detailed ion-donor interaction is important for the quenching process. Zinc-tetraphenylporphyrin is quenched in pyridine with k_q = 1.4 × 10^6 M^{-1} s^{-1}, and Co^{2+} also quenches singlet β-naphtholsulphonic acid [146]. Singlet benzohydroquinone fluorescence is quenched by $Co(CN)_6^{3-}$ in water, with a rate constant which is *p*H independent between *p*H 1 and *p*H 6. The quoted rate constant for the quenching process is high (k_q = 1.3 × 10^{10} M^{-1} s^{-1}) but this is possibly due to the value which was estimated for the lifetime of singlet benzohydroquinone, of 5.5 × 10^{-9} s, from a comparison of the benzohydroquinone spectrum with that of indole, and may well be in error by a factor of ten or more. The activation energy for the quenching was 5.2 kcal mol^{-1}, which suggests that in water the process cannot have a rate constant of 1.3 × 10^{10} M^{-1} s^{-1}. The authors suggest that the quenching mechanism is one involving electron transfer to produce Co^{II} and the semi-quinone, but the evidence is not conclusive [36].

Tris-oxalato cobalt(III) ions quench triplet eosine (E_T ~ 14 kK) with an overall quenching rate constant of 9.2 × 10^9 M^{-1} s^{-1}. There is evidence that the quenching involves both energy transfer and a path (with a rate constant of 3.2 × 10^9 M^{-1} s^{-1}) which leads to bleaching of the eosine, and which may be due to electron transfer from triplet eosine to the cobalt complex [156].

In benzene, triplet benzophenone (E_T = 24.0 kK) is quenched by some cobalt complexes but not by all. $Co(acac)_3$ and $Co(DPM)_3$ are inefficient quenchers (the ratios of the quenching rate constant to that for the reduction of benzhydrol are 47 and ~ 0) but $Co(DPM)_2$ is as efficient as other complexes of this kind (quenching ratio 296) [150].

Singlet oxygen is quenched by $CoCl_2$ in 2-butoxyethanol at 0°C. The quenching rate constant is 4.8 × 10^7 M^{-1} s^{-1}. The energy of singlet O_2 is only ca. 8 kK and an energy transfer mechanism is probably involved [153].

(g) Nickel complexes

While nickel(II) ions quench triplet naphthalene (E_T = 21.3 kK) in water and ethylene glycol at the same rate (k_q in both solvents, 2.4 × 10^7 M^{-1} s^{-1}) [143], and have quenching efficiencies for triplet naphthalene which are similar to Co^{2+}, triplet acridine (E_T = 15.8 kK) is quenched somewhat better by Ni^{2+} ions in water (k_q = 3.4 × 10^7 M^{-1} s^{-1}) than by Co^{2+} ions [144]. Once again the quenching rate constant for quenching by the ammine complex is higher than that for the aquo ion (k_q = 3.3 × 10^8 M^{-1} s^{-1}), but the relative increase in efficiency from the aquo to the ammine complex is less than for Co^{2+}. The increased quenching efficiency of $Ni(NH_3)_6^{2+}$ has been attributed to increased orbital overlap between the donor and quencher [144]. The influence of solvation on the quenching of triplet anthracene and triplet tetraphenylporphyrin by Ni^{2+} ions parallels that for Co^{2+} ions; for anthracene, k_q is almost the same in pyridine (1.2×10^8 M^{-1} s^{-1}) and THF (1.6×10^8 M^{-1} s^{-1}) [146]. For triplet TPP the quenching efficiency is always smaller, but the fall with increasing water content is again apparent. The triplet state of the zinc—TPP complex is quenched with rate constants of 9.8×10^6 M^{-1} s^{-1} in pyridine and 2.5×10^7 M^{-1} s^{-1} in THF [146]. Singlet riboflavin (E_S = 20 kK) is quenched less effectively by Ni_{aq}^{2+} ions than by Fe_{aq}^{2+} or Co_{aq}^{2+} ions (k_q = 5.5×10^8 M^{-1} s^{-1}) and the activation energy for the quenching process is 1.5 kcal mol^{-1}. The quenching rate constant decreases as the viscosity of water—glycerol mixtures increases but, in view of the small activation energy and the rather low rate constant, the process cannot be unambiguously attributed to diffusion controlled quenching [10].

In benzene the $Ni(DPM)_2$ complex quenches the triplet state of benzophenone (E_T = 24.0 kK) with an efficiency (relative to the reduction of benzhydrol) of 246, about the same as that for the Co^{II} complex [150]. The same complex quenches triplet benzil (E_T = 18.8 kK) in benzene with a rate constant of 3×10^8 M^{-1} s^{-1} [148].

In a very careful comparative study [157] of the quenching of a number of triplet donors by a variety of planar nickel complexes ($Ni(S\text{-}1)_2$ to $Ni(S\text{-}5)_2$, see abbreviation list) in benzene, a definite correlation was found between the donor triplet energy and the quenching rate constants for these Schiff base complexes, and it was suggested that the quenching may be due to quenching by different energy levels in the complexes, as below a particular donor energy the quenching rate constant became almost constant at between one-half and one-third of that for the highest energy donor, benzophenone. The effect of spin and stereochemistry was investigated [157] with the paramagnetic Schiff base complex $Ni(S\text{-}6)_2$ for which k_q fell to less than 10^7 M^{-1} s^{-1} for 1,2-benzanthracene (E_T = 16.5 kK). A similar effect was found for the octahedral nickel complex $Ni(S\text{-}2)_2(py)_2$ and the authors attribute these effects to the quenching of the high-energy donors by triplet ligand states, for which there would be little steric hindrance for any of the complexes, while the lower-energy triplets are quenched by triplet ligand field levels, where the change from square planar to octahedral configuration would involve considerable reduction in orbital overlap between donor and acceptor (see also Sect. D(ii)(c)).

The quenching of triplet and singlet donor states by a number of Ni complexes which are of interest as stabilizers of polymers against UV degradation is of current interest. Quenching of excited states of diethyl ketone in solution and in glasses at 77 K by $Ni(L\text{-}1)_2$ is apparently independent of viscosity and temperature, the quenching effectiveness being similar in solution at room temperature and in the glass at 77 K [149]. In benzene the quenching of triplet ketones by nickel complexes has been measured by competition with the triplet sensitized isomerisation of piperylene [158]. The initial energy transfer step in the piperylene isomerization has a rate constant which is diffusion controlled (5 × 10^9 M^{-1} s^{-1}) and Ni(BTC)$_2$ quenches the excited ketones with about the same efficiency. It may also be possible for Ni(BTC)$_2$ to quench the singlet precursor state of the ketone. There is no correlation between the quenching efficiency and the magnetic moment of the complexes, and the relative efficiencies are Ni(BTC)$_2$ > Ni(L-1)(n-$C_4H_9NH_2$) > Ni(L-1)$_2$, with Ni(L-2)$_2$ being of about the same efficiency as Ni(L-1)(n-$C_4H_9NH_2$). Polypropylene is photostabilized by nickel oxime complexes and may involve energy transfer from the excited carbonyl group to the nickel complex [159].

Singlet O_2 is quenched by similar nickel compounds. Ni(acac)$_2$ and Ni^{2+} ions quench singlet O_2 with rate constants of 7.5 × 10^7 M^{-1} s^{-1} and 3.1 × 10^7 M^{-1} s^{-1} in butoxyethanol, and Ni(L-1)(n-$C_4H_9NH_2$), Ni(S-7)$_2$, Ni(BTC)$_2$, Ni(L-1)$_2$ and Ni(L-3)$_2$ quench singlet O_2 in a variety of solvents with rate constants between 10^9 and 10^7 [155]. The nickel complexes with sulphur donor ligands appear to be good quenchers of singlet O_2 in bromobenzene solution, the quenching efficiencies relative to the reaction of rubrene with singlet O_2 being 2.0 (Ni(BTC)$_2$), 1.0 (Ni(L-1)(n-$C_4H_9NH_2$)), 0.3 (Ni(L-1)$_2$), 0.1 (Ni(L-2)$_2$), 1.8 (Ni(TAA)$_2$) and 0.5 (Ni(acac)$_2$). The efficiencies parallel those for the quenching of ketone donors by the same complexes [160].

Quenching of singlet O_2 (the concentration of singlet O_2 was monitored by the disappearance of 1,3-diphenyl-iso-benzofuran, which reacts readily with singlet O_2) by Schiff base nickel complexes shows that they are as effective in quenching singlet O_2 as they are in quenching donors such as triplet benzophenone despite the very much lower donor energy for singlet O_2. The rates of quenching are effectively diffusion controlled for Ni(S-1)$_2$ and Ni(S-2)$_2$ (3 × 10^9 M^{-1} s^{-1} and 2.7 × 10^9 M^{-1} s^{-1}) approaching the quenching efficiency of β-carotene for which k_q is 1.3 × 10^{10} M^{-1} s^{-1} [155].

(h) Copper complexes

As with other transition metal ions in aqueous solution the only studies on quenching of organic donors in aqueous solutions involve triplet naphthalene and acridine, and singlet riboflavin. Cu_{aq}^{2+} ions quench triplet naphthalene (E_T = 21.3 kK) with the same rate constant in both water and ethylene glycol (k_q = 7.5 × 10^7 M^{-1} s^{-1}), but the diamagnetic copper(I)—cyano complex, $Cu(CN)_2^-$, has a very low or zero quenching efficiency (k_q = 0 ± 0.1 × 10^7 M^{-1} s^{-1}) [143]. Triplet acridine (E_T = 15.8 kK) is quenched by Cu_{aq}^{2+} ions at the same rate as triplet naphthalene (k_q = 7.4 × 10^7 M^{-1} s^{-1}) but the copper(II)—ammine complex, $Cu(NH_3)_4^{2+}$, is very much more efficient, with a quenching rate constant of 4 × 10^8 M^{-1} s^{-1}, and this, like the increased efficiency recorded for other ammine over aquo ions, is attributed to the nephelauxetic effect [144]. Cu_{aq}^{2+} is one of the most effective quenchers among the divalent first-row transition metal ions of singlet riboflavin (E_S =

20.0 kK), with a quenching rate constant of 1.2×10^9 M^{-1} s^{-1} and an activation energy of 3.0 kcal mol^{-1} [10].

In mixed solvent the quenching efficiency for triplet anthracene decreases with increasing water content, showing the same dependency on the ionic solvation for Cu^{2+} as for the other divalent transition metal ions [146]. The k_q is 4.6×10^8 M^{-1} s^{-1} in pyridine and 3.2×10^8 M^{-1} s^{-1} in THF. Similar quenching efficiencies have been found for triplet zinc-tetraphenylporphyrin, k_q being 1.2×10^8 M^{-1} s^{-1} in pyridine and 2×10^8 M^{-1} s^{-1} in THF. Cu^{2+} ions are reported to be far more effective than Mn^{2+} and Ni^{2+} ions in quenching triplet β-naphtholsulphonic acid [146]. In pyridine the Cu^{II} almost certainly exists principally as $Cu(py)_2^{2+}$, and this ion and the $Cu(en)^{2+}$ ion have about the same quenching rate constants (4.6×10^8 and 2.2×10^8 M^{-1} s^{-1}) for triplet anthracene (E_T = 14.9 kK). The phenanthroline complex, $Cu(phen)^{2+}$, is much more efficient, quenching triplet anthracene with a rate constant of 1.3×10^9 M^{-1} s^{-1}. It has been suggested that this is due to the more efficient charge transfer quenching mechanism by the more "conducting" phen ligand, but the effect may be due to other causes [161]. In ethanol glasses at 77 K Cu^{2+} ions are less efficient than Co^{2+} and Ni^{2+} ions in quenching triplet perdeuteronaphthalene, and the efficiency is concentration dependent [145].

The $Cu(DPM)_2$ complex quenches triplet benzophenone (E_T = 24.0 kK) in benzene solution with about half the efficiency of the corresponding Co^{II} and Ni^{II} complexes (the ratio of k_q to the rate of reduction of benzhydrol, is ca. 130) [150], and this complex is rather less efficient than $Cu(acac)_2$ in quenching a variety of triplet donors in benzene, where $Cu(acac)_2$ has almost diffusion controlled efficiency [148].

(i) Zinc complexes

As might be expected from the d^{10} configuration, Zn^{II} is not an efficient quencher, most complexes having neither appropriate energy levels nor spin states for quenching. The generalized heavy-metal quenching by external spin—orbit coupling appears to be quite inefficient for zinc, perhaps because the atomic number is still relatively low. Triplet naphthalene (E_T = 21.3 kK) and acridine (E_T = 15.8 kK) are not quenched by Zn^{2+} [143, 144] and in THF triplet anthracene (E_T = 14.9 kK) is quenched [146], if at all, with a maximum rate constant of 4×10^4 M^{-1} s^{-1}. It is likely that complexes such as Zn-porphyrins will act as acceptors, but in this case the effect is predominantly due to the organic moiety of the ligand. $Zn(BTC)_2$ does not apparently quench triplet ketones in benzene [158].

(j) Molybdenum complexes

Although triplet naphthalene (E_T = 21.3 kK) is quenched by $Mo(CN)_8^{4-}$ with accompanying sensitized aquation (Sect. B(i)), a 10^{-3} M solution of the complex reduces triplet biacetyl (E_T = 19.6 kK) emission by about 40% with no detectable reaction. The difference in the energies of triplet naphthalene and biacetyl is sufficient for the quenching to be through the $^3B_1$ state of the complex in the one case and through the unreactive $^3A_2$ state in the other [44].

(k) Rhodium complexes

Singlet riboflavin (E_S = 20.0 kK) is quenched by Rh^{3+} in water at a rate less than that of the other trivalent ions, Cr^{3+} and Fe^{3+} (k_q = 6.4 × 10^8 M^{-1} s^{-1}). The $Rh(NH_3)_6^{3+}$ complex (10^{-2} M) reduces the emission intensity from triplet biacetyl slightly (ca. 10%), and, as the estimated triplet level for the complex is 20.3 kK, and that for triplet biacetyl is 19.6 kK, the quenching may be due to exciplex formation or thermally activated energy transfer [47]. However, the extent of the quenching is small, and could be due to impurities. A full investigation of this system would be valuable in order to establish definitively the existence of an exciplex between an organic donor and a transition metal complex.

(l) Palladium complexes

For a *trans*-planar Schiff base complex, $Pd(S\text{-}8)_2$, the quenching of a number of triplet donors of varying energy is very similar [162] to the effect observed with planar Ni Schiff bases [157]. The quenching rate constants fall with donor energy and then become constant as quenching by triplet ligand states is replaced by quenching by triplet ligand field states of the metal [162]. Singlet O_2 is also quenched by $Pd(S\text{-}8)_2$, but the quenching efficiency is very much lower than that of the Ni^{II} complexes; k_q is 6 × 10^7 M^{-1} s^{-1}, only ca. one-hundredth of the rate of quenching by the Ni^{II} complexes [155].

(m) Platinum complexes

Quenching of triplet donors by platinum complexes is usually accompanied by sensitized reaction, but in one case quenching does not appear to bring about reaction. $Pt(C_2H_4)Cl_3^-$ photoaquates at the ethylene ligand, and the reaction is sensitized by triplet acetone and triplet acetophenone (Sect. B(i)(c)). Triplet biacetyl (E_T = 19.6 kK), however, is ineffective as a sensitizer, although a 5 × 10^{-5} M solution of the complex is sufficient to reduce the biacetyl emission by two-thirds [52].

(n) Mercury complexes

For heavy metals the general external spin—orbit coupling mode becomes a favourable mode for quenching, and the effect is to make quenching of singlet states very much more favourable than quenching of triplet states. In ethanol and benzene singlet anthracene is quenched at diffusion controlled rates by $Hg(CH_3)_2$ (k_q = 8.7 × 10^9 M^{-1} s^{-1} in ethanol and 1.47 × 10^{10} M^{-1} s^{-1} in benzene). Triplet anthracene quenching is very much less efficient and k_q is only 1.2 × 10^3 M^{-1} s^{-1} for $Hg(CH_3)_2$, in paraffin oil [163]. Hg^{2+} ions also quench the emission from copper-free azurin [164].

(o) Lanthanide complexes

In solution lanthanide metal ions tend to be rather poorer acceptors than first-row transition metal ions, even for similar conditions of relative energy of acceptor and donor, magnetic moment, and so on. This is probably due to the greater difficulty of orbital interactions between donor and the lanthanide *f* orbitals, and quenching via ligand-to-metal energy transfer or complex formation is common (see also Sects. B(ii)(d) and B(iv)(b)). In water the ions are relatively tightly solvated, and energy transfer via the ligands is virtually precluded. Gd^{3+} and Nd^{3+} quench triplet naphthalene (E_T = 21.3 kK) in ethylene glycol with quenching rate constants of 7×10^4 M^{-1} s^{-1} and 4×10^5 M^{-1} s^{-1}, very much less effectively than first-row transition metal ions of similar magnetic moment (Cr^{3+} has a magnetic moment almost the same as that of Gd^{3+}, but the quenching rate constant is 7×10^7 M^{-1} s^{-1}) [143]. $GdCl_3$, $SmCl_3$ and $PrCl_3$ quench triplet anthracene (E_T = 14.9 kK) in pyridine with rates of less than 10^5 M^{-1} s^{-1} (k_q for Co^{2+} is 100 times larger) and the same ions are poor quenchers of chlorophyll [146, 165]. Triplet β-naphtholsulphonic acid is quenched somewhat more effectively by these ions [146]. Ce^{3+} ions quench singlet riboflavin (E_S = 20.0 kK) in water (*p*H 2.6) with a k_q of 1.3×10^8 M^{-1} s^{-1} [10].

In benzene solutions, the tris DPM complexes of Gd, Er and La quench triplet benzophenone (E_T = 24.0 kK) with efficiencies (relative to the reduction of benzhydrol) which are about the same as that of $Co(DPM)_3$ (31, 30 and 28, respectively) [150]. For a number of nucleotides and bases energy transfer to Eu^{3+} results in sensitized fluorescent emission, but tryptophan is quenched at a diffusion controlled rate (k_q = 5×10^9 M^{-1} s^{-1}) without emission by the Eu^{3+} [90]. The effects of solvation are so marked for quenching by lanthanide ions that comparisons between donors can be completely masked by the use of different solvents. The photoelimination from triplet *p*-methoxyvalerophenone is quenched in methanol with relative efficiencies much less than that of the diffusion controlled quenching by 2,5-dimethyl-2,4-hexadiene, the Stern—Volmer constants being 50 ($SmCl_3$), 375 ($EuCl_3$), 62 ($TbCl_3$), 75 ($DyCl_3$) and 70 ($ErCl_3$) M^{-1}, which are 30 to 200 times smaller than that for the diene. The higher efficiency of Eu is perhaps due to the possibility of quenching by an electron transfer process in this case. Similar results have been observed for the quenching of the reduction of triplet benzophenone [93].

The quenching of the donor emission and lifetimes for singlet and triplet acridine yellow, perylene and anthracene in acetone do not always lead to the same Stern—Volmer slopes, and in some cases the Stern—Volmer plots are curved, suggesting that the quenching mechanism for these donors by a variety of lanthanide ions may not be simple. The singlet quenching rates are several orders of magnitude higher than the quenching rate constants for the triplet states of the donors, and a variety of mechanisms has been invoked to explain the different quenching efficiencies [166]. For quenching by Eu^{3+} of a very wide range of donors the quenching rate constants appear to be related to the ionization potential of the singlet state which is quenched, suggesting that the quenching takes place by electron transfer to produce a cation radical and Eu^{2+} with high efficiency. In the case of perylene, the perylene cation radical has been observed following flash photolysis of perylene in the presence of Eu^{3+}, under conditions in which perylene alone does not yield the cation, and these experiments are a direct proof of the quenching by electron transfer in this case [167].

For aromatic ketones on the other hand, quenching by lanthanide ions in acetone is related to the magnitude of the exchange overlap integral, and this may imply that the mechanism of energy transfer is one of exchange resonance, although the integral is small for Ce^{3+}, and the authors suggest an electron transfer mechanism in this case [168].

The importance of the solvent in quenching studies using lanthanide metal ions is indicated by the fact that the quenching rate constant for triplet diphenyl ketone and derivatives quenched by Eu^{3+} decreases in going from dimethyl ketone to methanol as solvent, as the ions are more solvated in methanol, and the extent of orbital overlap possible for interaction with the donor is reduced [79].

(p) Transition metal complexes as donors

There are very few examples of processes involving energy transfer from transition metal complexes as donors and non-metal species as acceptors without observable quenching of a photoreaction or luminescence of the complex. Ferrocene causes sensitization of the isomerization and dimerization of olefins and the systems are markedly solvent dependent. In benzene, the photochemical stationary state *cis/trans* ratio for piperylene is 0.82 [169], but in *trans*-1,2-dimethylcyclohexane the ratio is 0.41 [170]. While it has been suggested [169] that absorption by a ground-state ferrocene—olefin complex may be responsible for the photosensitization, energy transfer from ^3E_g ferrocene to a triplet state of the olefin is a more probable mechanism [170].

By comparing the yields for sensitized delayed fluorescence by a number of acceptors from the triplet charge transfer state of $Cu(2,9\text{-dmp})^+$, the energy of the lowest triplet charge-transfer state has been established as 13.8 kK. Comparison with donors of known intersystem crossing efficiency also indicates that the intersystem crossing from the singlet charge transfer to the triplet charge transfer state for $Cu(2,9\text{-dmp})^+$ in ethanol is about 0.25, and that internal conversion to the ground state is the principal mode of deexcitation of the singlet charge transfer state [171]. These results, however, are reported in a short communication from which it is impossible to know whether all the necessary conditions were met (light absorbed only by the donor; equal exciting light intensities for the "standard" molecules and the complex of interest; complete quenching of the donor triplets; the same rate constants for the quenching of the "standard" molecules and the complex by the selected acceptors; quenching occurring only by energy transfer).

TABLE 2

Quenching of excited states by coordination compounds

Quencher [a]	Excited molecule [a]	Observed phenomena [b]	Ref.
Vanadium			
V^{3+} [c]	riboflavin	D_f	10
Chromium			
$Cr(CO)_6$	benzophenone	Q_r	38
Cr^{3+} [c]	anthracene	D_T	146
	naphthalene	D_T	143
	$C_{10}D_8$	D_p	145
	riboflavin	D_f	10
$Cr(urea)_6^{3+}$	anthracene	D_T	147
	benzil	D_p	58
	chrysene	D_T	147
	naphthalene	D_T	147
	triphenylene	D_T	147
$Cr(NH_3)_6^{3+}$	$Co(CN)_6^{3-}$	Q_l	71, 72
	naphthalene	Q_r	6
$Cr(NCS)_6^{3-}$	$Cr(urea)_6^{3+}$	Q_p	64
	$Cr(en)_3^{3+}$	Q_p	64
	$Ru(dipy)_3^{2+}$	Q_p	172
	anthracene	Q_p	58
	benzil	Q_p, D_p	58, 59
	biacetyl	Q_r	9
	erythrosin	Q_p, D_p	59
$Cr(CN)_6^{3-}$	$Cr(atp)_6^{3+}$	Q_p, D_f	63, 65
	$Cr(imid)_6^{3+}$	Q_p, D_p	63
	$Cr(NH_3)_6^{3+}$	Q_p, D_p	63
	$Cr(urea)_6^{3+}$	Q_p, D_l	62, 63
	$Cr(en)_3^{3+}$	Q_p, D_p	63
	$Cr(pn)_3^{3+}$	Q_p, D_p	63
	$Cr(tn)_3^{3+}$	Q_p, D_p	63
	$Cr_xCo_{n-x}(CN)_6^{3-}$	D_p	66, 73
	$t\text{-}Cr(NCS)_4(NH_3)_2^-$	Q_p, D_r, D_p	60, 97
	Zn-UP	D_T, D_r	14
	$Ru(dipy)_3^{2+}$	Q_p, D_p	12, 13, 61, 70, 111–113
	$Rh(dipy)_3^{3+}$	Q_p, D_p	70
	acridine	Q_r	13
	anthracene	Q_p, D_T	58, 147
	benzil	Q_p, D_p	58

TABLE 2 (continued)

	chrysene	D_T	147
	eosin	D_T	147
	erythrosin	Q_p	13
	naphthalene	Q_p, D_T, D_f	13, 147
	pyrazine	Q_r	12, 13
	triphenylene	D_T	147
	xanthone	Q_r	12, 13
$Cr(acac)_3$	2-acetonaphthone	D_T	148
	anthracene	Q_p, D_T	58, 148
	benzil	Q_p, D_p, D_T	58, 148
	benzophenone	D_r	150
	benzanthrone	D_T	148
	fluorenone	D_T	148
	erythrosin	D_p	59
	triphenylene	D_T	148
$Cr(DBM)_3$	benzophenone	D_c	151
$Cr(dipy)_3^{3+}$	$Ru(dipy)_3^{2+}$	D_p	173
$Cr(DPM)_3$	benzophenone	D_r	150
$Cr(en)_3^{3+}$	$Co(CN)_6^{3-}$	Q_l	72
	$Ru(dipy)_3^{2+}$	D_p	111, 173
	anthracene	Q_p, D_T	58, 147
	benzil	Q_p, D_p	58
	biacetyl	Q_p, Q_r, D_p	11
	naphthalene	D_T	147
c-$Cr(fba)_3$	methyl *o*-benzyloxyphenylglyoxylate	Q_r, D_r	16
$Cr(L\text{-}1)_3$	diethylketone	D_c	149
$Cr(mal)_3^{3-}$	$Cr(urea)_6^{3+}$	Q_p	64
	$Cr(en)_3^{3+}$	Q_p	64
	$Ru(dipy)_3^{2+}$	Q_p, D_p	70, 111
$Cr(ox)_3^{3-}$	$Ru(dipy)_3^{2+}$	Q_p, Q_r, D_p	15, 69, 70, 111
	acridine	D_T	144
$Cr(8\text{-}quinO)_3$	erythrosin	D_p	59
$Cr(NH_3)_5Cl^{2+}$	$Cr(NH_3)_6^{3+}$	Q_p, D_p	67, 68
	anthracene	D_T	147
	naphthalene	Q_r, D_T	6, 147
	riboflavin	Q_r, D_f	7
$Cr(NH_3)_5Br^{2+}$	$Cr(NH_3)_6^{3+}$	Q_p, D_p	68
$Cr(NH_3)_5I^{2+}$	$Cr(NH_3)_6^{3+}$	Q_p, D_p	68
$Cr(NH_3)_5(NO_3)^{2+}$	$Cr(NH_3)_6^{3+}$	Q_p, D_p	68
$Cr(NH_3)_5(NCS)^{2+}$	acridinium ion	Q_r, D_f	8, 9

TABLE 2 (continued)

Quenching of excited states by coordination compounds

Quencher [a]	Excited molecule [a]	Observed phenomena [b]	Ref.
	biacetyl	Q_r, D_p	8, 9
	Michler's ketone	Q_r	9
	riboflavin	Q_r, D_f	7, 10
t-$Cr(NCS)_4(NH_3)_2^-$	anthracene	D_T	147
	biacetyl	Q_r	9
	benzil	Q_p, D_p	59
	crysene	D_T	147
	erythrosin	Q_p, D_p	59
	methylene blue	Q_r	9
	naphthalene	D_T	147
	triphenylene	D_T	147
$Cr(NCS)_4(aniline)_2^-$	benzil	Q_p, D_p	59
	erythrosin	Q_p, D_p	59
t-$Cr(en)_2F_2^+$	$Ru(dipy)_3^{2+}$	D_p	113
t-$Cr(en)_2Cl_2^+$	$Ru(dipy)_3^{2+}$	D_p	113
c-$Cr(en)_2Cl_2^+$	$Ru(dipy)_3^{2+}$	D_p	113
	naphthalene	D_T	147
t-$Cr(en)_2Br_2^+$	$Ru(dipy)_3^{2+}$	D_p	113
t-$Cr(en)_2(NCS)_2^+$	$Ru(dipy)_3^{2+}$	Q_p, D_p	113
c-$Cr(en)_2(NCS)_2^+$	$Ru(dipy)_3^{2+}$	D_p	113
t-$Cr(en)_2(NCS)Cl^+$	$Ru(dipy)_3^{2+}$	D_p	113
c-$Cr(en)_2(NCS)Cl^+$	$Ru(dipy)_3^{2+}$	D_p	113
Manganese			
Mn^{2+} [c]	UO_2^{2+}	D_l, D_r	100
	benzophenone	D_p, D_r	152
	chlorophyll	D_T	165
	naphthalene	D_T	143
$Mn(CN)_6^{3-}$	Zn-UP	D_T, D_r	14
$Mn(DPM)_3$	benzophenone	D_r	150
Iron			
ferrocene	$^1O_2$	D_c	155
	2-acetonaphthone	D_T	148
	anthrone	D_T	148
	benzanthrone	D_T	148
	benzil	D_T	148
	fluorenone	D_T	148
	naphthalene	Q_r, D_f	39
	triphenylene	D_T	148
styrylferrocene	benzophenone	Q_r	40

TABLE 2 (continued)

Fe^{2+} [c]	$Cr(en)_3^{3+}$	D_r, D_p	95, 103
	$Ru(dipy)_3^{2+}$	Q_r, D_p, D_r	114, 115
	UO_2^{2+}	D_l	174
	$^1O_2$	Q_r	41
	benzophenone	D_r	152
	naphthalene	D_T	143
	riboflavin	D_f	10
$Fe(CN)_6^{4-}$	Zn-UP	D_T, D_r	14
c-$Fe(CNCH_3)_4(CN)_2$	biacetyl	Q_r, D_p	42a
t-$Fe(CNCH_3)_4(CN)_2$	biacetyl	Q_r, D_p	42a
Fe^{3+} [c]	naphthalene	D_T	143
	riboflavin	Q_r, D_f	10
$Fe(CN)_6^{3-}$	Zn-UP	D_T, D_r	14
$Fe(AC)_3$	benzophenone	D_c	150
$Fe(acac)_3$	2-acetonaphthone	D_T	148
	anthracene	D_T	148
	benzanthrone	D_T	148
	benzil	D_T	148
	benzophenone	D_c	150
	fluorenone	D_T	148
	naphthalene	D_T	148
	1-naphthaldehyde	D_T	154
	phenanthrene	D_T	148
$Fe(DBM)_3$	benzophenone	D_c	151
$Fe(DPM)_3$	benzophenone	D_c, D_T	150, 154
	1-naphthaldehyde	D_T	154
$Fe(MAA)_3$	benzophenone	D_c	150
$Fe(ox)_2^-$	$Ru(dipy)_3^{2+}$	D_p	15
$Fe(HEDTA)(H_2O)$	$Ru(dipy)_3^{2+}$	D_p	30
Cobalt			
Co^{2+} [c]	$Cr(en)_3^{3+}$	D_p, D_r	95, 103
	UO_2^{2+}	D_l, D_r	100
	Zn-TPP	D_T	146
	$^1O_2$	D_c	153
	acridine	D_T	144
	anthracene	D_T	146
	chlorophyll	D_T	165
	naphthalene	D_T	143
	$C_{10}D_8$	D_p	145
	β-naphtholsulphonic acid	D_f	146
	riboflavin	D_f	10

TABLE 2 (continued)

Quenching of excited states by coordination compounds

Quencher [a]	Excited molecule [a]	Observed phenomena [b]	Ref.
$Co(NH_3)_6^{2+}$	acridine	D_T	144
$Co(DPM)_2$	benzophenone	D_c	150
$Co(NH_3)_6^{3+}$	$Ru(dipy)_3^{2+}$	D_p	25
	benzophenone	Q_r	19
	biacetyl	Q_r, D_p	19—21
	biphenyl	Q_r	20
	naphthalene	Q_r, D_f	18
	quinoline	Q_r, D_f	21
	t-stilbene-4-carboxylic acid	Q_r	19
$Co(CN)_6^{3-}$	Zn-UP	D_c	14
	UO_2^{2+}	Q_r, D_i	35
	acetone	Q_r	34
	benzohydroquinone	Q_r, D_f	36
	biacetyl	Q_r, D_p	32—34
$Co(acac)_3$	benzophenone	D_c	150
$Co(ox)_3^{3-}$	$Ru(dipy)_3^{2+}$	Q_r, Q_p	15, 111
	eosin	D_p, D_r	156
$Co(phen)_3^{3+}$	phen	Q_r, D_f	37
$Co(EDTA)^-$	$Ru(dipy)_3^{2+}$	Q_r, D_p	24, 29—31
$Co(NH_3)_5(OCHO)^{2+}$	benzophenone	Q_r	28
$Co(NH_3)_5(H_2O)^{3+}$	$Ru(dipy)_3^{2+}$	D_p	25
	benzil	Q_r	19
	benzophenone	Q_r	19, 28
	t-stilbene-4-carboxylic acid	Q_r	19
$Co(NH_3)_5Cl^{2+}$	$Ru(dipy)_3^{2+}$	Q_r	22, 25
$Co(NH_3)_5Br^{2+}$	$Ru(dipy)_3^{2+}$	Q_r, D_p	22—25
$Co(NH_3)_5(NO_2)^{2+}$	acetone	Q_r	26
	benzaldehyde	Q_r	26
	biacetyl	D_p	26
	biphenyl	Q_r	26
$Co(CN)_5(H_2O)^{2-}$	biacetyl	D_p	33, 34
$Co(CN)_5(NCS)^{3-}$	biacetyl	Q_r, D_p	34
$Co(CN)_5(N_3)^{3-}$	biacetyl	Q_r, D_p	34
$Co(CN)_5(py)^{2-}$	biacetyl	D_p	34
$Co(CN)_5(CH_3CN)^{2-}$	biacetyl	D_p	34
$Co(HEDTA)Cl^-$	$Ru(dipy)_3^{2+}$	Q_r, D_p	22, 24, 29, 31

TABLE 2 (continued)

$Co(HEDTA)Br^{-}$	$Ru(dipy)_3^{2+}$	Q_r, D_p	24, 29, 31
$Co(HEDTA)(NO_2)^{-}$	$Ru(dipy)_3^{2+}$	Q_r, D_p	29, 31
Nickel			
Ni^{2+} [c]	Zn-TPP	D_T	146
	c-Pt(gly)$_2$	D_r	51
	$^1O_2$	D_c	153
	acridine	D_T	144
	anthracene	D_T	146
	chlorophyll	D_T	165
	naphthalene	D_T	143
	$C_{10}D_8$	D_p	145
	riboflavin	D_f	10
	TPP	D_T	146
$Ni(NH_3)_6^{2+}$	acridine	D_T	144
Ni(acac)$_2$	$^1O_2$	D_c	153, 160
Ni(BTC)$_2$	$^1O_2$	D_c	153, 160
	benzophenone	D_c	158
	4-methylpentanone	D_c	158
Ni(DPM)$_2$	benzil	D_T	148
	benzophenone	D_f	150
Ni(gly)$_2$	$Ru(dipy)_3^{2+}$	D_p	113
Ni(TAA)$_2$	$^1O_2$	D_c	160
Ni(L-1)$_2$	$^1O_2$	D_c	153, 160
	benzophenone	D_c	158
	diethylketone	D_c, D_p	149
	4-methylpentanone	D_c	158
Ni(L-1)(n-$C_4H_9NH_2$)	$^1O_2$	D_c	153, 160
	benzophenone	D_c	158
	4-methylpentanone	D_c	158
Ni(L-2)$_2$	$^1O_2$	D_c	160
	benzophenone	D_c	158
	4-methylpentanone	D_c	158
Ni(L-3)$_2$	$^1O_2$	D_c	153
Ni(S-1)$_2$	$^1O_2$	D_c	155
	arenes	D_T	157
	benzophenone	D_T	157
	methylene blue	D_T	157
Ni(S-2)$_2$	$^1O_2$	D_c	155
	arenes	D_T	157, 162
	benzophenone	D_T	157, 162
	methylene blue	D_T	157

TABLE 2 (continued)

Quenching of excited states by coordination compounds

Quencher [a]	Excited molecule [a]	Observed phenomena [b]	Ref.
$Ni(S\text{-}2)_2(py)_2$	arenes	D_T	157
$Ni(S\text{-}3)_2$	arenes	D_T	157
	benzophenone	D_T	157
$Ni(S\text{-}4)_2$	arenes	D_T	157
	benzophenone	D_T	157
$Ni(S\text{-}5)_2$	arenes	D_T	157
	benzophenone	D_T	157
	methylene blue	D_T	157
$Ni(S\text{-}6)_2$	arenes	D_T	157
	benzophenone	D_T	157
$Ni(S\text{-}7)_2$	$^1O_2$	D_c	153
Copper			
$Cu(CN)_2^-$	naphthalene	D_T	143
Cu^{2+} [c]	Zn-TPP	D_T	146
	$Ru(phen)_2(CN)_2$	D_p	116
	UO_2^{2+}	D_r, D_l	100
	acridine	D_T	144
	anthracene	D_T	146
	azurin	D_l	164
	chlorophyll	D_T	165
	naphthalene	D_T	143
	$C_{10}D_8$	D_p	145
	β-naphtholsulphonic acid	D_p	146
	pyO	D_r	175
	riboflavin	D_f	10
$Cu(NH_3)_4^{2+}$	acridine	D_T	144
$Cu(acac)_2$	2-acetophenone	D_T	148
	anthracene	D_T	148
	benzanthracene	D_T	148
	benzil	D_T	148
	fluorenone	D_T	148
	triphenylene	D_T	148
$Cu(DPM)_2$	2-acetophenone	D_T	148
	anthracene	D_T	148
	benzophenone	D_c	150
$Cu(en)Cl_2$	anthracene	D_T	161
$Cu(phen)Cl_2$	anthracene	D_T	161

TABLE 2 (continued)

$Cu(py)_2Cl_2$	anthracene	D_T	161
$Cu(mal)_2(H_2O)_2^{2-}$	$Fe(ox)_3^{3-}$	Q_r	176
$Cu(mal)(SO_4)(H_2O)_3^{2-}$	$Fe(ox)_3^{3-}$	Q_r	176
$Cu(DDQ)_2$	biacetyl	Q_r, D_p	43
Zinc			
Zn-EP	Zn-EP	D_l	128, 129
Niobium			
$Nb^{3+\ c}$	$Eu^{3+\ c}$	D_l	134
	$Tb^{3+\ c}$	D_l	134
	aromatic ketones	D_p	134
Molybdenum			
$Mo(CN)_8^{4-}$	$Ru(dipy)_3^{2+}$	D_p	117
	anthraquinone	Q_r	44
	benzophenone	Q_r	44
	biacetyl	D_p	44
	naphthalene	Q_r	44
	phenanthrene	Q_r	44
Ruthenium			
$Ru(NH_3)_6^{3+}$	$Ru(dipy)_3^{2+}$	Q_r, D_p, D_r	25
$Ru(NH_3)_5Cl^{2+}$	$Ru(dipy)_3^{2+}$	Q_r, D_p, D_r	25
$Ru(dipy)_2$- (c-4-stilbazole)$_2^{2+}$	Zn-EP	Q_r, D_T	45, 46
	EP	Q_r, D_T	45, 46
	Michler's ketone	Q_r	45, 46
$Ru(dipy)_2$- (t-4-stilbazole)$_2^{2+}$	Zn-EP	Q_r, D_T	45, 46
	EP	Q_r, D_T	45, 46
	Mickler's ketone	Q_r	45, 46
Rhodium			
$Rh^{3+\ c}$	riboflavin	D_f	10
$Rh(NH_3)_6^{3+}$	pyrazine	Q_r	47
$Rh(NH_3)_5Cl^{2+}$	biacetyl	Q_r, D_p	48
$Rh(NH_3)_5Br^{2+}$	biacetyl	Q_r, D_p	48
$Rh(NH_3)_5I^{2+}$	biacetyl	Q_r, D_p	48
$Rh(NH_3)_4I_2^{+}$	biacetyl	Q_r, D_p	48
Palladium			
Pd-MP	Pd-MP	D_l	129
$Pd(S\text{-}8)_2$	$^1O_2$	D_r	155
	acridine	D_T	162
	anthracene	D_T	162
	1,2-benzanthracene	D_T	162
	benzophenone	D_T	162

TABLE 2 (continued)

Quenching of excited states by coordination compounds

Quencher [a]	Excited molecule [a]	Observed phenomena [b]	Ref.
	chrysene	D_T	162
	1,2,3,4-dibenzanthracene	D_T	162
	1,2,5,6-dibenzanthracene	D_T	162
	phenanthrene	D_T	162
	pyrene	D_T	162
Silver			
Ag^{+} [c]	azurin	D_l	164
Lanthanum			
$La(DPM)_3$	benzophenone	D_c	150
Iridium			
$IrCl_6^{3-}$	$Ru(dipy)_3^{2+}$	D_p	117
Platinum			
$PtCl_4^{2-}$	$Ru(dipy)_3^{2+}$	Q_r, D_p	50, 117
	biacetyl	Q_r, D_p	49
$Pt(gly)_2$	biacetyl	D_l	51
	pyrazine	Q_r	51
	xanthone	Q_r	51
$Pt(C_2H_4)Cl_3^{-}$	acetone	Q_r	52
	acetophenone	Q_r	52
	biacetyl	D_p	52
Pt-EP	Pt-EP	D_l	129
Mercury			
$Hg(CH_3)_2$	anthracene	D_f, D_T	163
Hg^{+} [c]	UO_2^{2+}	D_l, D_r	100
Hg^{2+} [c]	azurin	D_l	164
Cerium			
Ce^{3+} [c]	rare earth ions or complexes	D_l	136, 177
	2-acetonaphthone	D_T	168
	riboflavin	D_f	10
Praseodymium			
Pr^{3+} [c]	Eu^{3+} and Sm^{3+} complexes	D_l	177
	rare earth ions	D_l	132, 178
	2-acetonaphthone	D_T	168
	acridine yellow	D_f	166
	anthracene	D_l	146, 166

TABLE 2 (continued)

	9-anthrylmethylketone	D_T	168
	perylene	D_f	166
	4-phenylbenzophenone	D_T	168
Neodymium Nd^{3+} [c]	Eu^{3+} and Sm^{3+} complexes	D_I	177
	rare earth ions	D_I	132, 138–141, 178
	2-acetonaphthone	D_T	168
	acridine yellow	D_f	166, 167
	anthracene	D_I	166
	9-anthrylmethylketone	D_T	168
	chlorophyll	D_T	165
	naphthalene	D_T	143
	perylene	D_I	166
	4-phenylbenzophenone	D_T	168
Samarium Sm^{3+} [c]	rare earth ions	D_I	132, 178
	2-acetonaphthone	Q_I, D_T	80, 168
	acetophenone and derivatives	Q_I	57, 75, 88
	acridine yellow	D_f	166
	aldehydes	Q_I	57, 88
	anthracene	D_f	166
	9-anthrylmethylketone	D_T	168
	benzophenone and derivatives	Q_I	57, 80
	flavone	Q_I	88
	p-MVP	D_r	93
	4-phenylbenzophenone	D_T	168
Europium Eu^{3+} [c]	rare earth ions	Q_I, D_I	86, 138–140, 178, 179
	UO_2^{2+}	Q_I, D_I	81
	1- and 2-acetonaphthone	Q_I, D_I, D_T	57, 76, 77, 80, 87, 88, 168, 180
	acetophenone and derivatives	Q_I, D_c	57, 74–78, 80, 88, 90, 91

TABLE 2 (continued)

Quenching of excited states by coordination compounds

Quencher [a]	Excited molecule [a]	Observed phenomena [b]	Ref.
	2- and 9-acetylfluorene	Q_l, D_l	88, 180
	3- and 9-acetylphenanthrene	Q_l	88
	2-acetylthiophene	Q_l	88
	acridine yellow	D_f	166
	aldehydes	Q_l	57, 76, 80, 88
	anthracene and derivatives	D_f	166, 167
	aromatic hydrocarbons	D_f	167
	benzophenone and derivatives	Q_l, D_p, D_c	57, 74—80, 91, 168
	benzoylpyridine	Q_l, D_c	78, 80
	deoxybenzoin	Q_l	76
	dyes	Q_l, D_f	167, 181
	flavone	Q_l	88
	p-MVP	D_r	93
	2,5-NSNa$_2$	D_f	91
	nucleotides	Q_l	90—92
	orotic acid	Q_l, D_r	14, 90—92
	perylene	D_f	166, 167
	propiophenone	Q_l	74
	tryptophan	Q_l, D_f	90, 91
	uridine monophosphate	Q_l,	14
	various aromatic ketones	Q_l	134, 182
Eu(DBM)$_3$	La(DBM)$_3$	Q_l, D_l	183
	amines	Q_l, D_l	184
Eu(EDTA)$^-$	*p*-benzoylbenzoate	Q_l	185
Eu(HFA)$_3$	acetophenone	Q_l	83
	benzaldehyde	Q_l	83
	benzophenone	Q_l, D_p	82, 83
Eu(TTA)$_3$(phen)	naphthalene	Q_l	84, 85
	2-naphthol, methyl ether	Q_l	84
	2-naphthylketone	Q_l	84
Gadolinium			
Gd^{3+} [c]	acetophenone	D_c	78
	2-acetonaphthone	D_l	168
	acridine yellow	D_f	166

TABLE 2 (continued)

	anthracene	D_T	146
	benzophenone and derivatives	D_c	78
	benzoylpyridine	D_c	78
	naphthalene	D_T	143
$Gd(DPM)_3$	benzophenone	D_r	150
Terbium			
Tb^{3+} [c]	acetophenone and derivatives	Q_l, D_c	57, 74, 75, 78—80, 88, 90
	9-acetylfluorene	Q_l	88
	2-acetylthiophene	Q_l	88
	aldehydes	Q_l	57, 79, 88
	benzophenone and derivatives	Q_l, D_r, D_c	57, 74, 77—80, 86, 89, 90, 168
	benzoylpyridine	D_c	78
	deoxybenzoin	Q_l	79
	dyes	Q_l	181
	flavone and derivatives	Q_l	57, 88
	methoxy benzoic acids	Q_l	88
	p-MVP	D_r	93
	propiophenone	Q_l	74
	tryptophan	Q_l, D_f	90
	various aromatic ketones	Q_l	182
Dysprosium			
Dy^{3+} [c]	Nd^{3+} [c]	D_l	178
	acetophenone and derivatives	Q_l	57, 75, 88
	anthracene	D_f	166
	aldehydes	Q_l	57
	benzophenone and derivatives	Q_l	57
	p-methoxy benzoic acids	Q_l	88
	p-MVP	D_r	93
Holmium			
Ho^{3+} [c]	rare earth ions	D_l	132, 138—140, 177, 178

TABLE 2 (continued)

Quenching of excited states by coordination compounds

Quencher[a]	Excited molecule[a]	Observed phenomena[b]	Ref.
Holmium			
	2-acetonaphtone	D_T	168
	acridine yellow	D_f	166
	9-anthrylmethylketone	D_T	168
	perylene	D_f	166
	4-phenylbenzophenone	D_T	168
Erbium			
Er^{3+} [c]	rare earth ions	D_l	132
	2-acetonaphthone	D_T	168
	acridine yellow	D_f	166
	anthracene	D_f	166
	9-anthrylmethylketone	D_T	168
	p-MVP	D_r	93
$Er(DPM)_3$	benzophenone	D_r	150
Ytterbium			
Yb^{3+} [c]	9-anthrylmethylketone	D_T	168
Uranium			
U^{4+} [c]	UO_2^{2+}	D_l	125
UO_2^{2+}	UO_2^{2+}	D_l	174

[a] For the abbreviations used see the list at the beginning of the article. [b] Q, quencher; Q_r, reaction of the quencher; Q_l, quencher luminescence; Q_f, quencher fluorescence; Q_p, quencher phosphorescence; D, excited molecule (donor); D_r, reaction of the donor; D_l, quenching of the donor luminescence; D_f, quenching of the donor fluorescence; D_p, quenching of the donor phosphorescence; D_T, quenching of the donor triplet state measured by triplet—triplet absorption; D_c, quenching of the sensitizer ability of the donor (from competition experiments). [c] The actual species present in the solution depends on the nature of the counter ion and solvent.

TABLE 3

Quenching of coordination compound excited states

Excited coordination compound [a]	Quencher [a]	Observed phenomena [b]	Ref.
Chromium			
$Cr(urea)_6^{3+}$	$Cr(CN)_6^{3-}$	D_p, Q_p	62, 63
	$Cr(NCS)_6^{3-}$	Q_p	64
	$Cr(mal)_3^{3-}$	Q_p	64
$Cr(NH_3)_6^{3+}$	$Cr(CN)_6^{3-}$	D_p, Q_p	63
	$Cr(NH_3)_5Cl^{2+}$	D_p, Q_p	67, 68
	$Cr(NH_3)_5Br^{2+}$	D_p, Q_p	68
	$Cr(NH_3)_5I^{2+}$	D_p, Q_p	68
	$Cr(NH_3)_5(NO_3)^{2+}$	D_p, Q_p	68
	OH^-	D_p, D_r	94
$Cr(atp)_6^{3+}$	$Cr(CN)_6^{3-}$	D_f, Q_p	63, 65
$Cr(imid)_6^{3+}$	$Cr(CN)_6^{3-}$	D_p, Q_p	63
$Cr(NCS)_6^{3-}$	O_2	D_p	109
$Cr(CN)_6^{3-}$	H_2O (in DMF)	D_p	104, 108
	O_2	D_p	104, 108, 109
	naphthacene	D_p	108
$Cr(acac)_3$	O_2	D_p	109
$Cr(en)_3^{3+}$	$Cr(CN)_6^{3-}$	D_p, Q_p	63
	$Cr(NCS)_6^{3-}$	Q_p	64
	$Cr(mal)_3^{3-}$	Q_p	64
	Fe^{2+} [c]	D_p, D_r	95, 103
	Co^{2+} [c]	D_p, D_r	95, 103
$Cr(phen)_3^{3+}$	I^-	D_p, D_r	96
$Cr(pn)_3^{3+}$	$Cr(CN)_6^{3-}$	D_p, Q_p	63
$Cr(tn)_3^{3+}$	$Cr(CN)_6^{3-}$	D_p, Q_p	63
t-$Cr(NCS)_4(NH_3)_2^-$	$Cr(CN)_6^{3-}$	D_p, D_r, Q_p	60, 97
	O_2	D_p	109
Iron			
Ferrocene	isoprene	Q_r	169
	piperylene	Q_r	169, 170
$Fe(ox)_3^{3-}$	$Cu(mal)_2(H_2O)_2^{2-}$	Q_r	176
	$Cu(mal)(SO_4)(H_2O)_3^{2-}$	Q_r	176
Cobalt			
$Co(CN)_6^{3-}$	$Cr(NH_3)_6^{3+}$	Q_p	71, 72
	$Cr(CN)_6^{3-}$	D_p	66, 73
	$Cr(en)_3^{3+}$	Q_p	72
	biacetyl	D_r, Q_r	98

TABLE 3 (continued)

Quenching of coordination compound excited states

Excited coordination compound [a]	Quencher [a]	Observed phenomena [b]	Ref.
Copper			
Cu(2,9-dmp)$^+$	chlorophyll a	Q_l	171
	chlorophyll b	Q_l	171
	perylene	Q_l	171
Zinc			
Zn-EP	Ru(dipy)$_2$-(*c*-4-stilbazole)$_2^{2+}$	D_T, Q_r	45, 46
	Ru(dipy)$_2$-(*t*-4-stilbazole)$_2^{2+}$	D_T, Q_r	45, 46
	Zn-EP	D_l	129
	organic molecules	D_f	128
Zn-TPP	Co^{2+} [c]	D_T	146
	Ni^{2+} [c]	D_T	146
	Cu^{2+} [c]	D_T	146
Zn-UP	$Cr(CN)_6^{3-}$	D_T, D_r	14
	$Mn(CN)_6^{3-}$	D_T, D_r	14
	$Fe(CN)_6^{3-}$	D_T, D_r	14
	$Co(CN)_6^{3-}$	D_T, D_r	14
Ruthenium			
Ru(dipy)$_3^{2+}$	$Cr(CN)_6^{3-}$	D_p, Q_p	12, 13, 61, 70, 111—173
	$Cr(NCS)_6^{3-}$	D_p, Q_p	70
	$Cr(en)_3^{3+}$	D_p	111, 113
	$Cr(dipy)_3^{3+}$	D_p	173
	$Cr(mal)_3^{3-}$	D_p, Q_p	70, 111
	$Cr(ox)_3^{3-}$	D_p, Q_p, Q_r	15, 69, 70, 111
	$Cr(phen)_3^{3+}$	D_p, Q_p	96
	t-Cr(en)$_2$F$_2^+$	D_p	113
	t-Cr(en)$_2$Cl$_2^+$	D_p	113
	c-Cr(en)$_2$Cl$_2^+$	D_p	113
	t-Cr(en)$_2$Br$_2^+$	D_p	113
	t-Cr(en)$_2$(NCS)$_2^+$	D_p, Q_p	113
	c-Cr(en)$_2$(NCS)$_2^+$	D_p	113
	t-Cr(en)$_2$(NCS)Cl$^+$	D_p	113
	c-Cr(en)$_2$(NCS)Cl$^+$	D_p	113
	Fe_{aq}^{2+}	D_p	114

TABLE 3 (continued)

	Fe^{3+}_{aq}	D_p, D_r, Q_r	114, 115
	$Fe(ox)_2^-$	D_p	15
	$Fe(HEDTA)(H_2O)$	D_p	30
	$Co(NH_3)_6^{3+}$	D_p	25
	$Co(ox)_3^{3-}$	D_p, Q_r	15, 111
	$Co(EDTA)^-$	D_p, Q_r	24, 29—31
	$Co(NH_3)_5(H_2O)^{3+}$	D_p	25
	$Co(NH_3)_5Cl^{2+}$	D_p, Q_r	22, 25
	$Co(NH_3)_5Br^{2+}$	D_p, Q_r	22—25, 25
	$Co(HEDTA)Cl^-$	D_p, Q_r	24, 29, 31
	$Co(HEDTA)Br^-$	D_p, Q_r	24, 29, 31
	$Co(HEDTA)(NO_2)^-$	D_p, Q_r	29, 31
	$Ni(gly)_2$	D_p	113
	$Mo(CN)_8^{4-}$	D_p	117
	$Ru(NH_3)_6^{3+}$	D_p, D_r, Q_r	25
	$Ru(NH_3)_5Cl^{2+}$	D_p, D_r, Q_r	25
	$IrCl_6^{3-}$	D_p	117
	$PtCl_4^{2-}$	D_p, Q_r	50, 117
	O_2	D_p, Q_r	15, 118
	Tl^{3+}_{aq}	D_p, D_r, Q_r	114
	anthracene	D_p	119
	t-stilbene	D_p, Q_r	119
	t-2-styrylpyridine	D_p	119
	t-4-styrylpyridine	D_p	119
$Ru(phen)_3^{2+}$	O_2	D_p	118
$Ru(dipy)_2(CN)_2$	O_2	D_p	118
$Ru(phen)_2(CN)_2$	Cu^{2+} [c]	D_p	116
	O_2	D_p, Q_r	118
Rhodium			
$Rh(dipy)_3^{3+}$	$Cr(CN)_6^{3-}$	D_p, Q_p	70
$Rh(phen)_3^{3+}$	ethanol	Q_r	186
Palladium			
Pd-MP	Pd-MP	D_l	129
Lanthanum			
$La(DBM)_3$	$Eu(DBM)_3$	D_l, Q_l	183

TABLE 3 (continued)
Quenching of coordination compound excited states

Excited coordination compound [a]	Quencher [a]	Observed phenomena [b]	Ref.
Wolfram			
$W(CO)_5py$	c-1,3-pentadiene	D_p	130
Iridium			
$Ir(phen)_2Cl_2^+$	$Cr(CN)_6^{3-}$	D_p	99
	O_2	D_p	99
$Ir(5,6\text{-dmp})_2Cl_2^+$	$Cr(ox)_3^{3-}$	D_p	99
	O_2	D_p	99
Platinum			
c-$Pt(gly)_2$	Ni^{2+} [c]	D_r	51
Pt-EP	Pt-EP	D_l	129
Cerium			
Ce^{3+} [c]	organic acids	D_l	142
Praseodymium			
Pr^{3+} [c]	rare earth ions	D_l	178
Neodymium			
Nd^{3+} [c]	rare earth ions	D_l	178
Samarium			
Sm^{3+} [c]	rare earth ions	D_l	177, 178
$Sm(acac)_3$	naphthalene	D_l	131
$Sm(DBM)_4^-$	anthracene	D_l	131
$Sm(TTA)_4^-$	anthracene	D_l	131
$Sm(TTA)_3(phen)$	anthracene	D_l	131
Europium			
Eu^{3+} [c]	rare earth ions	D_l	132, 134, 141, 177
	acridine	D_l	133
	amines	D_l	133
	anthracene and derivatives	D_l	133
	HDAC	D_l	90
	organic radicals	D_l	136
$Eu(acac)_3$	naphthalene	D_l	133
$Eu(BA)_4^-$	1-acetylanthracene	D_l	133
	anthracene	D_l	131, 133
	N,N-dimethylaniline	D_l	133
	piperidine	D_l	133

TABLE 3 (continued)

$Eu(BTFA)_4^-$	anthracene	D_1	131, 133, 187
$Eu(DBM)_4^-$	anthracene	D_1	131, 187
$Eu(phen)_3^{3+}$	anthracene	D_1	133
	fluorene	D_1	133
	naphthalene	D_1	133
$Eu(TTA)_4^-$	anthracene	D_1	131, 133, 187
	β-chloronaphthalene	D_1	187
$Eu(TTA)_3(phen)$	amines	D_1	133
	anthracene	D_1	131, 133
Terbium			
$Tb^{3+\ c}$	rare earth ions	D_1, Q_1	86, 132, 134, 139—141, 179
	anthracene	D_1	133
	acridine	D_1	133
	aromatic molecules	D_1	134
	benzophenone	D_1	133
	diphenylaniline	D_1	133
	dyes	D_1	135, 137
	fluorenone	D_1	133
	naphthalene and derivatives	D_1	87, 133
	organic radicals	D_1	136
	phenazine	D_1	133
$Tb(acac)_3$	naphthalene and derivatives	D_1	131, 133, 187
$Tb(sal)_3$	dyes	D_1	135, 188
Dysprosium			
$Dy^{3+\ c}$	rare earth ions	D_1	178
	2-acetonaphthone	D_1	133
	fluorenone	D_1	133
$Dy(acac)_3$	naphthalene	D_1	131
Uranium			
$UO_2^{2+\ c}$	$Mn^{2+\ c}$	D_1	100
	$Fe^{2+\ c}$	D_1	174
	$Co^{2+\ c}$	D_1	100
	$Co(CN)_6^{3-}$	D_1, Q_r	35
	$Cu^{2+\ c}$	D_1	100
	$Hg^{+\ c}$	D_1	100
	$Eu^{3+\ c}$	D_1, Q_1	81
	Eu(EDTA)	D_1, Q_1	81

TABLE 3 (continued)

Quenching of coordination compound excited states

Excited coordination compound[a]	Quencher[a]	Observed phenomena[b]	Ref.
	U^{4+} [c]	D_l	125
	UO_2^{2+} [c]	D_l	174
	Tl^{+} [c]	D_l	100
	$H_2PO_2^-$	D_l	123
	acetaldehyde	D_l	120
	acetic acid	D_l	123
	acetophenone	Q_r	121
	aliphatic alcohols	D_l, Q_r	122, 124, 126
	aromatic molecules	D_l	121, 122
	C_6H_6, C_6D_6	D_l	121, 122
	CH_3OH, CD_3OH	D_l	120, 123
	ethanol	D_l	123
	formaldehyde	D_l	120
	isopropanol	D_l	120
	lactic acid	D_l	100, 123
	stilbenes	D_l	127

[a] For the abbreviations used see the list at the beginning of the article. [b] D, excited coordination compound (donor); D_r, reaction of the donor; D_l, quenching of the donor luminescence; D_f, quenching of the donor fluorescence; D_p, quenching of the donor phosphorescence; D_T, quenching of the donor triplet state measured by triplet—triplet absorption; Q, quencher; Q_r, reaction of the quencher; Q_l, quencher luminescence; Q_f, quencher fluorescence; Q_p, quencher phosphorescence. [c] The actual species present in the solution depends on the nature of the counter ion and solvent.

C. KINETIC ASPECTS OF QUENCHING AND SENSITIZATION

(i) Dynamic collisional quenching

A dynamic collisional quenching process is a bimolecular interaction between an electronically excited state of a molecule (donor, D) and another species (quencher, Q), in which the excited molecule is deactivated or converted into a different compound*:

$$D^* + Q \rightarrow D \text{ (or products of D)} + \ldots \tag{8}$$

Such processes are usually studied by measuring at different quencher concentrations one or more of the following quantities: (i) the emission intensi-

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* For the sake of simplicity, self-quenching processes (Q = D) and quenching processes involving two excited molecules are not taken into consideration.

ty of the excited donor under constant illumination; (ii) the decay of the emission of the excited donor after a pulse excitation; (iii) the decay of the absorbance of the excited donor after pulse excitation; (iv) the quantum yield of a photochemical reaction of the donor.

In order to discuss such experimental data, reference is usually made to a postulated mechanism which consists of a number of elementary transformations (steps) of the excited donor and other species in the system [189].

The postulated mechanism must be considered as a working hypothesis whose reliability is judged by the amount of experimental data for which it is able to account. The object of this section is to show the algebraic relations between the experimental and the mechanistic quantities [189]*. When the experiments are carried out under continuous illumination conditions a stationary concentration of all the donor excited states involved in the mechanism is assumed (steady state approximation). For the pulse experiments, the duration of the excitation flash must be very short compared with the decay time of the observed phenomenon, and it is assumed to be practically instantaneous. In the relations between the experimental and mechanistic quantities, the experimental data generally appear as ratios of the value obtained in the absence of quencher to the value obtained in the presence of a given amount of quencher. The former value is indicated by the superscript 0. The algebraic relation between these ratios and the quencher concentration is called the "Stern—Volmer equation", and the plots of these ratios vs. [Q] are called "Stern—Volmer plots". Whenever a linear Stern—Volmer plot is obtained, its slope is called the "Stern—Volmer constant", k_{SV}. Under constant experimental conditions, and in the absence of light absorption by the quencher, the emission intensity is proportional to the emission quantum yield, so that the I^0/I ratio is equal to ϕ^0/ϕ.

We shall consider here only the most common kinetic quenching mechanism, which is shown in Fig. 1. Two distinct excited states of the donor are considered, D_1 and D_2, the higher energy one (D_1) being that reached directly by irradiation. I_0 is the intensity of the absorbed light. In most cases, the two excited states have different multiplicity such as, for example, the lowest singlet and lowest triplet excited state of an organic molecule. The unimolecular deactivation steps which have been taken into consideration for each excited state are the non-radiative deactivations to the ground state (k_{1d} and k_{2d}), the radiative emissions (k_{1e} and k_{2e}, that may represent fluorescence and phosphorescence, respectively), the chemical reactions (k_{1r} and k_{2r}, both of which are assumed to lead to the same products), and the forward (k_{1c}) and back (k_{2c}) non-radiative transitions between the two excited states (generally, these steps are intersystem crossing). The sum of the rate constants of all the unimolecular steps which depopulate D_1 and D_2 will be indicated by K_1 and K_2, respectively. The quantities $\tau_1^0 = 1/K_1$ and

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* The definitions of the mechanistic and experimental quantities are given in ref. 189. The nomenclature suggested in that paper is adopted here.

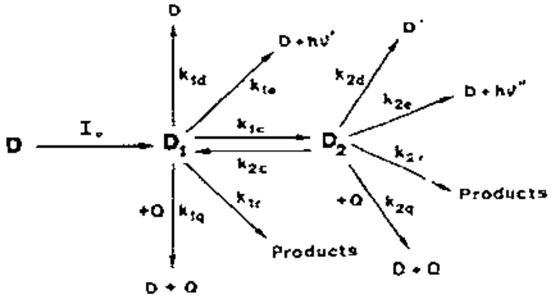

Fig. 1. Scheme for the discussion of the quenching processes (see text).

$\tau_2^0 = 1/K_2$ represent the lifetimes of D_1 and D_2, respectively. Both the excited states are subjected to quenching by the same quencher, Q. In the scheme of Fig. 1 only one quenching path has been considered for each excited state. However, different types of quenching processes (e.g. energy transfer, chemical reactions, etc., see Sect. D) can occur simultaneously between a given donor excited state and the quencher. In this case k_q represents the sum of the bimolecular rate constants of the simultaneous quenching processes, i.e.

$$k_{1q} = k'_{1q} + k''_{1q} + \ldots$$
$$k_{2q} = k'_{2q} + k''_{2q} + \ldots$$

In our system, the measurable quantities are the quantum yield of the photoreaction, and the intensity and decay of the two different luminescent emissions.

Note that any phenomenon that originates only from D_1 or D_2 behaves in exactly the same way as the corresponding emission.

Case 1. In this first case, the quenching of D_1 and the non-radiative transition from D_2 to D_1 are assumed to be negligible with respect to the competing steps ($k_{1q}[Q] \ll K_1$; $k_{2c} \ll K_2$). On this assumption, under steady state conditions one obtains

$$\frac{d[D_1]}{dt} = I_0 - K_1[D_1] = 0 \tag{9}$$

$$\frac{d[D_2]}{dt} = k_{1c}[D_1] - (K_2 + k_{2q}[Q])[D_2] = 0 \tag{10}$$

$$\phi_{1e} = \frac{k_{1e}[D_1]}{I_0} = \frac{k_{1e}}{K_1} \tag{11}$$

$$\phi_{2e} = \frac{k_{2e}[D_2]}{I_0} = \frac{k_{1c}}{K_1}\,\frac{k_{2e}}{K_2 + k_{2q}[Q]} \tag{12}$$

$$\frac{\phi_{1e}^{0}}{\phi_{1e}} = 1 \tag{13}$$

$$\frac{\phi_{2e}^{0}}{\phi_{2e}} = 1 + \frac{k_{2q}}{K_2}[\mathrm{Q}] = 1 + k_{2q}\tau_2^0[\mathrm{Q}] \tag{14}$$

Equation (14) is an example of the most common type of Stern—Volmer equation. The corresponding Stern—Volmer plot is linear provided that the bimolecular quenching constant (k_{2q}) does not depend on time or [Q] (see Sect. C(ii)), and the Stern—Volmer constant is given by k_{2q}/K_2.

The experimental quantum yield of the chemical reaction, ϕ_r, is the sum of the quantum yield of the reactions that originate from D_1 (φ_{1r}, which is unquenchable) and D_2 (φ_{2r}), respectively.

$$\phi_r = \varphi_{1r} + \varphi_{2r} = \frac{k_{1r}}{K_1} + \frac{k_{1c}}{K_1}\,\frac{k_{2r}}{K_2 + k_{2q}[\mathrm{Q}]} \tag{15}$$

$$\begin{aligned}\frac{\phi_r^0}{\phi_r} &= \left(1 + \frac{k_{2q}}{K_2}[\mathrm{Q}]\right)\left(1 + \frac{k_{1r}k_{2q}}{k_{1r}K_2 + k_{1c}k_{2r}}[\mathrm{Q}]\right)^{-1}\\ &= \frac{\phi_{2e}^0}{\phi_{2e}}\left(1 + \frac{k_{1r}k_{2q}}{k_{1r}K_2 + k_{1c}k_{2r}}[\mathrm{Q}]\right)^{-1}\end{aligned} \tag{16}$$

A careful analysis of the Stern—Volmer plot for ϕ_r^0/ϕ_r has been reported in refs. 190 and 191. In the second paper, the possibility of evaluating the two components of ϕ_r is also discussed. In this regard it is to be noted that, since $\varphi_{1r} = \varphi_{1r}^0$ and $\varphi_{2r} = \varphi_{2r}^0\phi_{2e}/\phi_{2e}^0$, the following equation can be obtained:

$$\phi_r = \varphi_{1r}^0 + \varphi_{2r}^0\,\frac{\phi_{2e}}{\phi_{2e}^0} \tag{17}$$

Therefore, if both the quantum yield of the chemical reaction and the emission intensity can be measured in the same experimental conditions, a plot of ϕ_r vs. ϕ_{2e}/ϕ_{2e}^0 gives φ_{1r}^0 as intercept and φ_{2r}^0 as slope.

For the decay experiments we have

$$\frac{\mathrm{d}[\mathrm{D}_1]}{\mathrm{d}t} = -K_1[\mathrm{D}_1] \tag{18}$$

$$\frac{\mathrm{d}[\mathrm{D}_2]}{\mathrm{d}t} = -(K_2 + k_{2q}[\mathrm{Q}])[\mathrm{D}_2] + k_{1c}[\mathrm{D}_1] \tag{19}$$

At $t = 0$ (i.e. just after the "instantaneous" light pulse), $[\mathrm{D}_1] = [\mathrm{D}_1]^0$ and $[\mathrm{D}_2] = 0$. Therefore,

$$[\mathrm{D}_1] = [\mathrm{D}_1]^0 \exp(-K_1 t) \tag{20}$$

$$[D_2] = [D_1]^0 \frac{k_{1c}}{K_1 - (K_2 + k_{2q}[Q])} \{\exp[-(K_2 + k_{2q}[Q])t\} - \exp(-K_1 t) \quad (21)$$

D_1 follows exactly a first-order decay, and its unquenchable lifetime is

$$\tau_1 = \tau_1^0 = \frac{1}{K_1} \quad (22)$$

The equation for $[D_2]$ is much more complicated, since D_2 is produced from D_1 and, at the same time, is consumed via K_2 and k_{2q}. If $K_1 \gg K_2$, as in general happens, the decay of D_2 long after the maximum of the $[D_2]$ vs. time curve is given by*

$$[D_2] = [D_1]^0 \frac{k_{1c}}{K_1 - (K_2 + k_{2q}[Q])} \exp[-(K_2 + k_{2q}[Q])t] \quad (23)$$

In these conditions D_2 follows a first-order decay, and its lifetime is given by

$$\tau_2 = \frac{1}{K_2 + k_{2q}[Q]} \quad (24)$$

It follows that

$$\frac{\tau_2^0}{\tau_2} = 1 + \frac{k_{2q}}{K_2}[Q] = 1 + k_{2q}\tau_2^0[Q] \quad (25)$$

We can note that the right-hand sides of eqns. (14) and (25) are equal. This means that, in this case, the decay of the quenchable excited state and each phenomenon which only originates from that state show the same linear quenching:

$$k_{SV(\phi_{2e})} = k_{SV(\tau_2)} = k_{2q}\tau_2^0 \quad (26)$$

The bimolecular quenching constant, k_{2q}, can be calculated, when the lifetime τ_2^0 is known.

Processes like the photochemical reaction which originates from both the quenchable and unquenchable excited states show non-linear quenching equations.

Case 2. In this case, we assume that only D_1 is quenched ($k_{2q}[Q] \ll K_2$) and that the radiationless transition from D_2 to D_1 is negligible ($k_{2c} \ll K_2$). On these assumptions, all the observable phenomena are quenched in parallel, with the exception of τ_2 which is not quenched at all:

$$\frac{\phi_{1e}^0}{\phi_{1e}} = \frac{\phi_{2e}^0}{\phi_{2e}} = \frac{\phi_r^0}{\phi_r} = \frac{\tau_1^0}{\tau_1} = 1 + \frac{k_{1q}}{K_1}[Q] = 1 + k_{1q}\tau_1^0[Q] \quad (27)$$

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* The error due to this approximation is ~ 1% when $K_1 t > 5$.

$$\tau_2 = \tau_2^0 = \frac{1}{K_2} \tag{28}$$

Therefore,

$$k_{SV(\phi_{1e})} = k_{SV(\phi_{2e})} = k_{SV(\phi_r)} = k_{SV(\tau_1)} = k_{1q}\tau_1^0 \tag{29}$$

The bimolecular quenching constant, k_{1q}, can be calculated when the lifetime τ_1^0 is known.

Case 3. Now we assume that both D_1 and D_2 are quenched and that the radiationless transition from D_2 to D_1 is negligible ($k_{2c} \ll K_2$).

Under stationary conditions we obtain

$$\frac{\phi_{1e}^0}{\phi_{1e}} = 1 + \frac{k_{1q}}{K_1}[Q] \tag{30}$$

$$\frac{\phi_{2e}^0}{\phi_{2e}} = \left(1 + \frac{k_{1q}}{K_1}[Q]\right)\left(1 + \frac{k_{2q}}{K_2}[Q]\right) = \frac{\phi_{1e}^0}{\phi_{1e}}\left(1 + \frac{k_{2q}}{K_2}[Q]\right) \tag{31}$$

$$\begin{aligned}\frac{\phi_r^0}{\phi_r} &= \left(1 + \frac{k_{1q}}{K_1}[Q]\right)\left(1 + \frac{k_{2q}}{K_2}[Q]\right)\left(1 + \frac{k_{1r}k_{2q}}{k_{1r}K_2 + k_{1c}k_{2r}}[Q]\right)^{-1} \\ &= \frac{\phi_{2e}^0}{\phi_{2e}}\left(1 + \frac{k_{1r}k_{2q}}{k_{1r}K_2 + k_{1c}k_{2r}}[Q]\right)^{-1}\end{aligned} \tag{32}$$

The Stern—Volmer plots for ϕ_{2e}^0/ϕ_{2e} and φ_r^0/ϕ_r have been analyzed in refs. 190 and 191. There is no unquenchable part of ϕ_r. However, since φ_{1r} is quenched as ϕ_{1e} and φ_{2r} as ϕ_{2e}, we have

$$\phi_r \frac{\phi_{1e}^0}{\phi_{1e}} = \varphi_{1r}^0 + \varphi_{2r}^0 \frac{\phi_{2e}}{\phi_{2e}^0}\frac{\phi_{1e}^0}{\phi_{1e}} \tag{33}$$

Thus the two parts of ϕ_r can be calculated if there are observable phenomena characteristic of the two excited states.

The decay of D_1 is exactly given by

$$\frac{\tau_1^0}{\tau_1} = 1 + \frac{k_{1q}}{K_1}[Q] = \frac{\phi_{1e}^0}{\phi_{1e}} \tag{34}$$

Within the same approximations discussed in Case 1, the decay of D_2 is given by

$$\frac{\tau_2^0}{\tau_2} = 1 + \frac{k_{2q}}{K_2}[Q] \tag{35}$$

In summary, the phenomena characteristic of the higher-energy excited state are quenched in the same linear way:

$$k_{SV(\phi_{1e})} = k_{SV(\tau_1)} = k_{1q}\tau_1^0 \tag{36}$$

The quenching constant for D_2 can be obtained from

$$k_{SV(\tau_2)} = k_{2q}\tau_2^0 \tag{37}$$

As far as the emission from D_2 is concerned, it is to be noted that whereas its lifetime is quenched linearly (eqn. (35)), its intensity is quenched according to a quadratic equation

$$\frac{\phi_{2e}^0}{\phi_{2e}} = (1 + k_{1q}\tau_1^0[Q])(1 + k_{2q}\tau_2^0[Q]) \tag{38}$$

Case 4. We assume here that the radiationless transition from D_2 to D_1 is present and that only D_2 is quenched ($k_{1q}[Q] \ll K_1$). It is to be noted that the radiationless transition from the lower-energy to the higher-energy state is a rather common process in Cr^{III} complexes ($^2E \rightarrow {}^4T_2$ back intersystem crossing, see Fig. 4). Under continuous illumination we obtain

$$\frac{\phi_{2e}^0}{\phi_{2e}} = 1 + \frac{K_1 k_{2q}}{K_1K_2 - k_{1c}k_{2c}}[Q] \tag{39}$$

$$\begin{aligned}\frac{\phi_{1e}^0}{\phi_{1e}} &= \left(1 + \frac{K_1 k_{2q}}{K_1K_2 - k_{1c}k_{2c}}[Q]\right)\left(1 + \frac{k_{2q}}{K_2}[Q]\right)^{-1} \\ &= \frac{\phi_{2e}^0}{\phi_{2e}}\left(1 + \frac{k_{2q}}{K_2}[Q]\right)^{-1}\end{aligned} \tag{40}$$

The quantum yield ϕ_{1e} can be divided into two parts: φ_{1e} (a), which is due to the D_1 molecules that emit directly after excitation ($D \xrightarrow{I_0} D_1 \xrightarrow{k_{1e}} D + h\nu'$), and φ_{1e} (b) that is due to the D_1 molecules which have passed, one or more times, through the D_2 state ($D \xrightarrow{I_0} D_1 \xrightarrow{k_{1c}} D_2 \xrightarrow{k_{2c}} D_1 \xrightarrow{k_{1e}} D + h\nu'$). The first part (eqn. (41)) is unquenchable, whereas the second part (eqn. (42)) is quenchable

$$\varphi_{1e}\,(a) = \varphi_{1e}^0\,(a) = \frac{k_{1e}}{K_1} \tag{41}$$

$$\varphi_{1e}\,(b) = \frac{k_{1e}}{K_1}\,\frac{k_{1c}k_{2c}}{K_1(K_2 + k_{2q}[Q]) - k_{1c}k_{2c}} = \varphi_{1e}^0\,(b)\,\frac{\phi_{2e}}{\phi_{2e}^0} \tag{42}$$

$$\phi_{1e} = \varphi_{1e}^0\,(a) + \varphi_{1e}^0\,(b)\,\frac{\phi_{2e}}{\phi_{2e}^0} \tag{43}$$

Therefore a plot of ϕ_{1e} vs. ϕ_{2e}/ϕ_{2e}^0 is linear, and its intercept and slope correspond to the unquenchable and quenchable part of the D_1 emission, respectively. Obviously the actual value of ϕ_{1e}, and not that of the emission intensity, is needed.

As far as the photoreaction is concerned, one obtains

$$\frac{\phi_r^0}{\phi_r} = \left(1 + \frac{K_1 k_{2q}}{K_1 K_2 - k_{1c} k_{2c}}[Q]\right)\left(1 + \frac{k_{1r} k_{2q}}{k_{1r} K_2 + k_{1c} k_{2r}}[Q]\right)^{-1}$$

$$= \frac{\phi_{2e}^0}{\phi_{2e}}\left(1 + \frac{k_{1r} k_{2q}}{k_{1r} K_2 + k_{1c} k_{2r}}[Q]\right)^{-1} \qquad (44)$$

Like the quantum yield of emission, the quantum yield of reaction can be written as the sum of distinct terms (for the meaning of the various terms, see above)

$$\phi_r^0 = \varphi_{1r}^0\ (a) + \varphi_{1r}^0\ (b) + \varphi_{2r}^0 \qquad (45)$$

$$\phi_r = \varphi_{1r}^0\ (a) + \varphi_{1r}^0\ (b) + \varphi_{2r}^0\ \frac{\phi_{2e}}{\phi_{2e}^0} \qquad (46)$$

$$\phi_r \frac{\phi_{1e}^0}{\phi_{1e}} = (\varphi_{1r}^0\ (a) + \varphi_{1r}^0\ (b)) + \varphi_{2r}^0\ \frac{\phi_{2e}}{\phi_{2e}^0}\ \frac{\phi_{1e}^0}{\phi_{1e}} \qquad (47)$$

The Stern—Volmer equations for ϕ_{1e}^0/ϕ_{1e} (eqn. (40)) and ϕ_r^0/ϕ_r (eqn. (44)) have been analyzed in ref. 192. The particular case of complete equilibration between the two excited states (i.e. $k_{1c} \approx K_1$ and $k_{2c} \approx K_2$) has also been discussed [190, 192].

For the decay measurements, we have

$$\frac{d[D_1]}{dt} = k_{2c}[D_2] - K_1[D_1] \qquad (48)$$

$$\frac{d[D_2]}{dt} = k_{1c}[D_1] - (K_2 + k_{2q}[Q])[D_2] \qquad (49)$$

Since, at $t = 0$, $[D_1] = [D_1]^0$ and $[D_2] = 0$, we have

$$[D_1] = [D_1]^0\ \frac{K_\alpha - K_1}{K_\alpha - K_\beta}\exp(-K_\beta t) - \frac{K_\beta - K_1}{K_\alpha - K_\beta}\ \exp(-K_\alpha t) \qquad (50)$$

$$[D_2] = [D_1]^0\ \frac{k_{1c}}{K_\beta - K_\alpha}\ [\exp(-K_\alpha t) - \exp(-K_\beta t)] \qquad (51)$$

where

$$K_\alpha = \frac{1}{2}[K_1 + (K_2 + k_{2q}[Q])] - \frac{1}{2}[K_1 - (K_2 + k_{2q}[Q])] \times$$

$$\times \left\{1 + \frac{4k_{1c}k_{2c}}{[K_1 - (K_2 + k_{2q}[Q])]^2}\right\}^{1/2} \qquad (52)$$

$$K_\beta = \frac{1}{2}[K_1 + (K_2 + k_{2q}[Q])] + \frac{1}{2}[K_1 - (K_2 + k_{2q}[Q])] \times$$
$$\times \left\{1 + \frac{4k_{1c}k_{2c}}{[K_1 - (K_2 + k_{2q}[Q])]^2}\right\}^{1/2} \tag{53}$$

Using the same approximation reported for Case 1 (note that $K_\beta - K_\alpha > K_1 - K_2$, when $[Q] = 0$)

$$[D_2] = [D_1]^0 \frac{k_{1c}}{K_\beta - K_\alpha} \exp(-K_\alpha t) \tag{54}$$

and then

$$\tau_2 = \frac{1}{K_\alpha} \tag{55}$$

By truncating after the second term the binomial expansion of the root in the equation for K_α, we obtain

$$K_\alpha = K_2 + k_{2q}[Q] - \frac{k_{1c}k_{2c}}{K_1} \tag{56}$$

This approximate value of K_α is higher than the true value by a factor which increases with increasing $4k_{1c}k_{2c}/[K_1 - (K_2 + k_{2q}[Q])]^2$ (about 6% for $4k_{1c}k_{2c}/[K_1 - (K_2 + k_{2q}[Q])]^2 = 1$). From a kinetic point of view, this last approximation corresponds to a steady state assumption for D_1 [193, 194] (i.e. the overall rate of depopulation of D_1 is equal to the rate of its repopulation from D_2), so that D_1 can no more function as "reservoir" for D_2 population. In this sense, this second approximation is valid when eqn. (54) is also valid. Thus we obtain

$$\tau_2^0 = \frac{K_1}{K_1K_2 - k_{1c}k_{2c}} \tag{57}$$

Note that τ_2^0 is *not* equal to the inverse of the sum of the rate constants of the steps which depopulate D_2. From eqns. (55), (56) and (57) we obtain

$$\frac{\tau_2^0}{\tau_2} = 1 + \frac{K_1k_{2q}}{K_1K_2 - k_{1c}k_{2c}}[Q] \tag{58}$$

Just after the flash, D_1 decays according to

$$\tau_1 = \frac{1}{K_1} \tag{59}$$

since its repopulation from D_2 is negligible. On the contrary, D_1 practically decays as D_2 does when eqns. (54) and (56) are valid. In summary, τ_2^0/τ_2 (eqn. (58)) and ϕ_{2e}^0/ϕ_{2e} (eqn. (39)) show the same linear dependence on [Q]

$$k_{SV(\phi_{2e})} = k_{SV(\tau_2)} = k_{2q}\tau_2^0 \tag{60}$$

Case 5. This case corresponds to the whole scheme of Fig. 1

Under stationary illumination

$$\frac{\phi_{2e}^0}{\phi_{2e}} = 1 + \frac{K_1 k_{2q} + k_{1q}K_2}{K_1K_2 - k_{1c}k_{2c}}[Q] + \frac{k_{1q}k_{2q}}{K_1K_2 - k_{1c}k_{2c}}[Q]^2 \tag{61}$$

$$\frac{\phi_{1e}^0}{\phi_{1e}} = \frac{\phi_{2e}^0}{\phi_{2e}}\left(1 + \frac{k_{2q}}{K_2}[Q]\right)^{-1} \tag{62}$$

$$\frac{\phi_r^0}{\phi_r} = \frac{\phi_{2e}^0}{\phi_{2e}}\left(1 + \frac{k_{1r}k_{2q}}{k_{1r}K_2 + k_{1c}k_{2r}}[Q]\right)^{-1} \tag{63}$$

The Stern—Volmer equations for ϕ_{1e}^0/ϕ_{1e}, ϕ_{2e}^0/ϕ_{2e}, and ϕ_r^0/ϕ_r have been analyzed in ref. 192. The complete equilibration between the two excited states has been discussed in refs. 191 and 195. The following relation also holds:

$$\phi_r \frac{\phi_{1e}^0}{\phi_{1e}} = \varphi_{1r}^0 + \varphi_{2r}^0 \frac{\phi_{2e}}{\phi_{2e}^0}\frac{\phi_{1e}^0}{\phi_{1e}} \tag{64}$$

For the decay of D_2, using the same approximations as in Case 4, we obtain

$$K_\alpha = K_2 + k_{2q}[Q] - \frac{k_{1c}k_{2c}}{K_1 + k_{1q}[Q]} \tag{65}$$

$$\tau_2^0 = \frac{K_1}{K_1K_2 - k_{1c}k_{2c}} \tag{66}$$

$$\frac{\tau_2^0}{\tau_2} = \frac{\phi_{2c}^0}{\phi_{2c}}\left(1 + \frac{k_{1q}}{K_1}[Q]\right)^{-1} \tag{67}$$

The decay of D_1 is given by

$$\tau_1 = \frac{1}{K_1 + k_{1q}[Q]} \tag{68}$$

just after the flash, while it is practically equal to the decay of D_2 when eqn. (67) is valid. It is to be noted that the ratios k_{2q}/K_2 and k_{1q}/K_1 can be calculated from eqns. (62) and (67), provided that the experimental data that appear in these equations are measurable. However, the bimolecular quenching rate constants k_{1q} and k_{2q} cannot be calculated, since K_1 and K_2 are not measurable quantities.

(ii) Relation between the bimolecular quenching rate constant and the diffusion rate constant

A collisional quenching requires a close approach (of the order of the collisional diameter) of the excited donor and the quencher. Assuming that no chemical bond is formed between the two partners, their contact is only maintained by the solvent cage. This situation corresponds to the so called "*encounter complex*" ($D^*.Q$). Such a situation is common when coordination compounds are involved. However, formation of bonds between D^* and Q is known to occur for organic molecules (exciplexes) [196, 197].

In the hypothesis that neither emission nor reaction occur from D^* during the encounter, the scheme of the quenching process is

$$D^* + Q \underset{k_{-\rm diff}}{\overset{k_{\rm diff}}{\rightleftharpoons}} (D^*.Q) \xrightarrow{k_i} D + \ldots \tag{69}$$

where $k_{\rm diff}$ is the diffusion rate constant, $k_{-\rm diff}$ is the (unimolecular) encounter dissociation rate constant, and k_i is the rate constant of the quenching process in the encounter (see also Fig. 3, Sect. D). The total quenching constant k_q (or the individual k'_q if more than one simultaneous quenching processes are present, Sect. C(i)) is given by

$$k_q = k_{\rm diff}\left(\frac{k_i}{k_{-\rm diff} + k_i}\right) = k_{\rm diff}.\alpha \tag{70}$$

where α represents the efficiency of the quenching process during the encounter. The theoretical value of the diffusion rate constant, $k_{\rm diff}$, may be calculated by means of the Debye equation [198]

$$k_{\rm diff} = \frac{8NkT}{3000\eta}\, b(e^b - 1)^{-1} \tag{71}$$

where $b = Z_D Z_Q E^2/r\epsilon kT$, η is the viscosity of the solution, Z_D and Z_Q are the ionic charge of the donor and the acceptor, E is the charge of the electron, r is the encounter distance between D and Q, and ϵ is the dielectric constant of the medium.

It is to be noted that, when both the donor and quencher are ionic species, $k_{\rm diff}$ depends on the product of their charge, $Z_D Z_Q$. The values of $k_{\rm diff}$ in aqueous solutions at 25°C for various values of $Z_D Z_Q$ are reported in Table 4. It should be emphasized that the diffusion rate constant between ionic species is influenced by the ionic strength of the medium. The value of $k_{\rm diff}$ given by eqn. (71) refers to zero ionic strength, and it may be corrected for the ionic strength influence by means of the well-known Debye—Bronsted equations [199]. The values calculated for $\mu = 0$ and $\mu = 0.002$ in Table 4 give an idea of the influence of the ionic strength on $k_{\rm diff}$. It follows that the influence of the ionic strength must be taken into consideration when dealing with quenching processes between ionic species. In fact, an increase of [Q] would cause an increase of μ if no appropriate correction is made. As

TABLE 4

Diffusion rate constant for various values of $Z_D Z_Q$, in water at 25°C, calculated from the Debye equation (eqn. (71), see text) with an encounter distance of 10Å

$Z_D Z_Q$	k_{diff} ($\times 10^{-9}$ M^{-1} s^{-1}) at $\mu = 0$	k_{diff} ($\times 10^{-9}$ M^{-1} s^{-1}) at $\mu = 0.002$ [a]
+9	0.08	0.21
+8	0.14	0.32
+6	0.44	0.83
+4	1.28	1.95
+3	2.11	2.89
+2	3.33	4.11
+1	5.07	5.63
0	7.41	7.41
−1	10.4	9.35
−2	13.9	11.3
−3	18.0	13.2
−4	22.5	14.8
−6	32.3	17.2
−8	42.6	18.4
−9	47.8	18.6

[a] Calculated by the simplified Brönsted—Debye equation: $\log k(\mu) = \log k(\mu = 0) + 1.02\, Z_D Z_Q \sqrt{\mu}$.

a consequence, when [Q] increases k_q also increases when D and Q are ions of the same sign, whereas it decreases when they have opposite sign. It follows that the experimental Stern—Volmer plot does not correspond to the "theoretical" mechanistic equation.

For the same reason, when two or more quenching constants are to be compared, they must be extrapolated to zero ionic strength, or, at least, refer to the same ionic strength, provided that they show the same dependence on the ionic strength.

The theoretical value of $k_{-\text{diff}}$ may be calculated by means of the Eigen equation [200]:

$$k_{-\text{diff}} = \frac{2kT}{\pi r^3 \eta}\, b(1 - e^{-b})^{-1} \tag{72}$$

Note that $k_{-\text{diff}}$ does not depend on the ionic strength.

The factors affecting k_i depend on the nature of the quenching process and will be discussed in Sect. D.

Equation (70) only holds when the steady state is reached, i.e. when a constant concentration gradient for the quencher molecules towards an excited donor molecule is established. But, at the moment that the donor molecules are excited, there is a statistical chance that each excited donor is the nearest neighbour of a quencher molecule. The quenching of this fraction of excited molecules does not follow diffusion kinetics, since the quenching time for diffusion controlled reactions is comparable with the time required to reach the steady state. This particular effect, which is usually called "transient effect", has been extensively discussed [196]. The transient effect cannot be seen in decay experiments because the time needed for reaching the steady state is lower by far than the lifetimes that can be measured with conventional apparatus. It affects, on the contrary, the quenching measurements carried out under continuous illumination in the sense that the observed intensity quenching is higher than that due to the diffusional mechanism alone. The "transient effect" increases with increasing quencher concentration, collisional distance, and efficiency of the quenching (α), while it decreases with increasing lifetime of the excited state [196]. In any case, no evidence for the presence of the transient effect has so far been reported in quenching experiments involving coordination compounds.

(iii) Static quenching

In the previous section, we have only considered dynamic quenching processes. However, a different situation may result when the donor and the quencher can give rise to a chemical or physical "association" in their ground state. This is particularly important when the donor and the quencher are ions of opposite sign since ion pairs can be easily formed.

In the simple case of an interaction leading to a 1:1 complex, the concentration of the new species, DQ, is related to the concentration of the "free" donor and quencher by the following equation:

$$K = \frac{[\mathrm{DQ}]}{[\mathrm{D}][\mathrm{Q}]} \qquad (73)$$

In the quenching experiments, the incident light is shared between the two absorbing species, D and DQ; in other words, the species DQ acts as an inner filter with respect to light absorption by D:

$$\begin{tikzcd} \mathrm{D} \arrow[r, "h\nu"] \arrow[d, shift left, "+\mathrm{Q}"'] & \mathrm{D}^* \arrow[r] & \ldots \\ \mathrm{DQ} \arrow[r, "h\nu"] \arrow[u, shift left] & \mathrm{DQ}^* \arrow[r] & \ldots \end{tikzcd} \qquad (74)$$

The fraction of incident light absorbed by D is

$$I_\mathrm{D} = I_0(1 + K[Q]\epsilon_\mathrm{DQ}/\epsilon_\mathrm{D})^{-1} \qquad (75)$$

and that absorbed by DQ is

$$I_\mathrm{DQ} = I_0\left(\frac{K[Q]\epsilon_\mathrm{DQ}/\epsilon_\mathrm{D}}{1 + K[Q]\epsilon_\mathrm{DQ}/\epsilon_\mathrm{D}}\right) \qquad (76)$$

where I_0 (see eqn. (9)) is the total light intensity absorbed by the solution and ϵ_DQ and ϵ_D are the molar extinction coefficients at the wavelength of excitation of the species DQ and D, respectively. If DQ^* does not behave as D^*, the light absorption by the donor—acceptor couple obviously results in a quenching of each phenomenon which originates from D^*. This effect is called *static quenching*.

On the assumption that the manifestations (emissions and/or reactions) of DQ^* can be experimentally distinguished from the emissions or reactions of the excited donor, the consequences of static quenching can easily be accounted for: the quantum yield of each phenomenon of the donor is decreased by a factor $(1 + K[Q]\epsilon_{DQ}/\epsilon_D)^{-1}$. Thus, if reference is made to Case 1 of Sect. C(i), we have

$$\frac{\phi^0_{1e}}{\phi_{1e}} = \left(1 + K[Q]\,\frac{\epsilon_{DQ}}{\epsilon_D}\right) \tag{77}$$

$$\frac{\phi^0_{2e}}{\phi_{2e}} = (1 + k_{2q}\tau^0_2[Q])\left(1 + K\,\frac{\epsilon_{DQ}}{\epsilon_D}[Q]\right) \tag{78}$$

which may be rewritten as follows:

$$\frac{\phi^0_{2e}}{\phi_{2e}} = 1 + \left(k_{2q}\tau^0_2 + K\,\frac{\epsilon_{DQ}}{\epsilon_D}\right)[Q] + k_{2q}\tau^0_2 K\,\frac{\epsilon_{DQ}}{\epsilon_D}[Q]^2 \tag{79}$$

and

$$\frac{\phi^0_r}{\phi_r} = (1 + k_{2q}\tau^0_2[Q])\left(1 + \frac{k_{1r}k_{2q}}{k_{1r}K_2 + k_{1c}k_{2r}}[Q]\right)^{-1}\left(1 + K[Q]\,\frac{\epsilon_{DQ}}{\epsilon_D}\right) \tag{80}$$

It must be noted that in these cases [Q] represents the "free" quencher concentration. However, this concentration may be considered practically equal to the total quencher concentration if K is very small or the total donor concentration is much lower than the total quencher concentration.

Contrary to what happens to the quenching measurements under stationary illumination, the static quenching has no influence on the decay measurements (see eqns. (18) and (19)), because when the depopulation steps exhibit a first-order dependence on the excited state, the lifetime obviously does not depend on the concentration of D^* just after the flash.

The few examples known up to date of static quenching involving coordination compounds have been studied by comparing the intensity and lifetime quenching of the emission which originates from the quenched excited states. As mentioned before, the Stern—Volmer plots obtained from the intensity and lifetime quenching measurements do not coincide (compare eqn. (78) with eqn. (25)). The real difference between the two Stern—Volmer plots depends on the relative magnitude of the terms $K\epsilon_{DQ}/\epsilon_D$ and $k_{2q}\tau^0_2$, and obviously it increases with increasing [Q]. When $K\epsilon_{DQ}/\epsilon_D$ is higher than or about equal to $k_{2q}\tau^0_2$ and [Q] is sufficiently small to neglect the third term on the right-hand side of eqn. (79), the intensity Stern—Volmer plot is almost linear, with slope $(k_{2q}\tau^0_2 + K\epsilon_{DQ}/\epsilon_D)$ higher than that $(k_{2q}\tau^0_2)$ of the lifetime Stern—Volmer plot (eqn. (25)). As [Q] increases, the quadratic term of eqn. (79)

is no longer negligible and the intensity plot shows an upward curvature. When $K\epsilon_{DQ}/\epsilon_D \ll k_{2q}\tau_2^0$, and [Q] is sufficiently small to neglect the third term on the right-hand side of eqn. (79), the intensity and lifetime plots may be practically coincident within the experimental error. When the third term cannot be neglected, the intensity plot shows an upward curvature and the difference between the two Stern—Volmer plots becomes appreciable.

It should also be noted that if the ground-state "complex", DQ, has an absorption spectrum that differs from that of the donor, the Stern—Volmer plot obtained from steady state measurements will generally vary with varying the exciting wavelength.

(iv) Sensitization processes

A quenching process may give rise to a "sensitized" process, i.e. to some phenomenon which is characteristic of the quencher. Such phenomena, which are generally studied under continuous illumination conditions, may be emissions or chemical reactions of the quencher. The presence of a sensitized emission is a clear demonstration that the quenching is, at least in part, due to an energy transfer process

$$D^* + Q \rightarrow D + Q^* \tag{81}$$
$$Q^* \rightarrow Q + h\nu \tag{82}$$

while a sensitized photoreaction may be due either to an energy transfer or to a direct bimolecular reaction between D^* and Q (chemical sensitization):

$$Q^* \rightarrow \text{products} \tag{83}$$
$$D^* + Q \rightarrow \text{products} \tag{84}$$

The discussion of the kinetic treatment of a sensitized process may be based on the scheme of Fig. 2, where φ_0 is the quantum yield of population

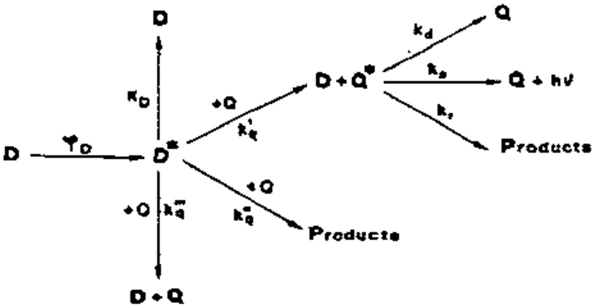

Fig. 2. Scheme for the discussion of the sensitization processes (see text).

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* If the emission (or the reaction) originates from a lower-energy excited state of Q, which is populated by means of radiationless transitions from Q^*, η_e (or η_r) must be the product of the efficiencies of all the steps which lead from Q^* to the observed phenomenon.

of D*, K_D is the sum of unimolecular deactivation processes of D*, k'_q represents an energy transfer process, k''_q a chemical sensitization and k'''_q a bimolecular quenching process which does not cause any phenomenon of Q. Q* may be depopulated through deactivation (k_d), emission (k_e) and reaction (k_r).

(a) Sensitization by energy transfer

In this case we assume that the chemical sensitization does not occur ($k''_q = 0$). The quantum yields for the sensitized emission and reaction are given by

$$\phi_e = \varphi_D \frac{k'_q [Q]}{K_D + (k'_q + k'''_q)[Q]} \eta_e \tag{85}$$

$$\phi_r = \varphi_D \frac{k'_q [Q]}{K_D + (k'_q + k'''_q)[Q]} \eta_r \tag{86}$$

where*

$$\eta_e = \frac{k_e}{k_d + k_e + k_r} \tag{87}$$

and

$$\eta_r = \frac{k_r}{k_d + k_e + k_r} \tag{88}$$

Sensitization experiments are generally interpreted by means of $1/\phi$ vs. $1/[Q]$ plots, which, by analogy with quenching plots (Sect. C(i)), are sometimes called *sensitization Stern—Volmer plots*:

$$\frac{1}{\phi_e} = \frac{1}{\varphi_D \eta_e} \frac{k'_q + k'''_q}{k'_q} + \frac{1}{\varphi_D \eta_e} \frac{K_D}{k'_q} \frac{1}{[Q]} \tag{89}$$

$$\frac{1}{\phi_r} = \frac{1}{\varphi_D \eta_r} \frac{k'_q + k'''_q}{k'_q} + \frac{1}{\varphi_D \eta_r} \frac{K_D}{k'_q} \frac{1}{[Q]} \tag{90}$$

Provided that φ_D does not depend on [Q] (see also below), linear sensitization Stern—Volmer plots are obtained*. Both the sensitized emission and the sensitized reaction show the same intercept/slope ratio, which is called *Stern—Volmer constant for the sensitization*:

$$k_{SV}(\text{sens}) = \frac{k'_q + k'''_q}{K_D} \tag{91}$$

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* It should be noted that, for a sensitized reaction, ϕ_r diminishes with time during the same experiment owing to the consumption of the quencher. In order to overcome this effect, the substitution of $1/[Q]$ by $\{[Q_0]/([Q_0] - [Q])\} \ln ([Q_0]/[Q])$, where $[Q_0]$ and $[Q]$ are the quencher concentrations at the beginning and the end of irradiation, respectively, has been proposed [19].

Extrapolation of the Stern—Volmer plot to $1/[\mathrm{Q}] = 0$ gives the *limiting quantum yield* of the sensitized process:

$$\phi_e(\lim) = \varphi_D \eta_s \eta_e \tag{92}$$

$$\phi_r(\lim) = \varphi_D \eta_s \eta_r \tag{93}$$

where

$$\eta_s = \frac{k'_q}{k'_q + k'''_q} \tag{94}$$

η_s may be called *limiting sensitization efficiency*[**] and the products $\eta_s\eta_e$ and $\eta_s\eta_r$ may be called *limiting sensitization yields* of the emission and reaction, respectively. A sensitization yield can also be obtained for conditions other than the limiting one.

The limiting sensitization quantum yields are generally compared with the quantum yields of the corresponding processes obtained upon direct irradiation of the quencher. This last quantum yield may be expressed [189] by

$$\phi(\mathrm{dir}) = \varphi' \eta(\mathrm{dir}) \tag{95}$$

where φ' is the quantum yield of the "direct" population of the quencher excited state which is also reached by energy transfer, and $\eta(\mathrm{dir})$ has the same meaning as η_e or η_r. Equation (95) must be compared with eqns. (92) or (93), which may be written in the general form

$$\phi(\lim) = \varphi_D \eta_s \eta \tag{96}$$

It is generally assumed that $\eta(\mathrm{dir}) = \eta$[*]. Therefore

$$\frac{\phi(\mathrm{dir})}{\phi(\lim)} = \frac{\varphi'}{\varphi_D \eta_s} \tag{97}$$

and since in several cases φ_D may be obtained by means of independent experiments, the following ratio may be calculated:

$$\varphi_D \frac{\phi(\mathrm{dir})}{\phi(\lim)} = \frac{\varphi'}{\eta_s} = \delta \tag{98}$$

A very simple situation occurs when $\delta = 1$; in this case, in fact, the by far most probable conclusion is that $\varphi' = \eta_s = 1$. When $\delta \neq 1$ and neither φ' nor η_s are independently known, the upper limit value of one of these quantities can be obtained assuming the other equal to unity.

The above equations only hold if φ_D does not depend on $[\mathrm{Q}]$. Such a situation occurs when (i) static quenching or transient effect are not present, (ii)

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[*] This assumption requires that the quencher excited state Q^* is produced in the same vibrational level and geometry by both energy transfer and direct excitation. Whenever this does not occur, the following statements may be meaningless.

[**] This quantity may also be called *limiting energy transfer efficiency*. In some papers [58, 61] it is simply called "energy transfer efficiency" and is indicated by γ.

the sensitization originates from a donor excited state that is the highest in energy among the quenched excited states of the donor, (iii) there are no back radiationless transitions *to* this state from other quenchable excited states, and (iv) there is no back radiationless transition *from* this state to a higher-energy excited state which is its precursor. The last condition, however, is not needed for obtaining a linear Stern—Volmer sensitization plot. Let us consider Case 4 of Sect. C(i) and assume that an energy transfer sensitization originates from D_2. Since the symbols K_2 and k_{2q} used in quenching equations correspond here to K_D and k'_q/η_s, respectively, one obtains

$$\varphi_{D_2} = \frac{k_{1c}(K_2 + k_{2q}[Q])}{K_1(K_2 + k_{2q}[Q]) - k_{1c}k_{2c}} \tag{99}$$

$$\frac{1}{\phi} = \frac{K_1 k_{2q}}{k_{1c}k'_q\eta} + \frac{K_1K_2 - k_{1c}k_{2c}}{k_{1c}k'_q\eta}\,\frac{1}{[Q]} \tag{100}$$

where ϕ and η refer to *sensitized* emission or reaction. It is evident that $1/\phi$ shows a linear dependence on $1/[Q]$, even if φ_{D_2} depends on $[Q]$. The limiting quantum yield is

$$\phi(\text{lim}) = \frac{k_{1c}}{K_1}\,\eta_s\eta \tag{101}$$

i.e. the same obtained when radiationless transitions from D_2 to D_1 are negligible ($k_{2c} \ll K_2$). The Stern—Volmer constant for the sensitization is

$$k_{SV}(\text{sens}) = \frac{K_1 k_{2q}}{K_1K_2 - k_{1c}k_{2c}} = \tau_2^0 k_{2q} \tag{102}$$

As a general rule, a linear Stern—Volmer sensitization plot requires that conditions (i), (ii) and (iii) above are obeyed. If this plot is linear even the quenching Stern—Volmer plots relative to the same donor excited state *must* be linear, and the sensitization Stern—Volmer constant *must* be equal to the quenching Stern—Volmer constant:

$$k_{SV}(\text{sensitization}) = k_{SV}(\text{quenching}) = \tau^0 k_q \tag{103}$$

As examples of non-linear sensitization Stern—Volmer plots, we shall examine Case 3 (sensitization from D_2) and Case 5 (sensitization from D_1) of Sect. C(i). For Case 3, we have

$$\frac{1}{\phi} = \frac{K_1}{k_{1c}\eta\eta_s} + \frac{k_{1q}K_2}{k_{1c}k'_q\eta} + \frac{k_{1q}}{k_{1c}\eta\eta_s}[Q] + \frac{K_1K_2}{k_{1c}k'_q}\,\frac{1}{[Q]} \tag{104}$$

Therefore, $\phi = 0$ for both $[Q] = 0$ and $[Q] = \infty$. The Stern—Volmer sensitization plot shows a minimum at

$$\frac{1}{[Q]} = \left(\frac{k_{1q}k_{2q}}{K_1K_2}\right)^{1/2} \tag{105}$$

For Case 5, we have

$$\frac{1}{\phi}=\frac{k_{1\mathrm{q}}}{k'_{\mathrm{q}}\eta}+\frac{K_1}{k'_{\mathrm{q}}\eta}\,\frac{1}{[\mathrm{Q}]}-\frac{k_{1\mathrm{c}}k_{2\mathrm{c}}}{(K_2+k_{2\mathrm{q}}[\mathrm{Q}])k'_{\mathrm{q}}\eta}\,\frac{1}{[\mathrm{Q}]} \tag{106}$$

The limiting quantum yield is

$$\phi(\mathrm{lim})=\frac{k'_{\mathrm{q}}\eta}{k_{1\mathrm{q}}}=\eta_{\mathrm{s}}\eta \tag{107}$$

i.e. equal to the value obtained when radiationless transitions from D_2 to D_1 are negligible ($k_{2\mathrm{c}} \ll K_2$).

(b) Sensitization by energy transfer and by chemical mechanism

If both energy transfer and chemical sensitization are simultaneously present, we obtain

$$\frac{1}{\phi_{\mathrm{e}}}=\frac{1}{\varphi_{\mathrm{D}}\eta_{\mathrm{e}}}\,\frac{k'_{\mathrm{q}}+k''_{\mathrm{q}}+k'''_{\mathrm{q}}}{k'_{\mathrm{q}}}+\frac{1}{\varphi_{\mathrm{D}}\eta_{\mathrm{e}}}\,\frac{K_{\mathrm{D}}}{k'_{\mathrm{q}}}\,\frac{1}{[\mathrm{Q}]} \tag{108}$$

$$\frac{1}{\phi_{\mathrm{r}}}=\frac{1}{\varphi_{\mathrm{D}}}\,\frac{k'_{\mathrm{q}}+k''_{\mathrm{q}}+k'''_{\mathrm{q}}}{k'_{\mathrm{q}}\eta_{\mathrm{r}}+k'''_{\mathrm{q}}}+\frac{1}{\varphi_{\mathrm{D}}}\,\frac{K_{\mathrm{D}}}{k'_{\mathrm{q}}\eta_{\mathrm{r}}+k'''_{\mathrm{q}}}\,\frac{1}{[\mathrm{Q}]} \tag{109}$$

Again, both the sensitization Stern—Volmer plots are linear provided that φ_{D} does not depend on [Q] (see above). The Stern—Volmer constant

$$k_{\mathrm{SV}}(\mathrm{sens})=\frac{\mathrm{intercept}}{\mathrm{slope}}=\frac{k'_{\mathrm{q}}+k''_{\mathrm{q}}+k'''_{\mathrm{q}}}{K_{\mathrm{D}}} \tag{110}$$

is the same for both the sensitized processes and is again equal to the quenching Stern—Volmer constant.

As a general rule, the Stern—Volmer constant for all the sensitized processes which originate from the same donor excited state is the same:

$$k_{\mathrm{SV}}(\mathrm{sens})=\frac{\Sigma k_{\mathrm{q}}}{K_{\mathrm{D}}} \tag{111}$$

independently of the number of quenching processes and the nature of the process(es) responsible for the sensitization. This constant must be equal to that obtained from the experiments on donor quenching.

The limiting quantum yields are given by

$$\phi_{\mathrm{e}}(\mathrm{lim})=\varphi_{\mathrm{D}}\eta'_{\mathrm{s}}\eta_{\mathrm{e}} \tag{112}$$

$$\phi_{\mathrm{r}}(\mathrm{lim})=\varphi_{\mathrm{D}}\eta'_{\mathrm{s}}\eta_{\mathrm{r}}+\varphi_{\mathrm{D}}\eta''_{\mathrm{s}} \tag{113}$$

where η'_{s} and η''_{s} (the limiting sensitization efficiency for the energy transfer and the chemical sensitization, respectively) are given by

$$\eta'_{\mathrm{s}}=\frac{k'_{\mathrm{q}}}{k'_{\mathrm{q}}+k''_{\mathrm{q}}+k'''_{\mathrm{q}}} \tag{114}$$

$$\eta_s'' = \frac{k_q''}{k_q' + k_q'' + k_q'''} \tag{115}$$

While $\phi_e(\text{lim})$ may be compared with $\phi_e(\text{dir})$ in the same way as we have seen in Sect. C(iv)(a), a similar comparison is much less useful in the case of $\phi_r(\text{lim})$ because of the presence of the chemical sensitization (i.e. of the term $\varphi_D \eta_s''$ in eqn. (113)). In fact by comparing eqns. (95) and (113), we obtain

$$\varphi_D \frac{\phi(\text{dir})}{\phi(\text{lim})} = \frac{\varphi' \eta(\text{dir})}{\eta_s' \eta_r + \eta_s''} \tag{116}$$

The only deduction which can be inferred from eqn. (116) is that, if $\varphi_D \phi(\text{dir})/\phi(\text{lim}) < 1$ and $\varphi' = 1$, some chemical sensitization must be present.

Finally it is to be noted that the limiting quantum yield is sometimes calculated by means of

$$\varphi(\text{lim}) = \phi\left(1 - \frac{\phi_e}{\phi_e^0}\right)^{-1} \tag{117}$$

where ϕ_e^0/ϕ_e is the quenching ratio for donor emission, measured at the same experimental conditions (and particularly, with the same quenching concentration) as the sensitization quantum yield, ϕ.

This equation obviously requires that $(1 - \phi_e/\phi_e^0)$ represents the fraction of donor excited molecules which are quenched in the excited state that leads to sensitization and, therefore, that φ_D does not depend on [Q]. In these conditions, however, a linear Stern—Volmer sensitization plot can be obtained, and a more accurated value of $\phi(\text{lim})$ can thus be calculated by extrapolating this plot.

D. DISCUSSION OF THE QUENCHING AND SENSITIZATION MECHANISMS

(i) Types of mechanisms

The discussion of the quenching mechanisms will be limited to the complexes of the *d* transition series in fluid solutions because the authors' interest mainly concerns this specific area. For a recent discussion concerning the quenching processes involving rare earth ions, see ref. 201.

The bimolecular quenching of an excited-state molecule may take place by several distinct mechanisms [2, 3, 197], the most important of which (Fig. 3) are (i) electronic energy transfer, (ii) chemical reaction, (iii) spin-catalyzed deactivation, (iv) external heavy-atom effect and (v) complex (excimer and exciplex) formation. Generally, while it is possible to show that a mechanism is important, it is very difficult, if not impossible, to establish that a mechanism is completely ineffective.

In the following sections, the participation of each one of these mechanisms in the quenching processes will be discussed, with particular emphasis on the factors which determine their occurrence and their relative importance.

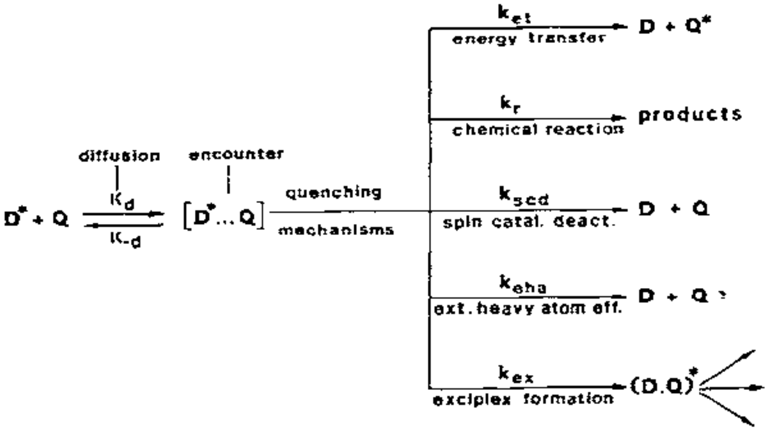


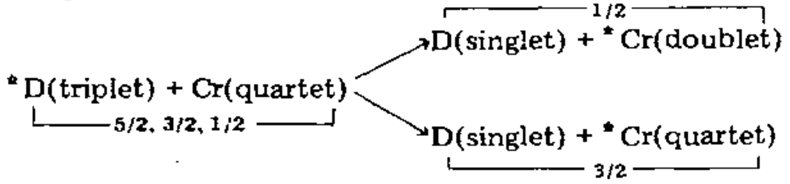
Fig. 3. Bimolecular quenching mechanisms for an excited-state molecule.

(ii) Electronic energy transfer

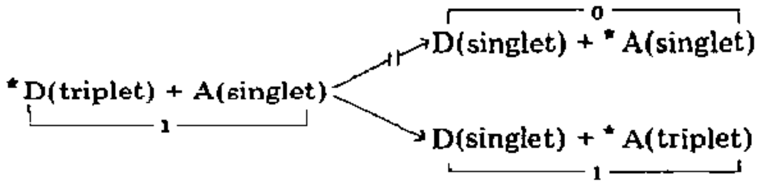
(a) Introduction

In fluid solutions, electronic energy transfer may occur by means of Coulombic (dipole—dipole) or exchange interactions [2, 3, 197]. The Coulombic interactions can take place over intermolecular distance much larger than the molecular diameter, but they are important only in the case in which the transitions in the donor and acceptor are allowed. The exchange interaction can only take place over distances of the order of the collision diameters and its magnitude is not related to the oscillator strength of the transition in the donor and acceptor. The general weakness of the low-energy absorption bands of transition metal complexes (in which the lowest spin-allowed bands are usually symmetry-forbidden) excludes the Coulombic interactions from an important role in energy transfer. Therefore, in most cases the electronic energy transfer processes involving transition metal complexes take place through exchange interactions which require a collisional mechanism.

It is also important to notice that, unlike most organic molecules, the ground state of a transition metal complex may have a high multiplicity, e.g. the ground state is a quartet for Cr^{III} complexes, it is a quintet for Mn^{III} complexes, etc. This causes a loss of selectivity of Wigner's spin rules for electronic energy transfer [2, 201]. For example, energy transfer from triplet donors to both spin-forbidden (doublet) and spin-allowed (quartet) excited states of Cr^{III} complexes is allowed



whereas when the ground state of the acceptor is a singlet, energy transfer from triplet donors is only allowed to spin-forbidden (triplet) excited states of the acceptor



In order to be certain that electronic energy transfer from the donor to the acceptor has occurred, a manifestation of an excited state of the acceptor must be observed. Physical events like acceptor luminescence or absorption by acceptor excited states give such definite evidence, but a sensitized chemical reaction of the acceptor is not by itself a proof that electronic energy transfer has occurred, since the observed reaction could be due to a chemical interaction between excited donor and ground-state acceptor or to some catalytic effect on the ground-state reactivity of the acceptor.

Of course when the occurrence of a reaction in the acceptor critically depends on the energy of the donors and not on their chemical nature, electronic energy transfer is most probably involved.

The results available (Tables 2 and 3) show that transition metal complexes can participate in electronic energy transfer processes as both donors and acceptors. In dealing with organic molecules in fluid solutions it has usually been found (and is commonly assumed) that electronic energy transfer is nearly diffusion controlled when spin and energy requirements are satisfied [2, 3, 197]. This, however, is not generally true when transition metal complexes are involved.

As is shown in Tables 5, 6 and 7, the quenching rate constants (which are upper limiting values for the energy transfer rate constants) may be up to three orders of magnitude lower that the diffusion controlled rates when one of the partners is a transition metal complex, and even lower when both the donor and acceptor are transition metal complexes. Evidently in these cases there are factors which reduce the quenching efficiency during the encounter lifetime. As far as the quenching by electronic energy transfer is concerned, the factors which may be involved in principle include (a) the nature of the ligands, (b) the nature of the metal, (c) the ionic charge, (d) the orbital nature of the excited states involved, (e) the geometry of the complex, (f) the coordination number and (g) the nature of the solvent. Unfortunately, it is impossible to assess the role played by each one of these factors because of the small number of results available. It may also be worth while recalling that the quenching rate constants strongly depend on the ionic strength of the solution when both the donor and acceptor are charged species (Sect. C(ii)). It follows that only k_q values extrapolated to zero ionic strength or measured at the same ionic strength can be compared.

(b) Energy transfer between transition metal complexes

For systems in which both the donor and the acceptor are transition metal complexes, only in the case of the $Ru(dipy)_3^{2+}$—$Cr(CN)_6^{3-}$ couple (Sect. E(iv)) is there experimental evidence that electronic energy transfer is the *principal* mechanism which causes the observed donor quenching [61], and in some 20 cases there is experimental evidence for the participation of electronic energy transfer in the quenching process. However, it can be confidently assumed that electronic energy transfer is also involved in other cases. For example, in the quenching of the ^3CT state of $Ru(dipy)_3^{2+}$ by Cr^{III} complexes which are not able to exhibit luminescence in fluid solution, no sensitized luminescence is of course observed, but there is no reason to believe that the quenching mechanism is different from that involved for $Cr(CN)_6^{3-}$ [12, 61] and *trans*-$Cr(en)_2(NCS)_2^+$ [113] where sensitized emission is observed. The other important bimolecular quenching mechanism for (^3CT)-$Ru(dipy)_3^{2+}$, namely electron transfer to the acceptor (Sect. D(iii)), is not favoured with Cr^{III} complexes which are generally not easily reduced. Therefore it can be assumed that the quenching of the $Ru(dipy)_3^{2+}$ phosphorescence by most Cr^{III} complexes is mainly due to electronic energy transfer.

On this assumption, the rate constants collected in Table 5 for the quenching of the $Ru(dipy)_3^{2+}$ phosphorescence by various Cr^{III} complexes can give some information on the role played by some of the factors mentioned above in determining the energy transfer efficiency. For such systems, only three properties of the acceptor complexes change, namely the nature of the ligands, the ionic charge, and the geometry. Within each one of the *cis*- and *trans*-$Cr(en)_2XY^+$ families only the nature of the X and Y ligands changes, and for each *cis*—*trans* couple the two complexes only differ, of course, in the geometry. The data shown in Table 5 for the $Ru(dipy)_3^{2+}$—Cr^{III} systems clearly indicate that the nature of the ligands is a very important factor. For the ligands involved, the quenching ability increases in the series $F^- < Cl^- < NCS^- < Br^-$, which does not exactly coincide with the nephelauxetic series [113]. A change in the ligands seems to cause a larger effect in the *cis* family. The quenching ability of the *cis* isomer is higher than that of the corresponding *trans* isomer for each one of the three couples which have been examined, showing that geometric factors play some role in determining the energy transfer efficiency. Owing to the very important ligand effect, it is not possible to establish the role played by a change in the ionic charge. For example, the great difference between the quenching constants of $Cr(CN)_6^{3-}$ and $Cr(en)_3^{3+}$ and more generally the decrease in the quenching constant with decreasing negative charge of the acceptor (note that the donor is a cation) cannot be attributed simply to an ionic charge effect since the change in the ionic charge is necessarily accompanied by a change in the nature of the ligands. On the other hand, the high quenching ability of $Cr(dipy)_3^{3+}$ does not prove that the ionic charge is unimportant, since in this case a chemical quenching mechanism could be predominant [173]. As fas as the ligand effect is concerned, it may be interesting to note that the quenching constant of the $Ru(dipy)_3^{2+}$

TABLE 6

Rate constants for the quenching of transition metal complex excited states by transition metal complexes (selected systems [a])

Donor	Acceptor	k_q (M^{-1} s^{-1})	k_d (M^{-1} s^{-1}) [b]	Experimental conditions	Ref.
$Ru(dipy)_3^{2+}$	$Mo(CN)_8^{4-}$	9×10^9	8.9×10^9	22°C, H_2O, $\mu = 0.01$	117
	$Cr(CN)_6^{3-}$	2.1×10^{10}	3.2×10^{10}	22°C, H_2O, $\mu \to 0$	112
	$PtCl_4^{2-}$	1×10^{10}	1.6×10^{10}	22°C, H_2O, $\mu = 0.002$	117
	$Co(EDTA)^-$	3×10^8	$>2 \times 10^9$	25°C, H_2O, $\mu \approx 2$	31
	$Ni(gly)_2$	4×10^7	7.4×10^9	22°C, H_2O	113
	$Cr(en)_3^{3+}$	$\leqslant 10^6$	4.4×10^8	22°C, H_2O, $\mu \to 0$	173
	$Cr(dipy)_3^{3+}$	5×10^8	4.4×10^8	22°C, H_2O, $\mu \to 0$	173
	t-$Cr(en)_2F_2^+$	3×10^6	3.3×10^9	22°C, H_2O, $\mu \to 0$	113
	t-$Cr(en)_2Cl_2^+$	3.6×10^7	3.3×10^9	22°C, H_2O, $\mu \to 0$	113
	t-$Cr(en)_2(NCS)Cl^+$	7.4×10^7	3.3×10^9	22°C, H_2O, $\mu \to 0$	113
	t-$Cr(en)_2(NCS)_2^+$	9.1×10^7	3.3×10^9	22°C, H_2O, $\mu \to 0$	113
	t-$Cr(en)_2Br_2^+$	1.2×10^8	3.3×10^9	22°C, H_2O, $\mu \to 0$	113
	c-$Cr(en)_2Cl_2^+$	4.9×10^7	3.3×10^9	22°C, H_2O, $\mu \to 0$	113
	c-$Cr(en)_2(NCS)Cl^+$	1.4×10^8	3.3×10^9	22°C, H_2O, $\mu \to 0$	113
	c-$Cr(en)_2(NCS)_2^+$	5.0×10^8	3.3×10^9	22°C, H_2O, $\mu \to 0$	113
$Cr(en)_3^{3+}$	$Co(H_2O)_6^{2+}$	1.5×10^5	4.4×10^8 [c]	20°C, H_2O, $\mu \approx 2$	103
	$Co(H_2O)_5Cl^+$	5×10^6	2.1×10^9 [c]	20°C, H_2O, $\mu \approx 2$	103
	$Co(H_2O)_2Cl_2$	8×10^7	7.4×10^9	20°C, H_2O	103
	$Co(H_2O)Cl_3^-$	$\sim 2 \times 10^8$	$>1 \times 10^9$	20°C, H_2O, $\mu \approx 2$	103

[a] For each one of these systems, except the $Ru(dipy)_3^{2+}$—$Cr(dipy)_3^{3+}$ couple, electronic energy transfer is believed to be the main or the only quenching mechanism (see text). [b] Calculated for the experimental conditions given in the fifth column by means of the Debye equations (see Sect. C(ii)), with an encounter radius of 5 Å for each complex. [c] At $\mu = 0$.

phosphorescence by $Co(NH_3)_5X^{2+}$ complexes increases in the series $F^- < Cl^- < Br^-$ [22], and that $Co(HEDTA)Br^-$ is a better quencher than $Co(HEDTA)Cl^-$ [31]. These results are in line with the quenching ability series previously reported for the $Cr(en)_2XY^+$ acceptors. However, apart from the possibility that a chemical quenching takes place for the Co^{III} complexes [15, 22] (Sect. D(iii)), the availability of orbitally different (i.e. CT and MC) excited states for the acceptor should also be taken into consideration [31]. The elucidation of these and other aspects of electronic energy transfer between transition metal complexes will largely depend on the discovery and the characterization of other complexes which can replace $Ru(dipy)_3^{2+}$ as a suitable donor.

(c) Energy transfer from organic molecules to transition metal complexes

For systems in which the donor is an organic molecule and the acceptor is a transition metal complex, only in the case of the benzil—$Cr(CN)_6^{3-}$ couple is there experimental evidence that electronic energy transfer is the *principal* mechanism which causes the observed donor quenching [58, 61, 73]. In several other cases, however, there is experimental evidence for the participation of electronic energy transfer in the quenching process. For many of these cases there is no reason to believe that chemical quenching or other quenching mechanisms occur, so that we can reasonably assume that electronic energy transfer is the main (or the only) quenching mechanism. On this assumption, the quenching rate constants reported in Table 6 can give some indication as to the role played by the various factors (see Sect. D(ii)(a)) in determining the energy transfer efficiency. Like electronic energy transfer between transition metal complexes, the change in the ligands certainly affects the quenching constants: for ML_6^{2+} complexes, the quenching ability of NH_3 is higher than that of H_2O [144], and for Cr^{III} complexes aniline is more efficient than NH_3 [59]. The experiments of organic triplet quenching by Ni^{II} chelates carried out by Wilkinson [157] give information about the role played by some of the other factors. The decrease in the quenching constant with decreasing energy of the triplet donor (e.g. from phenanthrene to 1,2-benzanthracene, Table 6) is attributed to the possibility of the high-energy donors transferring energy to ligand-centred or charge transfer states of the acceptor, whereas the low-energy donors can only transfer energy to the metal-centred states. A very similar effect has been found for Pd^{II} complexes of the same type [162]. The relatively high values of the quenching constant even when only metal-centred excited states of the donor are available for the energy transfer is attributed to the square planar structure of the Ni chelates $Ni(S\text{-}2)_2$ and $Ni(S\text{-}3)_2$ which permits good interactions with the donor orbitals through the *d* metal orbitals perpendicular to the molecular plane [157]. This hypothesis is supported by the strong decrease in the quenching constant for the same low-energy donor (e.g. 1,2-benzanthracene) when the geometry or the coordination number of the complex are changed so as to shield all the *d* metal orbitals. When high-energy donors (e.g. phenanthrene) are used, the

TABLE 6

Rate constants for the quenching of organic molecule excited states by transition metal complexes (selected systems [a])

Donor	Acceptor	k_q $(M^{-1}\ s^{-1})$	k_d [b] $(M^{-1}\ s^{-1})$	Experimental conditions	Ref.
acridine	$Co(H_2O)_6^{2+}$	1.0×10^7	7.4×10^9	22°C, H_2O	144
	$Co(NH_3)_6^{2+}$	3.6×10^8	7.4×10^9	22°C, H_2O	144
	$Ni(H_2O)_6^{2+}$	3.4×10^7	7.4×10^9	22°C, H_2O	144
	$Ni(NH_3)_6^{2+}$	3.3×10^8	7.4×10^9	22°C, H_2O	144
erythrosin	$Cr(NCS)_4(NH_3)_2^-$	6.2×10^6	—	−72°, 90% EtOH·H_2O	59
	$Cr(NCS)_4(aniline)_2^-$	1.2×10^7	—	−72°, 90% EtOH·H_2O	59
phenanthrene	$Ni(S\text{-}3)_2$ (square planar)	8.1×10^9	1×10^{10}	22°C, benzene	157
	$Ni(S\text{-}2)_2$ (square planar)	3.9×10^9	1×10^{10}	22°C, benzene	157
	$Ni(S\text{-}2)_2(py)_2$ (octahedral)	1.4×10^9	1×10^{10}	22°C, benzene	157
	$Ni(S\text{-}6)_2$ (tetrahedral)	2.5×10^9	1×10^{10}	22°C, benzene	157
1,2-benzanthracene	$Ni(S\text{-}3)_2$ (square planar)	3.2×10^9	1×10^{10}	22°C, benzene	157
	$Ni(S\text{-}2)_2$ (square planar)	2.0×10^9	1×10^{10}	22°C, benzene	157
	$Ni(S\text{-}2)_2(py)_2$ (octahedral)	$<1 \times 10^7$	1×10^{10}	22°C, benzene	157
	$Ni(S\text{-}6)_2$ (tetrahedral)	$<1 \times 10^7$	1×10^{10}	22°C, benzene	157

TABLE 6 (continued)

anthracene	Cr(acac)$_3$	1.3×10^9	1×10^{10}	~20°C, benzene	148
	$Cr(NCS)_4(NH_3)_2^-$	5.6×10^8	$\sim 5 \times 10^9$	~20°C, 70% EtOH—H_2O	147
	$Cr(NH_3)_5Cl^{2+}$	3.0×10^7	$\sim 5 \times 10^9$	~20°C, 70% EtOH—H_2O	147
	$Cr(CN)_6^{3-}$	5.9×10^7	$\sim 5 \times 10^9$	~20°C, 70% EtOH—H_2O	147
	$Cr(en)_3^{3+}$	1.1×10^7	$\sim 5 \times 10^9$	~20°C, 70% EtOH—H_2O	147
	$Cr(urea)_6^{3+}$	5.7×10^6	$\sim 5 \times 10^9$	~20°C, 70% EtOH—H_2O	147
naphthalene	$Cr(NCS)_4(NH_3)_2^-$	1.3×10^9	$\sim 5 \times 10^9$	~20°C, 50% EtOH—H_2O	147
	$Cr(en)_2Cl_2^+$	2.0×10^8	$\sim 5 \times 10^9$	~20°C, 50% EtOH—H_2O	147
	$Cr(NH_3)_5Cl^{2+}$	2.0×10^8	$\sim 5 \times 10^9$	~20°C, 50% EtOH—H_2O	147
	$Cr(urea)_6^{3+}$	5.6×10^8	$\sim 5 \times 10^9$	~20°C, 50% EtOH—H_2O	147
	$Cr(CN)_6^{3-}$	1.7×10^8	$\sim 5 \times 10^9$	~20°C, 50% EtOH—H_2O	147
	$Cr(en)_3^{3+}$	6.2×10^7	$\sim 5 \times 10^9$	~20°C, 50% EtOH—H_2O	147

[a] For each one of these systems, electronic energy transfer is believed to be the main or the only quenching mechanism (see text). [b] Calculated using the simplified Debye equation [198] for the experimental conditions given in the fifth column.

quenching constant is almost unaffected by a change in the geometry or coordination number since the donor—acceptor interaction takes place through ligand orbitals [157].

As happens for energy transfer between transition metal complexes (Sect. D(ii)(b)), it is not clear what is the role played by the ionic charge of the complex. The main reason for this, of course, is that again any change in the ionic charge also causes a change in the nature of the ligands. In any case, we can note that for the anthracene—Cr^{III} systems, increasing the ionic charge (either positive or negative) decreases the quenching efficiency [147]. This effect could be attributed to increased shielding by (polar) solvent molecules with increasing ionic charge. However, this effect is much less evident in the naphthalene—Cr^{III} systems (Table 6) [147]. In general, the role of the solvent in the energy transfer processes has not yet been clarified, but the effects of solvation are known to be very important, especially for "uncomplexed" ions such as those of the rare earths (Sect. B(v)(o)).

(d) Energy transfer from transition metal complexes to other species

Evidence for the participation of electronic energy transfer in the quenching of excited states of transition metal complexes by other molecules (generally oxygen) has also been reported. For example, the quenching of the $Ru(dipy)_3^{2+}$ or $Ru(phen)_2(CN)_2$ luminescence by oxygen has been shown to yield singlet oxygen [118]. For the quenching of Cr^{III} complexes by oxygen, systematically investigated by Pfeil [109], there is no experimental proof that the process is due to electronic energy transfer, but this mechanism is nevertheless the most likely one even for these systems. On this assumption, the quenching rate constants (Table 7) show once again that there are factors which reduce the energy transfer efficiency. The nature of the ligands seems to play again an important role [109], but it should be noted that in this series the change in the ligands is generally accompanied by a change in the ionic charge.

(iii) Quenching by chemical mechanisms

(a) Introduction

Consideration of the quenching of donor excited states by "chemical" rather than "physical" processes directs attention to one aspect of the chemistry of donor excited states: the reactivity of the excited state towards the acceptor substrate. The range of possible reaction types is much more limited when coordination compounds are donors or acceptors than when donors and acceptors are organic compounds. By far the largest classes of reactions which coordination compounds undergo in the ground state are ligand substitution and oxidation—reduction reactions, and these might be expected to play equivalent roles in the reactions of excited states of coordination compounds or of organic donors with coordination compounds.

TABLE 7

Rate constants for the quenching of transition metal complex excited states by other species (selected systems [a])

Donor	Acceptor	k_q (M^{-1} s^{-1})	k_d (M^{-1} s^{-1}) [b]	Experimental conditions	Ref.
$Ru(dipy)_3^{2+}$	O_2	3.3×10^9	7.4×10^9	21°C, H_2O	118
$Ru(dipy)_2(CN)_2$	O_2	4.5×10^9	7.4×10^9	21°C, H_2O	118
$Ru(phen)_3^{2+}$	O_2	4.7×10^9	7.4×10^9	21°C, H_2O	118
$Ru(phen)_2(CN)_2$	O_2	5.5×10^9	7.4×10^9	21°C, H_2O	118
$Ir(phen)_2Cl_2^+$	*t*-stilbene	5×10^8	8.3×10^9	22°C, DMF	99
	2-acetonaphthone	2×10^7	8.3×10^9	22°C, DMF	99
$Cr(acac)_3$	O_2	10^{11} [c]	—	[c]	109
t-$Cr(NCS)_4(NH_3)_2^-$	O_2	2×10^9 [c]	—	[c]	109
$Cr(CN)_6^{3-}$	O_2	2×10^8 [c]	—	[c]	109
$Cr(en)_3^{3+}$	O_2	$\leqslant 10^7$ [c]	—	[c]	109
$Cr(tn)_3^{3+}$	O_2	$\leqslant 10^7$ [c]	—	[c]	109

[a] For each of these systems, electronic energy transfer is believed to be the main-or the only quenching mechanism (see text). [b] Calculated using the simplified Debye equation [198] for the experimental conditions given in the fifth column. [c] Extrapolated values at 25°C, in methanol—water—ethylene glycol (2:1:1).

Ligand substitution reactions involving excited-state donors which are ligands or potential ligands (eqn. (118)) have not been observed

$$D^* + ML_n \rightarrow ML_{n-1}D + L \tag{118}$$

and the nature of ligand substitution processes at metal centres makes reactions of this type unlikely. Substitution in coordination compounds normally involves the displacement of one or more already coordinated ligands or solvent molecules. If the incoming ligand is in an excited state the substitution reaction must, for quenching to occur by the substitution reaction, compete with the natural lifetime of the excited state ($< 10^{-6}$ s in general). This requires that the substitution reaction have a second-order rate constant $\geqslant 10^6$ M^{-1} s^{-1}. For octahedral complexes the rate of substitution is normally only weakly dependent on the nature of the entering group, and substitution reactions of excited-state donors might be expected to have rates which are of the same order of magnitude as the substitution rates of ground-state ligands. For inert complexes of cobalt(III) and chromium(III), for example, the rate constants for substitution are many orders of magnitude below the rates which could compete with the natural decay of excited donor states and quenching by this mechanism is impossible.

Even for more labile metal centres the rates of substitution are normally too low to compete with excited-state decay. For example, in the first transition series, V^{II}, Fe^{III}, Mn^{III} and Ni^{II} have solvent exchange rates of the order of 10^2—10^4 s^{-1}, while Mn^{II}, Fe^{II} and Co^{II} have solvent exchange rates of about 10^6—10^7 s^{-1}. For ions such as Cr^{2+} and Cu^{2+}, with solvent exchange rates of about 10^8—10^9 s^{-1}, substitution by an excited donor might provide a feasible path for donor quenching, but to date no such reactions have been observed. The observation of substitution quenching in the case of Cr^{2+} and Cu^{2+} would be experimentally very difficult; even for ground-state substitution reactions of these ions there have been very few measurements of the rates of substitution reactions.

For excited-state donors which are themselves coordination compounds "chemical" quenching by ligand substitution in the excited state (eqn. (119)) also implies high second-order rate constants and high ligand concentrations. The rates of ligand substitution for

$$^*ML_n + A \rightarrow ML_{n-1}A + L \tag{119}$$

transition metal excited states are not known. Most studies of photochemical substitution reactions of transition metal coordination compounds have been confined to photosolvation reactions, where the very high solvent concentration masks direct measurement of the substitution process, and from continuous photolysis experiments only indirect information on the dynamics of the photosolvation process from the excited state is obtained. This quenching mechanism is a possible one, particularly by solvent molecules, but remains one which has yet to be demonstrated experimentally.

Only one common class of bimolecular reactions of coordination compounds is able to provide reasonably probable paths for chemical quenching. Oxidation—reduction reactions (electron transfer reactions) more commonly than substitution reactions have rates which can compete with excited-state decay. Intermolecular electron transfer reactions of transition metal complexes occur by one of two limiting mechanisms: inner or outer sphere. In the inner sphere mechanism primary bonds are made and broken in the approach to the transition state, and the energetics of the transition state are similar to those for substitution reactions at the same metal centre; electron transfer takes place after the new coordination sphere has been formed, or concurrently with it. In the outer sphere mechanism, electron transfer between two metal centres (or between an electron donor or acceptor and a metal centre) takes place through ligands in coordination spheres which retain their integrity during the passage up to, and through, the transition state. After the electron transfer the coordination spheres may or may not retain their integrity. Inner sphere electron transfer reactions are frequently substitution controlled, and even if electron transfer controlled (so that electron transfer after substitution is the rate-determining step) cannot be faster than the substitution step. For this reason inner sphere electron transfer reactions (eqn. (120)) are as unlikely as substitution reactions to be able to compete with excited-state decay.

$$^{*}ML_6 + M'A_6 \rightarrow [L_5M{-}L{-}M'A_5]^{\ddagger} \rightarrow M^{+}L_6 + M'^{-}A_6 \qquad (120)$$

The rates of outer sphere electron transfer reactions are not subject to limitations of dependency on the substitution rate, and as the coordination spheres remain intact during the electron transfer process may be very fast (even diffusion controlled) between substitution inert complexes such as hexacyano-iron complexes, or first-row transition metal complexes involving phenanthroline and dipyridyl ligands. Outer sphere electron transfer reactions

$$^{*}ML_6 + M'A_6 \rightarrow M^{+}L_6 + M'^{-}A_6 \qquad (121)$$

can also take place by pathways which directly involve the ligands in the electron transfer, with electron transfer between one of the metal centres and a ligand of the other metal centre, producing reduced or oxidized ligand species still bound to the metal, which then undergo intramolecular electron transfer to the metal centre.

Non-metal species can also act as the primary electron donors or acceptors in outer sphere reactions, and this increases the possibilities of reactions of this kind being able to quench excited states of both organic and coordination compound donors. The rates of outer sphere electron transfer reactions are governed by "intrinsic" factors (the self-exchange rates of the reactants) and "extrinsic" factors (the overall free energy change of the reaction) and are well interpreted by the Marcus theory [203] of these processes. However, for reactions involving excited species, the self-exchange rates are still unknown, even when ΔG^0 for the reaction can be estimated. Systematic data for the rates of electron transfer reactions of excited states will allow the relative importance of the intrinsic and extrinsic factors to be evaluated in some cases.

It is difficult to demonstrate conclusively a chemical quenching mechanism, even if the quenching involves electron transfer, because of the formal similarity (or even identity) with energy transfer processes especially where the excited state involved is a charge transfer state. In charge transfer excited states of metal complexes there is a relative separation of charge between the metal and ligand compared with the ground state. This charge separation will, in the limit, be the same as for an intramolecular electron transfer reaction. If, as is frequently the case, the two oxidation states of the metal differ widely in lability (as is certainly true for the +2 and +3 oxidation states of the first-row metals from Cr through Co) it may be experimentally extremely difficult to distinguish between an energy transfer process which results in the formation of an excited charge transfer state of the acceptor complex which then undergoes intramolecular electron transfer (eqns. (122) to (125))

$$D^* + ML_6 \rightarrow (CT)^*ML_6 + D \tag{122}$$
$$(CT)^*ML_6 \rightarrow M^-L_5L^+ \tag{123}$$
$$M^-L_5L^+ \rightarrow M^- + 5L + L^+ \tag{124}$$
$$D + L^+ \rightarrow D^+ + L \tag{125}$$

and electron transfer from the donor to the acceptor directly (eqns. (126) and (127)). In the first case, following intramolecular electron transfer (eqn.

$$D^* + ML_6 \rightarrow D^+ + M^-L_6 \tag{126}$$
$$M^-L_6 \rightarrow M^- + 6L \tag{127}$$

(123)), the acceptor metal will be found in the new oxidation state together with a ligand radical. The ligand radical can frequently oxidize the ground-state donor (eqn. (125)), and the products of these reactions will be indistinguishable from those of the direct electron transfer quenching which results in the change in oxidation state of the donor and acceptor directly (eqns. (126) and (127)). Because of the more general lability of cobalt(II) than cobalt(III), those systems which have been most frequently studied apart from chromium(III) systems (in which photochemical electron transfer reactions have rarely been observed) have been liable to conflicting interpretations of this kind. Experimentally the distinction between energy transfer and charge transfer quenching in such systems is dependent on distinguishing between the intramolecular electron transfer step (eqn. (123)) and the intermolecular electron transfer step (eqn. (126)). Evidence for the ligand radical in the solutions, or for the subsequent oxidation of the ground-state donor molecule at rates different from the quenching rate is needed to show definitely that the quenching is an energy transfer process, and normally only a combination of dynamic flash photolysis, phosphorescence quenching and scavenger studies can provide this in the general case. Only in very exceptional circumstances can the mechanism be deduced with certainty from product analysis alone, and even scavenger studies may require the short timescales of flash photolysis if they are to be correctly interpreted. The secondary reactions are unrelated to the quenching process but greatly add to the experimental complexity.

The possible reactions which might be responsible for quenching by a chemical process have been discussed so far on the assumption that the metal centre of either donor, quencher or both is involved, but another class of possible quenching reactions are those in which the primary chemical reaction takes place with bound ligands. In the general case, such reactions may be of any of the types which have frequently been demonstrated for interactions between organic donors and acceptors [204]. Hydrogen atom abstraction from a bonded ligand by an excited-state organic donor, for example, will provide a path for chemical quenching [28]. Reactions of this sort can only take place with suitable ligands, and a systematic search for evidence of them has not yet been undertaken. Frequently the restrictions outlined above for the distinction between electron transfer and energy transfer modes, such as the rapidity of secondary reactions, will have to be taken into account, and the production of radical species, either free, or bonded to the metal centre, will increase the probability of secondary intermolecular and intramolecular oxidation—reduction reactions.

(b) Quenching by electron transfer processes

The number of systems for which a chemical quenching mechanism has been definitely established is very small, and as anticipated (Sect. D(iii)(a)) these are all electron transfer processes. The establishing of the true mode of the quenching process is no easier, and in many cases is harder, than the determination of the intimate mechanism of an inorganic reaction, but very few experimental studies have been undertaken with the degree of concern for the testing of a reaction scheme which is commonplace in other mechanistic investigations. In particular the chemistry of oxidation—reduction reactions of organic and inorganic free radicals has not always been properly understood and relevant data for pertinent free radical reactions [205] which are available from organic systems or from pulse radiolysis experiments have frequently been ignored. An important factor which has been largely overlooked in the discussion of possible quenching mechanisms is that for many free radicals which may be generated in inorganic systems the labels "oxidizing radical" or "reducing radical" have little meaning: the radicals are frequently capable of rapid disproportionation reactions, and may act both as electron donors and as electron acceptors with widely different standard potentials. Even H atoms, widely regarded as reducing agents, are capable of oxidizing Fe^{2+} to Fe^{3+} in acid solution [206]. In many cases the quenching mechanism must provisionally be regarded as still to be established by further experimental observations in which all the possible complications have been taken into account. In nearly all cases dynamic photolysis studies are needed to complement the results already obtained. The chemistry of excited states of coordination compounds is still largely unexplored. There is only one example at present of the quenching of an organic donor by a coordination compound which has definitely been shown to take place by an electron transfer mechanism. The quenching of triplet perylene by Eu^{3+} ions takes place at near diffusion controlled rates and flash photolysis experiments have shown that the perylene cation radical is the primary product of the quenching reaction, definitely establishing electron transfer from triplet perylene to Eu^{3+} as the quenching mechanism [167]

$$\text{(T)perylene} + Eu^{3+} \rightarrow Eu^{2+} + \text{(S)perylene}^{+} \tag{128}$$

Flash photolysis experiments have also shown that the triplet state of zinc-uroporphyrin can be quenched by a number of one-electron oxidizers or reducers to produce the cation radical $ZnUP^{+}$ (eqn. (129)) or the anion $ZnUP^{-}$·

$$\text{(T)ZnUP} + M(CN)_6^{3-} \rightarrow M(CN)_6^{4-} + ZnUP^{+} \tag{129}$$

The results are interesting because for the series of quenchers $Cr(CN)_6^{3-}$, $Mn(CN)_6^{3-}$, $Fe(CN)_6^{3-}$ and $Co(CN)_6^{3-}$ the quenching and electron transfer rate constants were 2.2×10^5, 4.9×10^7, 1.9×10^7 and 2.6×10^3 M^{-1} s^{-1} at *p*H 10.8 [14] and the reduction of Cr^{III} by an excited-state charge transfer process does not appear to have been reported previously. At lower *p*H, $Fe(CN)_6^{4-}$ was found to reduce triplet ZnUP to $ZnUP^{-}$. These results represent the first series of data for electron transfer reactions of the same excited state for a number of different quenchers, and more information of this kind is needed if the chemistry of such reactions is to be as well understood as that of ground-state electron transfer reactions.

In some favourable cases such as the quenching of triplet $Ru(dipy)_3^{2+}$ by Tl^{3+} (see Sect. B(iv)(b)) the energy levels of the quencher may preclude quenching by energy transfer and the observation of an electron transfer reaction on continuous photolysis may be sufficient to show that quenching takes place by an electron transfer mechanism. The problems of interpreting the results of continuous photolysis experiments of this type are well illustrated by the quenching of triplet charge transfer $Ru(dipy)_3^{2+}$ by Fe^{3+} ions [114]. The quenching rate constant is 2×10^9 M^{-1} s^{-1} but no overall chemical change is observed in continuous irradiation. Although the quenching reaction has been shown to be one of electron transfer by flash photolysis [115]

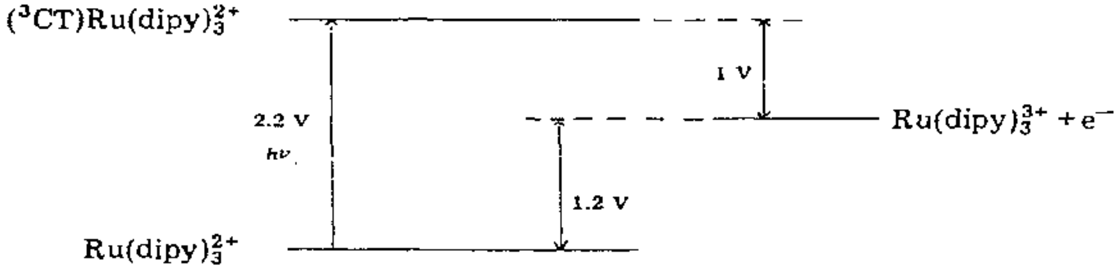
$$(^3CT)Ru(dipy)_3^{2+} + Fe^{3+} \rightarrow Ru(dipy)_3^{3+} + Fe^{2+} \tag{130}$$

the rate constant for the reduction of the $Ru(dipy)_3^{3+}$ produced by the quenching, by the Fe^{2+}, is 7.2×10^5 M^{-1} s^{-1} [25]

$$Fe^{2+} + Ru(dipy)_3^{3+} \rightarrow Fe^{3+} + Ru(dipy)_3^{2+} \tag{131}$$

and under these conditions no overall change results in continuous photolysis experiments. In dynamic flash photolysis studies, however, reaction (131) is readily observed, and it is possible to demonstrate that the quenching reaction is indeed one of electron transfer [115].

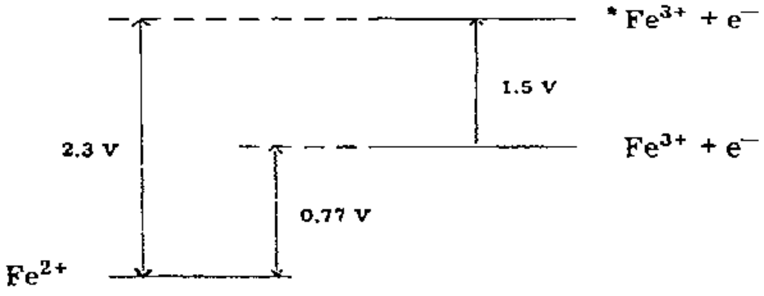
It should be noted that arguments based on the expected (hypothetical) reduction potentials of excited states of donor species in relation to possible electron transfer quenching mechanisms are not in themselves of value, because exactly the same arguments can be applied to the excited state of the quencher presumably formed by an energy transfer quenching process. The application of thermodynamic arguments to excited states which are not in equilibrium is open to objections on theoretical grounds, but the practice has some value if it is simply applied to energy level diagrams and true thermodynamic functions, such as ΔG^0 or equilibrium constants are not calculated for the excited-state species (for which the normal chemical potential in the presence of the radiation field is meaningless). It is always possible to formulate equivalent arguments from both the electron transfer quenching and the energy transfer quenching viewpoints, although fortunately the two models suggest different experimental observations. This can be illustrated in the case of the quenching of triplet $\mathrm{Ru(dipy)_3^{2+}}$ by $\mathrm{Fe^{3+}}$. If changes in entropy between ground state and excited states are small, the excitation energy can be considered as changing the standard reduction potential, and for triplet $\mathrm{Ru(dipy)_3^{2+}}$ the energy diagram is



with the reduction potential

$$\mathrm{Ru(dipy)_3^{3+}} + e \rightarrow (^3\mathrm{CT})\mathrm{Ru(dipy)_3^{2+}} \qquad (132)$$

being ca. − 0.9 V if the entropy differences between the states are small; so that the reduction of $\mathrm{Fe^{3+}}$ by triplet $\mathrm{Ru(dipy)_3^{2+}}$ is apparently much more favoured than the reduction by ground-state $\mathrm{Ru(dipy)_3^{2+}}$. However, if energy transfer from triplet $\mathrm{Ru(dipy)_3^{2+}}$ takes place to an excited state of $\mathrm{Fe^{3+}}$ (a suitable state lies 12.3 kK, i.e. 1.5 V, above the ground state) then the energy diagram is



and $^*Fe^{3+}$ will be now favoured to oxidize the ground-state $Ru(dipy)_3^{2+}$ and the sequence of reactions would be

$$(^3CT)Ru(dipy)_3^{2+} + Fe^{3+} \rightarrow Ru(dipy)_3^{2+} + {}^*Fe^{3+} \quad (133)$$
$$^*Fe^{3+} + Ru(dipy)_3^{2+} \rightarrow Ru(dipy)_3^{3+} + Fe^{2+} \quad (134)$$

Notice that the same products are formed from both quenching processes and that the electron transfer reactions of both the $Ru(dipy)_3^{2+}$ and Fe^{3+} ions have been rendered more favourable energetically. However, the dynamics of the two schemes are different, and the oxidation of the $Ru(dipy)_3^{2+}$ would take place in one case at the same rate as the quenching reaction, in the second case at the rate of the reaction between $^*Fe^{3+}$ and $Ru(dipy)_3^{2+}$. Of course, if the second reaction were faster than the quenching, then it would not be experimentally possible to distinguish the two processes kinetically.

The quenching of $Ru(dipy)_3^{2+}$ phosphorescence by cobalt(III) complexes, with the concomitant production of cobalt(II) was originally assumed by Gafney and Adamson [22] to proceed by an electron transfer mechanism (eqn. (135)), with quenching constants

$$(^3CT)Ru(dipy)_3^{2+} + Co(NH_3)_5Br^{2+} \rightarrow Ru(dipy)_3^{3+} + Co^{2+} + 5NH_3 + Br^- \quad (135)$$

which increased with the ease of reduction of the cobalt(III) complex. Natarajan and Endicott [24, 31] proposed an energy transfer mechanism for the quenching of $Ru(dipy)_3^{2+}$ phosphorescence by $Co(HEDTA)X^-$ ($X = Cl, NO_2$) complexes and by $Co(NH_3)_5Br^{2+}$ (eqns. (136) to (139)):

$$(^3CT)Ru(dipy)_3^{2+} + Co(NH_3)_5Br^{2+} \rightarrow Ru(dipy)_3^{2+} + (^3CT)Co(NH_3)_5Br^{2+} \quad (136)$$
$$(^3CT)Co(NH_3)_5Br^{2+} \rightarrow Co^{2+} + 5NH_3 + Br \quad (137)$$
$$Br + Br^- \rightleftharpoons Br_2^- \quad (138)$$
$$Br_2^- + Ru(dipy)_3^{2+} \rightarrow Ru(dipy)_3^{3+} + 2Br^- \quad (139)$$

In support of this mechanism, Natarajan and Endicott [24] have shown that Br_2^- radical ions and Br atoms oxidize $Ru(dipy)_3^{2+}$ with rate constants greater than $10^9\ M^{-1}\ s^{-1}$, and that the addition of 2-propanol (50%) as a radical scavenger decreased the yield of $Ru(dipy)_3^{3+}$ from the quenching by $Co(NH_3)_5Br^{2+}$, while the yield of Co^{2+}, which can be formed by the reaction of cobalt(III) complexes with the 2-hydroxy-2-propyl radical, was increased. The critical step in this mechanism is the energy transfer from the $(^3CT)Ru(dipy)_3^{2+}$ to triplet charge transfer states of the cobalt(III) complexes, which must imply that the cobalt(III) triplet states lie below the energy of the $(^3CT)Ru(dipy)_3^{2+}$. This assumption has been criticized by Navon and Sutin [25], who have investigated the quenching of the $Ru(dipy)_3^{2+}$ phosphorescence by $Co(NH_3)_5X^{3+}$ ($X = Br^-, Cl^-, H_2O, NH_3$) and the quantum yields for the oxidation of $Ru(dipy)_3^{2+}$ in 1 N sulphuric acid and 50% 2-propanol. In sulphuric acid, the ratio of the quenching rate constant determined from the phosphorescent intensity measurements to the rate constant for the oxidation of

$Ru(dipy)_3^{2+}$ was the same for all the cobalt(III) complexes, implying that the phosphorescence quenching and the oxidation of the $Ru(dipy)_3^{2+}$ proceed at the same relative efficiency for all the complexes studied. In 2-propanol it was found that the yield of $Ru(dipy)_3^{3+}$ in the presence of $Co(NH_3)_5Br^{2+}$ was reduced, but that the Stern—Volmer quenching constant was also reduced by the same factor, probably owing to differences in the encounter rate in 2-propanol. It was not necessary to invoke radical production to account for the reduced yield in 2-propanol, and the electron transfer quenching mechanism must be favoured for these reactions at least. Navon and Sutin [25] also compared the quenching by cobalt(III) complexes with that by the complexes $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_5Cl^{2+}$, and found that the quenching was essentially diffusion controlled, and much faster than for the corresponding cobalt(III) complexes, but that in these cases there was no net oxidation of $Ru(dipy)_3^{2+}$ because of the very efficient back electron transfer reaction between the products of the quenching reaction, $Ru(dipy)_3^{3+}$ and $Ru(NH_3)_6^{2+}$ or $Ru(NH_3)_5Cl^{+}$.

At present the balance of the evidence probably favours an electron transfer quenching mechanism for the quenching of triplet $Ru(dipy)_3^{2+}$ by cobalt(III) complexes of the type $Co(NH_3)_5X^{2+}$ and $Co(ox)_3^{3-}$, but the evidence is much less definite for quenching by complexes of the kind $Co(HEDTA)X^{-}$, for which the evidence for energy transfer followed by radical production and secondary electron transfer involving the radicals is greater.

More extended studies of electron transfer reactions of excited states are needed. Comparison between excited-state and ground-state electron transfer reactions leads to a better understanding of the potential energy surfaces of the excited states. Although outer sphere ground-state electron transfer reactions are relatively well understood in terms of the Marcus theory [203], a simple comparison between ground-state and excited-state electron transfer rates for even the same complex in terms of the expected standard free energy changes of the two electron transfer reactions is not possible, because the nature of the intersection of the ground- and excited-state potential surfaces with those of the products may be very different, and the activation free energy of the two reactions will not necessarily be well described by intersections which give rise to linear free energy relationships.

(c) General comments on quenching by chemical mechanisms

In a large number of cases of quenching involving coordination compound donors or acceptors it is possible that quenching takes place by a chemical rather than an energy transfer mechanism but experimental investigations have not been sufficiently detailed to enable the mechanism to be definitely assigned. It is common to assume that if the addition of radical scavengers has no effect on the system then the quenching mechanism is one of energy transfer, since for many organic donors (and for some coordination compound acceptors) an electron transfer mechanism would result in radical formation. But scavengers may also react with the radical product of an intramolecular electron transfer process following energy transfer from donor to a charge transfer excited state of the acceptor. The investigations of Natarajan and Endicott [24, 29, 31], on the mechanism of the quenching of triplet charge transfer $Ru(dipy)_3^{2+}$ by $Co(HEDTA)X^-$ ($X = Cl, NO_2$) are examples of the detailed experimental evidence which must be obtained in systems of this kind, using flash photolysis and scavenger studies, as well as quenching and continuous photolysis experiments, before the quenching mechanism (in these cases one of energy transfer to a triplet charge transfer state of the cobalt(III) complexes) can be known with any certainty.

Oxidations and reductions of transition metal ions by organic substrates have recently been much investigated and electron transfer reactions involving organic donors and metal acceptors are quite feasible. For donors which are capable of ground state electron transfer reactions of this kind, such as riboflavin, there can be no a priori reason for dismissing electron transfer as a possible quenching path for the excited state. In many cases more detailed experimental studies would be desirable. It has been reported that singlet riboflavin "catalyzes" the oxidation of Fe^{2+} to Fe^{3+} [10], and an electron transfer reaction may well be responsible. However, the yield of the riboflavin semi quinone transient produced on flash photolysis of riboflavin decreased in the presence of Fe^{2+} [10]. The quenching of singlet riboflavin by Cu^{2+} [10, 144], of triplet anthracene by $Cu(phen)^{2+}$ [161] and of aromatic ketones by Ce^{3+} [168] are other possible examples. Singlet oxygen, produced by the quenching of triplet eosin "catalyzes" the oxidation of Fe^{2+} to Fe^{3+} [41]. Singlet O_2 has an energy of 7.9 kK, and, while electron transfer is a strong probability, Fe^{2+} has an excited state 8.3 kK above the ground state and thermally activated energy transfer is possible. This system is another example in which the mechanism cannot be decided by discussion of the energetics of the possible reactions alone. The initial step in the reduction of O_2 is the formation of the peroxy anion, O_2^-, and the reduction potential for this step for O_2 is -0.88 V. For singlet O_2 the singlet excitation energy might make the equivalent reduction potential ~ 0 V, and increase the probability of electron transfer from Fe^{2+}. But the formation of excited Fe^{2+} would produce a species which itself would be a more powerful reducing agent than ground-state Fe^{2+}, and this would be more likely to reduce ground-state oxygen.

Even when redox products have been observed in a sensitized reaction, electron transfer has often been neglected as a quenching mechanism. Some Pt^{IV} production has been observed in the photosensitized reactions of Zeise's salt ($Pt(C_2H_4)Cl_3^-$) induced by triplet acetone [52]. It was assumed that the Pt^{IV} came from oxidation of the Pt^{II} by CH_3 radicals produced by photodecomposition of the acetone. However, the standard reduction potential of the one-electron intermediate Pt^{III} is probably about 1 V [172] which makes the oxidation of Pt^{II} by CH_3 unlikely. The Pt^{IV} production was suppressed in 0.1 M methyl methacrylate which scavenges CH_3 radicals. But Pt^{III} produced by a more direct electron transfer path could also be reduced back to Pt^{II} in the presence of 0.1 M methyl methacrylate. As Pt^{III} has been shown to be produced by charge transfer flash photolysis of $PtCl_6^{2-}$ [207] the mode of production of Pt^{IV} from Zeise's salt is of considerable interest.

In a study of the sensitized aquation of $Mo(CN)_8^{4-}$ [44] the quantum yield was higher for sensitization by triplet naphthalene when the sensitizer was irradiated at 286 nm than at longer wavelengths and the authors suggest that in this case the sensitization and quenching may be a modification of the electron transfer process observed in direct photolysis of the complex at 254 nm [4], but the details of the mechanism are obscure.

The quenching of a number of organic donors by $Co(CN)_6^{3-}$ presents some anomalies. Flash photolysis of benzohydroquinone in the presence of the complex [36] showed that the fluorescence was quenched at a diffusion controlled rate, and the yield of the semiquinone, which decays by a second-order process, was about 25% higher in the presence of the $Co(CN)_6^{3-}$ complex. It was considered that the increased yield of the semiquinone was evidence for quenching by an electron transfer mechanism, but no evidence of the production of Co^{II} was reported. In contrast, triplet biacetyl is quenched by $Co(CN)_6^{3-}$ by a mechanism which leads to the aquation of the complex [32]. In this case there is no apparent consumption of biacetyl, and the quenching rates for a number of cobalt(III) cyano complexes show an apparent correlation between the quenching rate constant and the energy of spin-allowed *d*—*d* transitions [33]. In organic systems triplet biacetyl is a powerful hydrogen atom abstraction reagent, and a search for evidence of hydrogen atom abstraction or electron transfer involving coordination complexes and this donor might be rewarding. In systems in which quenching by cobalt(III) complexes occurs the thermodynamic and kinetic parameters are such that if direct electron transfer (or energy transfer to a triplet charge transfer state followed by intramolecular electron transfer) occurs, the product cobalt(II) should almost always be able to be observed. Co^{2+} (high spin) is extremely labile and the production of a Co^{II} centre still bound to the ligands of the Co^{III} complex will be followed by dissociative steps with a first-stage rate constant of the order of ca. 10^6 s^{-1}. Co_{aq}^{2+} will be the normal product and is difficult to oxidize back to Co^{3+} ($E^0 = +1.85$ V). The absence of Co^{2+} in such cases is very good evidence that the quenching is proceeding neither by direct electron transfer (unless the back electron transfer is exceedingly efficient and takes place with almost 100% efficiency inside the encounter cage) nor by production of a charge transfer state of Co^{III} which then undergoes intramolecular electron transfer.

(iv) Quenching by spin-catalyzed deactivation

Spin-catalyzed deactivation of the excited state of the donor is considered as a special case of excited-state deactivation by a radiationless transition to the ground state without energy transfer to the quenching molecule or ion. As the quencher molecule is unchanged, the term "catalyzed spin conservation" was suggested for this process in a discussion of triplet)singlet conversion modes by Porter and Wright [143]. This effect must be distinguished from the breakdown of the normal spin selection rules because of the proximity of a heavy atom to the excited-state molecule (Sect. D(v)) and arises because only one of the components of the total spin must be the same before and after the encounter between the donor and quencher. A direct collisional process of the type given in eqn. (140)

$$^{3}\mathrm{D} + {}^{1}\mathrm{Q} \rightarrow {}^{1}\mathrm{D} + {}^{1}\mathrm{Q} \qquad (140)$$

is forbidden by the spin conservation rules if the quencher Q has only singlet multiplicity but is allowed for quenchers with higher multiplicities, subject only to the rule that

$$\mathrm{D}_{(S_\mathrm{d})} + \mathrm{Q}_{(S_\mathrm{q})} \rightarrow \mathrm{D}_{(S_\mathrm{d}-1)} + \mathrm{Q}_{(S_\mathrm{q})} \qquad (141)$$

where S_d and S_q are the integral or half-integral spin quantum numbers and $S_\mathrm{d} \geqslant 1$ and $S_\mathrm{q} > 0$. Most organic molecules have singlet ground states and cannot quench by this catalyzed deactivation process. On the other hand, the multiplicities of paramagnetic transition metal ions and complexes are greater than 1, so that the normally spin-forbidden change from triplet to ground-state singlet of an organic donor will be permitted in the presence of such species, and quenching may occur without energy transfer between the two. The rate of donor deactivation will be dependent on the degree of spin—spin coupling between donor and quencher and the lifetime of the encounter in the solvent cage, with an additional (statistical) term arising from the probability that the collision complex DQ has a spin momentum which correlates with the ground-state products D and Q. The larger the spin—spin coupling between donor and quencher the more efficient the quenching, and the quenching of triplet naphthalene by a number of transition metal ions in water was rationalized on this basis [143]. However, for many of the ions studied (see Sect. B(v)) quenching by energy transfer to low-lying states of the quencher ions is possible, and quenching by direct energy transfer has subsequently been shown to occur to these ions from donors with energies similar to triplet naphthalene, as well as from triplet naphthalene itself. For triplet acridine quenching rate constants of the same order as those for the quenching of triplet naphthalene have been found [144] and there was no correlation between the quenching rate constants and the ground-state multiplicities of the metal ions. Spin-catalyzed deactivation should be a general process independent of the relative energy levels of the donor and acceptor, but Mn^{2+} ions with an energy level at 19.4 kK quench triplet naphthalene (21.3 kK) but not triplet acridine (15.8 kK). Similarly the emission from $\mathrm{Cr(en)}_3^{3+}$ is quenched by Co^{2+} but not by Mn^{2+} [103] and the $\mathrm{Pt(gly)}_2^{2+}$ *cis—trans* isomerization is quenched by Ni^{2+} but not by Mn^{2+} [51]. These results suggest that the quenching of triplet naphthalene by transition metal ions is not due to spin-catalyzed deactivations as suggested by Porter and Wright [143] but to energy transfer of the more conventional type. The process of spin-catalyzed deactivation remains to be unequivocally demonstrated as an experimentally observable quenching mechanism, able to compete with quenching by other processes.

(v) Quenching by external heavy-atom effect

Spin—orbit coupling between an external atom and the excited state of the donor can increase the probability of de-excitation of the donor. Normally forbidden transitions may have non-zero probability integrals in systems in which there is considerable spin—orbit coupling and excited-state donors are therefore expected to be quenched by the influence of atoms of large atomic number in close proximity. Although this external heavy-atom effect has been expected [208] it has not been experimentally demonstrated for the quenching of excited states of transition metal complexes, and for the quenching of organic donors by transition metal ions or complexes of the first-row spin—orbit effects are small and so far unobserved. Only for mercury is there good evidence for quenching of this type. Singlet anthracene is quenched by $Hg(CH_3)_2$ at diffusion controlled rates by this mechanism [163] and the process is much more efficient than the quenching of triplet anthracene by the same organo-metallic compound, for which the quenching rate constant is only $1.2 \times 10^3\ M^{-1}\ s^{-1}$.

For both the quantum mechanical quenching phenomena, spin-catalyzed quenching and spin—orbit quenching, involving transition metal coordination compounds, definite experimental evidence is at present rare, and it must be supposed that these processes are normally too inefficient to compete with the more usual energy transfer quenching mode.

(vi) Quenching by exciplex formation

The formation of complexes ("exciplexes") between excited-state donors and quencher molecules, with a resulting quenching of the donor, is a common phenomenon in organic systems [196, 197]. The formation of the excited-state complex may be followed by a variety of physical or chemical processes, such as exciplex emission or chemical reaction, and in organic systems it is common to attribute bimolecular photochemical processes, particularly those involving an excited singlet state, to exciplex formation. The effects of exciplex formation upon lifetimes and emission intensities have been reviewed [196]. Exciplex formation is difficult to demonstrate experimentally in the absence of emission by the exciplex, and for cases involving coordination compounds little evidence is available. The type of exciplex which could be formed may be considered in terms of the bond energy in the exciplex. For small interaction energies (that is for those less than or about the energy barrier to diffusion) then the exciplex is little more than an encounter phenomenon. When both donor and quencher are ions, there is the possibility of the formation of an ion pair (one is hesitant to introduce the terminology "exion pair") between excited-state donor and quencher, and even for cases in which only one of either donor or quencher is charged, there exists the possibility of ion—dipole interaction, but in general careful steady state and transient measurements at nanosecond times are needed to demonstrate exciplex formation. For the quenching of excited singlet UO_2^{2+} ions by a number of organic quenchers for which energy transfer from the excited uranyl ions is impossible, both physical and chemical quenching occurs and it was assumed that uranyl exciplex formation provides the initial pathway for both the physical and chemical quenching [126] but there was no direct experimental evidence of exciplex formation. For the quenching of some metal porphyrins, exciplex formation has been assumed as the mechanism. Zinc-etioporphyrin is quenched by a number of aromatic nitro compounds at near diffusion controlled rates [128] but the quenching efficiency falls rapidly for more sterically hindered substituted compounds. The nitro compounds (such as nitrobenzene) do not form complexes with the ground state of the zinc-porphyrin, unlike nitrogen bases which show strong ground-state interaction, and the initial donor—quencher interaction was assumed to be of the exciplex type with some charge transfer character. Similarly the self-quenching of the triplet states of platinum-, palladium- and zinc-mesoporphyrins and of platinum- and zinc-etioporphyrins can be interpreted as due to the formation of triplet excimers, but the difficulties of direct observation of the excimers have been emphasized [129], and exciplex formation involving coordination compound donors or quencher is speculative*.

E. EXAMPLES OF APPLICATIONS OF THE QUENCHING AND SENSITIZATION TECHNIQUES IN THE FIELD OF COORDINATION COMPOUNDS

In the following sections, many of the ways in which sensitization and quenching have been used in the field of coordination compounds are reviewed with specific examples. Emphasis will be given to the cases in which important mechanistic information or quantitative data have been obtained.

(i) Identification of the reactive state

Sensitization and quenching by energy transfer can lead to selective population and depopulation of excited states. This of course, is a very useful tool for the identification of the excited state responsible for a photochemical reaction. As far as sensitization is concerned, the selectivity is based on energy grounds (i.e. the process must be exothermic) and on spin selection rules. We have seen in Sect. D(ii)(a) that for some coordination compounds there is a loss of selectivity of the spin selection rules when the ground state of the complex has a high multiplicity. It should also be recalled that owing to the presence of the metal (heavy) atom and the consequent spin—orbit coupling, the spin labels may lose part of their validity**. However, for com-

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* Exciplex formation between *cis*-$Ir(phen)_2Cl_2^+$ and naphthalene has recently been found in our laboratory [209].

** For a recent paper on the loss of validity of the spin labels, see ref. 210.

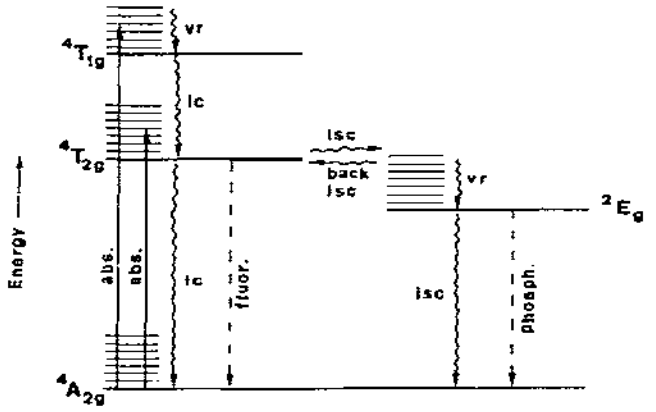

Fig. 4. Jablonski diagram for an octahedral Cr^{III} complex: solid arrows, absorptions; dashed arrows, radiative deactivations; waved arrows, non-radiative deactivations.

plexes which have singlet ground states and not too heavy metals, a selective population of the lowest triplet states has been obtained by means of suitable triplet donors. This, for example, has been possible for $Co(CN)_6^{3-}$ [33], $Co(NH_3)_6^{3+}$ [20], and $Rh(NH_3)_5X^{2+}$ (X = Cl, Br, I) [48]. In each case the same photoreactions were obtained as those observed upon direct irradiation in the singlet bands. This suggests that the lowest triplet excited states are responsible for the observed photoreactions, although it cannot be excluded that the excited singlets are also reactive. Selective quenching of the triplet states would have been much more diagnostic but it is hardly possible because of experimental limitations.

The excited state, responsible for the photosolvation reaction of $Cr(CN)_6^{3-}$ (eqn. (142))

$$Cr(CN)_6^{3-} + S \xrightarrow{h\nu} Cr(CN)_5S^{2-} + CN^- \qquad (142)$$

has clearly been individualized from both sensitization and quenching experiments. In this complex, the energy separation between the lowest excited quartet, $^4T_{2g}$, and the lowest doublet, ^2E_g, is large enough to allow a selective population of the doublet state by energy transfer and to prevent the back intersystem crossing $^2E_g \rightarrow {}^4T_{2g}$ from occurring (Fig. 4). The sensitization experiments were carried out in DMF solutions [12,13] where both the photosolvation reaction and the phosphorescence emission can be observed at room temperature. Two different series of donors were used (Fig. 5). The donors of the first series, represented in the figure by xanthone, were at higher energy than both the doublet and the quartet so that they were able to populate both these states by energy transfer. The donors of the second series, represented by $Ru(dipy)_3^{2+}$, were higher in energy than the doublet but lower than the quartet, so that they were able to transfer energy to the doublet in a selective way. The results obtained showed that xanthone and the other high-energy donors were able to sensitize *both* the photoreaction *and* the phosphorescence emission, whereas Ru(dipy)$_3^{2+}$ and the other low-energy donors were only able to sensitize the phosphoresence emission but not the photoreaction. This indicates that the reactive state must be the quartet. The same conclusion was arrived at by means of quenching experiments [104]. Working again on DMF, it was found that the phosphorescence emission is strongly quenched by oxygen and water, whereas the photoreaction is not quenched at all, so that it must originate from a state different from ^2E_g.

For other Cr^{III} complexes, where the energy gap between $^4T_{2g}$ and ^2E_g (Fig. 4) is small, the selective population of the doublet cannot be achieved by energy transfer. On the other hand, in these cases quenching experiments cannot give a precise answer because of the existence of the $^2E_g \rightarrow {}^4T_{2g}$ back intersystem crossing. In any case, the fact that part of the photoreaction is unquenched under conditions of complete quenching of the phosphorescence (Sect. B(iii)(b)) shows that at least part of the photoreaction originates from the quartet [211]. As an example, for Cr(en)$_3^{3+}$ 40% of the observed photoreaction is unquenchable and thus it directly originates from $^4T_{2g}$ prior to intersystem crossing to ^2E_g [95].

(ii) Intersystem crossing efficiency

The efficiency of intersystem crossing from the lowest spin-allowed excited state to the lowest spin-forbidden one can be evaluated in two different ways by means of sensitization and quenching techniques, i.e. (i) using the compound of interest as a donor in electronic energy transfer experiments and then measuring some properties of the donor [212] or of the acceptor [213—215], (ii) using the compound of interest as an acceptor in electronic energy transfer experiments and then comparing the direct and sensitized quantum

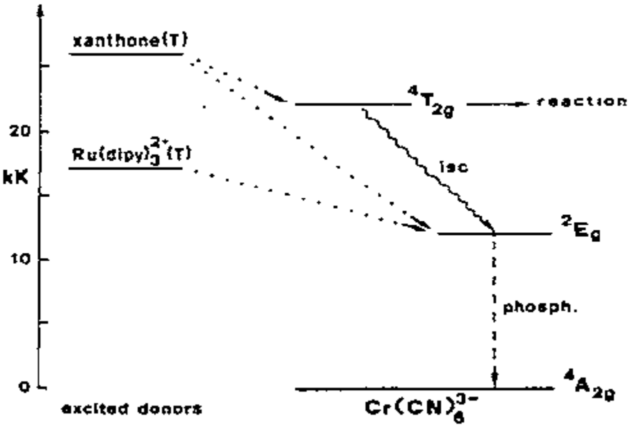

Fig. 5. Sensitization of the Cr(CN)$_6^{3-}$ phosphorescence and photoreaction [12, 13]: solid arrow, reaction; dashed arrow, phosphorescence; dotted arrows, intermolecular energy transfer.

yields of a phenomenon which is known to originate from the spin forbidden state of the acceptor [61].

A version of the first method has been used by Whery and Sundararajan [171] for measuring the intersystem crossing efficiency of Cu(2,9-dmp)$^+$ (for details, see Sect. B(v)(p)). This method, however, is impracticable for most coordination compounds because it usually requires high absorption intensities at long wavelengths and a long lifetime of the quenchable excited state. The first method was also used by Eisinger and Lamola for determining the intersystem crossing efficiency of organic donors using Eu^{3+} as acceptor and measuring the ratio between the direct and sensitized emission of this ion [91]. This version of the first method is based on eqn. (98), which is also the basis of the second method described below.

The second method has been recently applied to the evaluation of the intersystem crossing efficiency of Cr(CN)$_6^{3-}$ [61] (Fig. 6). The direct and Ru(dipy)$_3^{2+}$-sensitized phosphorescence intensities of Cr(CN)$_6^{3-}$ were measured in DMF at 20°C under the same experimental and instrumental conditions. Since under these conditions the ratio between the intensities of the direct and sensitized emission must be equal to the ratio of the respective quantum yields, eqn. (98) can be used:

$$\varphi' = \frac{\phi(\mathrm{dir})}{\phi(\mathrm{lim})}\varphi_\mathrm{D}\eta_\mathrm{s} \tag{143}$$

φ' is the quantum yield of direct population of ^2E_g which coincides with the $^4T_{2g} \rightarrow {}^2E_g$ intersystem crossing efficiency when the irradiation is carried out in $^4T_{2g}$, and is given by $k_{11}/(k_{11} + k_{10} + k_9)$ in Fig. 6, φ_D is the quantum yield of population of the ^{3}CT state of Ru(dipy)$_3^{2+}$, $k_3/(k_3 + k_2)$, and η_s is the limiting sensitization efficiency, $k_6/(k_6 + k_7)$. Since ϕ(dir)/ϕ(lim) was

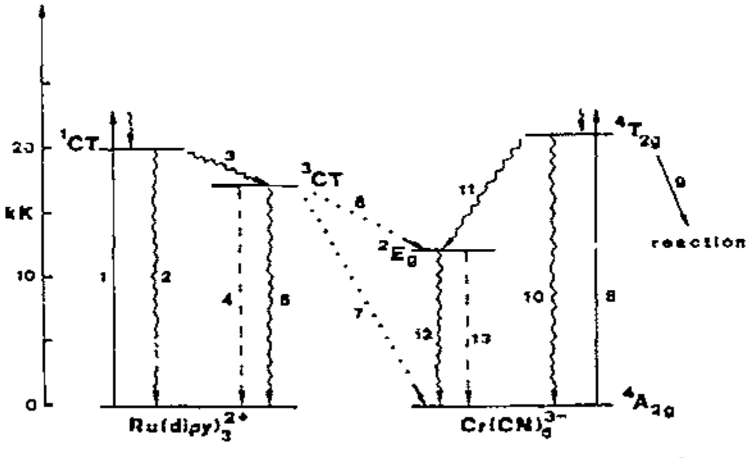

Fig. 6. Energy level diagram for the Ru(dipy)$_3^{2+}$—Cr(CN)$_6^{3-}$ system [61]: solid arrows, absorptions and reaction; dashed arrows, radiative deactivations; waved arrows, intramolecular radiationless deactivations; dotted arrows, intermolecular quenching processes.

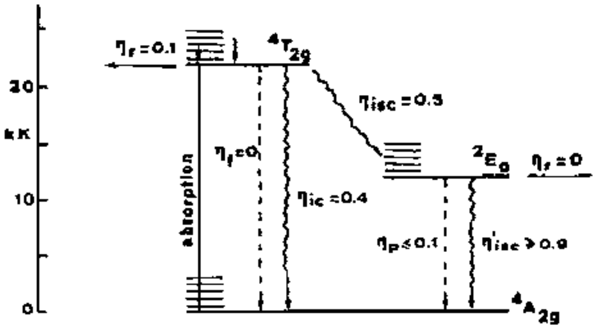

Fig. 7. Excited-state behaviour of $Cr(CN)_6^{3-}$ in DMF at 20°C [61].

found to be 0.5 and φ_D is known to be unity, the φ'/η_s ratio has also to be 0.5. On the other hand $\eta_s \leq 1$, so that 0.5 is the upper limit value for φ'. The same value (~ 0.5) for φ'/η_s was previously reported for the benzil—$Cr(CN)_6^{3-}$ system in a fluid mixed solvent at −113°C [58]. Since $Ru(dipy)_3^{2+}$ and benzil are very different donors from both a chemical and a physical point of view, it has been argued [61] that the η_s values for the two systems can only be equal if each of them is unity (i.e. if electronic energy transfer is the sole quenching mode). On such a reasonable hypothesis, the intersystem crossing efficiency of $Cr(CN)_6^{3-}$ is definitely established as about 0.5. This result together with the other available data for $Cr(CN)_6^{3-}$ in DMF at 20°C allow us to establish the role played by the $^4T_{2g}$ and ^2E_g states in determining the photochemical and photophysical behaviour of this complex (Fig. 7).

Photochemical data alone can also be useful in obtaining information on

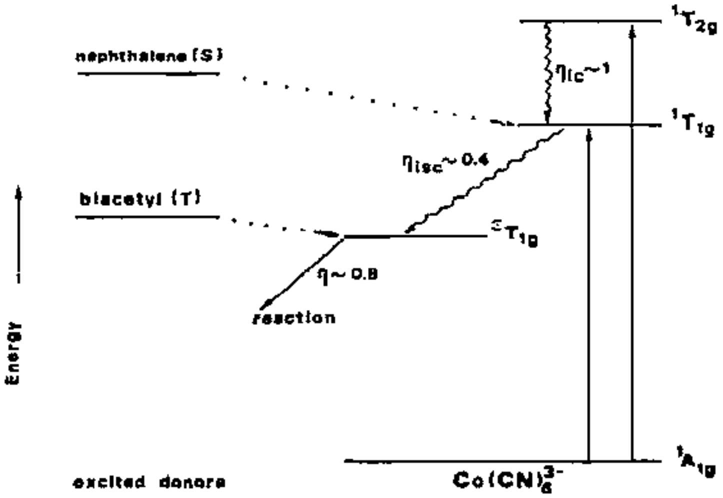

Fig. 8. Evaluation of the intersystem crossing efficiency from photochemical data (see text): solid arrows, absorptions or reaction; waved arrows, intramolecular radiationless deactivations; dotted arrows, intermolecular energy transfer. The exact energy of the $^3T_{1g}$ excited state of $Co(CN)_6^{3-}$ is unknown [34, 98].

the intersystem crossing efficiency. For $Co(CN)_6^{3-}$, the quantum yield of the direct photoaquation is 0.31 upon excitation in the $^1T_{2g}$ and $^1T_{1g}$ spin-allowed metal centred excited states (Fig. 8). The same value was obtained for the limiting sensitization efficiency upon singlet—singlet sensitization by naphthalene ($E_S \sim 31$ kK), whereas triplet—triplet sensitization by biacetyl ($E_T = 19.6$ kK) gave a limiting sensitization efficiency of about 0.8 [34]. Using eqn. (98), for this last case we obtain

$$\varphi' = \frac{0.31}{0.8}\varphi_D\eta_s \qquad (144)$$

Since φ_D for biacetyl is unity, if the $^3T_{1g}$ state is the only reactive state of $Co(CN)_6^{3-}$ and if η_s is assumed to be unity (i.e. if the deactivation of biacetyl only occurs by electronic energy transfer to $^3T_{1g}$), a value of about 0.4 can be obtained for the $^1T_{1g} \rightarrow {}^3T_{1g}$ intersystem crossing efficiency.

(iii) Excited-state lifetimes and quenching rate constants

In certain conditions the lifetime of an excited state can be measured by steady state quenching experiments. Consider for example Case 1 of Sect. C(i). The slope of the Stern—Volmer plot corresponding to eqn. (14) is given by $k_{2q}\tau_2^0$, where k_{2q} is the bimolecular quenching constant and τ_2^0 is the lifetime of the quenchable excited state. If one of the two quantities is known from independent experiments, the other quantity can easily be obtained (see e.g., the k_q values of Tables 5—7, Sect. D(ii)).

As mentioned in Sect. D(ii)(a), quenching processes between organic molecules in fluid solutions are usually found to be diffusion controlled when energy and spin requirements are satisfied. Therefore, when τ_2^0 is not known, k_{2q} is usually calculated from the Debye equation (eqn. (71)), and τ_2^0 is consequently obtained. Unfortunately, when coordination compounds are involved the quenching rate is usually much lower than the diffusion controlled limit and strongly dependent on the specific nature of the donor and the quencher (see Sect. D(ii)(a)). It follows that only a lower limit value for the excited-state lifetime can be obtained if the "calculated" k_{2q} value is used. Alternatively, competition experiments must be carried out, such as those described by Eisinger and Lamola [91].

(iv) Limiting energy transfer efficiency

As mentioned in Sect. D(i), the bimolecular quenching of an excited state may take place by several distinct mechanisms. Both in the organic and inorganic field there is a general but dangerous tendency to assume that the quenching occurs by electronic energy transfer whenever contrary evidence is lacking. What is worse, some authors still believe that a proof for the involvement of energy transfer alone is the equality of the Stern—Volmer constants obtained from the quenching and sensitization plots of the same systems. This is absolutely untrue, as we have seen in Sect. C(iv)(a). The only valid criterion for establishing whether or not electronic energy transfer is the sole quenching mechanism (in other words, for establishing whether η_s is equal to or lower than unity) is that of measuring the quantum yields of the direct and sensitized phenomenon of the acceptor, as shown by eqn. (98). According to such equation, η_s is given by

$$\eta_s = \frac{\phi(\text{dir})\varphi_D}{\phi(\text{lim})\varphi'} \qquad (145)$$

so that its value can only be obtained if φ_D and φ' are also known. However, to date there is no system for which all the quantities appearing in the right-hand side of eqn. (145) are known. As we have seen in Sect. E(i), the conclusion that $\eta_s = 1$ for the $Ru(dipy)_3^{2+}$—$Cr(CN)_6^{3-}$ and benzil—$Cr(CN)_6^{3-}$ systems is in fact the result of a "reasonable" assumption.

(v) Increasing quantum yield and increasing range of useful exciting light wavelength through sensitization

Suppose that the photoreaction of a complex originates from a spin-forbidden excited state which cannot be populated efficiently either by excitation in the corresponding spin-forbidden band, which is extremely weak, or by excitation in the intense spin-allowed bands because the intersystem crossing efficiency to the reactive state is very small. One can increase the reaction quantum yield by increasing the yield of the reactive state through the use of a sensitizer which possesses a high intersystem crossing efficiency and which is able to give an efficient transfer to the reactive state of the acceptor. An example of this situation has already been discussed in Sect. E(ii) and concerns the biacetyl—$Co(CN)_6^{3-}$ system (Fig. 8) [34]. The same system can also offer an example of increasing range of useful exciting light wavelength through sensitization. The cobalt complex does not absorb appreciably above 370 nm (the maximum of its lower-energy spin-allowed band is at 313 nm), whereas biacetyl absorbs up to about 450 nm. As a consequence, direct photoaquation of $Co(CN)_6^{3-}$ can only be carried out (with $\phi = 0.31$) with UV radiation whereas its sensitized photoaquation ($\phi(\text{lim}) = 0.8$) can also be obtained with visible light.

(vi) Quenching of undesired photoreactions

Protection against photosensitivity is an important problem both in nature and in technology. Chelates of transition metal ions are very interesting protecting agents because of (i) their photochemical stability, (ii) their high-intensity absorption in the UV region, (iii) the presence of very low-lying energy levels which allow these compounds to act as acceptors in energy transfer processes and (iv) the possibility of entering into electron transfer processes.

$\mathrm{Ni^{II}}$ chelates are the object of theoretical quenching investigations [149, 157,158] (Sects. B(v)(g) and D(ii)(c)) and are already used as commercial UV stabilizers [159, 216]. It is also worth mentioning the use of transition metal complexes for reaching the opposite but equally important goal of increasing the rate of plastic photodegradation [216]. $\mathrm{Ni^{II}}$ chelates are also used to quench singlet oxygen, ${}^1\Delta_g$ [153, 155, 160], which is responsible for a great variety of photooxidation reactions. The quenching rate constants depend on the specific nature of the ligands (Sect. B(v)(g)).

(vii) Study of equilibria in solution

As shown in Sect. C(iii), the luminescence quenching besides being due to dynamic processes may also be due to an association between the ground-state donor and acceptor (static quenching):

$$\mathrm{D + Q \rightleftharpoons DQ} \qquad K = \frac{[\mathrm{DQ}]}{[\mathrm{D}][\mathrm{Q}]} \tag{146}$$

When both dynamic and static quenching processes are important, the Stern—Volmer plot for the intensity quenching (see eqn. (78)) exhibits a slope higher than that of the corresponding lifetime Stern—Volmer plot (eqn. (25)). Dividing eqn. (78) by eqn. (25), one obtains

$$\frac{\phi_{2e}^0}{\phi_{2e}} \frac{\tau_2}{\tau_2^0} = \left(1 + K \frac{\epsilon_{\mathrm{DQ}}}{\epsilon_{\mathrm{D}}} [\mathrm{Q}]\right) \tag{147}$$

If the excitation is carried out in a spectral region where D and DQ have the same extinction coefficient, the association constant K can be obtained from the slope of the plot corresponding to eqn. (147). In this way, ion-pairing constants of 300 $\mathrm{M^{-1}}$ and 1000 $\mathrm{M^{-1}}$ have been obtained for the systems $\mathrm{Ru(dipy)_3^{2+}}$—$\mathrm{Mo(CN)_8^{4-}}$ in water and $\mathrm{Ru(dipy)_3^{2+}}$—$\mathrm{PtCl_4^{2-}}$ in DMF [117] (see also Sect. B(iv)). In a similar way the value 270 $\mathrm{M^{-1}}$ has been obtained for the association constant of $\mathrm{Ru(phen)_2(CN)_2}$ with $\mathrm{Cu^{2+}}$ [116]. It has been pointed out that this very sensitive technique, although not general because it requires a luminescent complex, can make an important contribution to the study of equilibria involving transition metal complexes in solution [116, 117].

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