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FLASH PHOTOLYSIS OF COORDINATION COMPOUNDS

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CONTENTS

ABBREVIATIONS

acac = acetylacetonate ion
bipy = α,α'-bipyridyl

biquin = 2,2′-biquinoline
EDTA = ethylenediaminetetraacetate ion
exan = ethylxanthogenate ion
N_4 = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene
ox = oxalate ion
phen = 1,10-phenanthroline
PNB = *p*-nitrobenzoate ion
py = pyridine

A. INTRODUCTION

In the flash photolysis technique, initiated by Norrish and Porter in 1949 [1,2] a photochemical reaction is induced by an intense, short-duration light flash which generates in the reaction cell a concentration of unstable products which may be about 10^6 times higher than for low intensity, steady state irradiation. The direct observation of the transient molecules, ions, radicals or excited states is thus possible using absorption spectroscopy or other fast detection methods. The intermediates generated by the flash are generally far from their equilibrium state; the fate of such species as the system proceeds to equilibrium can thus be studied or unstable species can be used to initiate reactions of interest.

Flash photolysis was recognized about twenty years ago as a useful, or in many cases unique, tool for the elucidation of reaction mechanisms in the photochemistry of coordination compounds: numerous intermediates, whose existence had been postulated only on the basis of indirect evidence were identified; the kinetics of photochemical and thermal reactions by which the unstable species decay were determined; and information about the faster processes by which the transient are formed was also gathered.

Much of this work has been mentioned occasionally in the various reviews dealing with the photochemistry of coordination compounds [3—6] and there are some recent, less extensive summaries in the field made by Gleria [7] and Semerano [8]. However, a comprehensive review of the flash photolytic studies on transition metal complexes involving a thorough literature search has not been published. It is the purpose of this article to attempt such a task and to discuss the extensive amount of experimental material in terms of the mechanisms of the photochemical reactions in coordination compounds.

In Section B of this article the experimental technique will be briefly discussed along with its recent development. Section C deals with the subject in a general way, outlining the differences between flash photolysis and steady illumination studies, as well as the peculiarities of the pertinent types of photochemical reactions. The descriptive section, D, is arranged by the types of photochemical processes found in transition metal complexes.

In order to keep the present article to a reasonable length we have omitted photoluminescence studies in which flash sources are also commonly used. This subject was recently comprehensively reviewed [9].

B. EXPERIMENTAL TECHNIQUE

It is not the object of this article to describe the large variety of apparatus available for flash photolysis studies, detailed descriptions of which may be found in numerous publications [2,7,10—30]. A typical apparatus, based essentially on the original design of Norrish and Porter [1,2] consists of three parts: (i) radiation source (photoflash), (ii) a reaction cell and (iii) an arrangement for physical detection and estimation of transient species.

(i) Radiation sources

The most conventional light sources are short duration (μs to ms) discharges in rare-gas-filled flash lamps. Experimental details are reported in the reviews mentioned above [7,11—13] and in many other papers [2,31—35].

Since the flash light is frequently used without any filtration, which is accompanied by a severe decrease in light intensity, a knowledge of the spectral distribution of the flash is necessary. For most discharge lamps the light includes the prevailing contribution of visible and near ultraviolet radiation up to about 30 000 cm^{-1} [2,26,32,35—37]. The particular spectral characteristic can be regulated by the type and power of lamp. Some flash lamps generating light enriched with ultraviolet [37], or vacuum ultraviolet radiation [17,38, 39], have recently been constructed. Partial filtration of flash light is also a common practice with the use of band-pass [11,40] or cut-off filters [24,36, 41—44].

Conventional flash sources have been developed in recent years to increase the flash energy without an expansion of the pulse width [15,31,36,45], as well as to shorten the pulse width without a considerable loss in light intensity [28,46—48].

Greatest progress in reducing the pulse duration has occured, however, through the use of laser sources. These possess three advantages over other sources, spatial coherence, monochromicity and a high peak power. With laser sources the resolution time has been shortened to a few nanoseconds in the case of Q-switched systems [49—58], and to the ps range for mode-locked lasers [49,55,59—62].

(ii) Reaction vessels

The method is applicable to gases, liquids or solids and to systems of almost any geometry and size, from microscopically small samples to those with several meters path length. For coordination compounds in solution, or in the gaseous phase, cylindrical quartz cells with optically flat windows, connected to degassing equipment are in common use. These are usually placed parallel to one or more flash lamps. In addition spiral flash lamps with the reaction cell in the centre have also been constructed [20,38,63]. Reaction cells, fitted with jackets for passing a thermostatic or filter liquid [21, 24,41—44,64], are also employed.

(iii) Detection methods

The most typical detection method is absorption spectroscopy. It was first applied by Norrish and Porter [1,2] who conceived the idea of identifying the initial photolysis products by taking optical absorption spectra of the system using a delayed light flash (spectroflash) as a spectroscopic or monitoring source. A photographic record of the absorption spectra of transient species over a wide spectral range was obtained with the aid of a spectrograph. This variation of the flash photolysis technique is known as flash spectroscopy. In another variant, kinetic spectrophotometry, the monitoring flash is replaced by an intense continuous source such as a xenon arc, and observations are made at a single wavelength using a monochromator, photomultiplier and oscilloscope. Flash spectroscopy is commonly used for recording transient spectra, whereas kinetic spectrophotometry is better suited for detailed kinetic studies since it is more accurate and gives a complete time history in a single experiment.

The spectral detection method has been improved recently by the use of a dual beam system [28], rapid scanning spectrophotometry [65], light scattering detection [66], a special high intensity monitoring light source [67] and various shutters to reduce scattering effects [2,19,68]. Infra-red absorption has also been adapted to record transient species generated on flashing [14,69].

Real progress in flash photolysis detection was achieved by the use of other physical methods to record the transient species generated. Perone et al. [70—74] described a time-delayed potentiostatic technique using a hanging, mercury-drop electrode to determine the kinetics of electroactive intermediates. Milewski [75] constructed an apparatus for measuring the photoconductivity decay of solutions irradiated by a flash lamp. The use of e.p.r. monitoring of paramagnetic transient species generated upon flash has been reported in numerous papers, e.g. [76—79]. Gunning and co-workers [80,81] adapted a mass spectrometer to flash photolysis studies. On this technique a conventional flash cell was attached through a small bleed to the ion source of a mass spectrometer modified for fast response of transient species. Recently, Fornstedt and Lindquist [82,83] extended the technique using time-of-flight mass spectrometry.

C. GENERAL SURVEY

When comparing the results obtained in coordination compound photochemistry from flash and continuous irradiation the following differences between the methods must be considered.

(1) The time scale of the observation is quite different: in flash photolysis it is at least 10^4 times shorter than in steady experiments and the difference may be extended as much as 10^{13} times.

(2) The concentration of unstable species upon flashing may be about 10^6

times higher than in steady state measurements. This allows direct observation of transients by the flash technique. It also makes it possible to detect and study photochemical processes in systems found to have no net sensitivity to continuous irradiation. This is the case for labile complexes in which the photostationary state concentration of product corresponds to virtually zero transformation; thus a non-stationary efficient method must be used to discover any photochemical reaction.

(3) The inconvenient accumulation of stable products of secondary thermal and photochemical reactions which frequently occurs in steady illumination is generally avoided with the use of the flash technique.

(4) The products generated from different excited states may be observed separately by continuous irradiation at different wavelengths or by using monochromatic laser sources. With unfiltered light from discharge lamps this is not possible, although some indications may be derived from the spectral characteristic of the flash light. The use of cut-off and band-pass filters, and flash sources enriched with UV radiation is also profitable.

(5) A flash pulse especially when high in UV radiation, may also generate a high concentration of radical species from solvent or other substances which are present e.g. halide ions or hydrogen peroxide. Such a situation may complicate the photochemical study of coordination compounds by the flash technique. On the other hand, however, the phenomenon was adapted to investigate reactions between transition metal complexes and radicals generated upon flashing.

The flash photolytic studies include, more or less, all the types of photochemical reactions of coordination compounds, i.e. (i) photosubstitution and substitution-related reactions, (ii) photooxidation—reduction pathways and (iii) ligand photoreactions. Besides following unstable products of photochemical reactions the flash technique is a suitable method for providing information about the precursor excited state. The attractive idea of a close correlation between irradiation range and the type of the photochemical reaction can no longer be considered as absolutely valid.

Photochemical pathways often proceed from excited states other than those presumably reached directly by the irradiating wavelength. This is often due to a considerable overlap of the charge-transfer, metal-centered and ligand-centered bands making selection irradiation difficult. Furthermore radiationless relaxation from higher excited states also occurs. The lack of a clear distinction in the excited state character is a frequent occurrence in coordination compounds, particularly in the case of heavier transition metals or those with an extensive metal—ligand covalency.

With these limitations in mind the correlation between the character of the precursor excited state and the photochemical reaction is still of practical significance, and will be used throughout this article. The material is organized according to the main types of photochemical processes mentioned above, but a few systems do not easily fit in any of these patterns and had to be classified arbitrarily.

(i) Excited state studies

The direct observation in flash studies of the transient absorption due to the excited states of the transition metal complexes is especially possible in the case of relatively long-lived excited states. Experimental data are unfortunately, as yet, scarce. More extensive progress in this study may be expected from the development of flash investigations at low temperature and with the use of laser sources.

(ii) Photosubstitution and substitution related reactions

This reaction mode commonly follows reactive decay of LF excited states although it may also occur following charge-transfer band irradiation.

The term "photosubstitution" is used here for all the pathways involving changes in the composition of the coordination sphere without changes in the oxidation number of the metal, ligand or solvent, as well as in ligand structure. Therefore, not only the simple photosubstitution processes such as photosolvation, photoanation, photoexchange, but also photodissociation and some kinds of photoisomerization are included.

Among photosubstitution and substitution related reactions, photodissociation and photoaquation are the most frequently studied using flash methods. Some experimental work has also been reported for photoisomerization.

Photodissociation is often assumed to be the first step in some photosubstitution reactions. In Section D(ii) (a) cases are only described where photodissociation products were observed directly in flash experiments.

(iii) Photooxidation—reduction reactions

This reaction pathway is expected to follow a charge-transfer excitation, although electronic relaxation from the higher energy CT states may populate the lower LF or ligand centered states and the chemical process need not always be due to reactive decay of the excited CT state.

Due to the very short lifetimes of transition metal CT excited-state species (commonly less than 1 μs) there have been very few direct observations of the charge-transfer excited state processes. Since photoredox decompositions lead to generation of reactive radicals and unstable metal fragments, flash photolysis has been used to follow these products and has been helpful in probing the nature of the primary process and the reactive excited state.

It is convenient to discuss the flash photolysis studies of photoredox reactions in two groups: (a) photoreduction of transition-metal central ion and oxidation of ligand or solvent and (b) photooxidation of central ion and reduction of ligand or solvent.

(a) Photoreduction of transition-metal central ion

Photoreduction of the central ion is generally induced by electron transfer from the ligand towards the metal center as a consequence of charge transfer to metal (CTTM) transitions. Such a reaction mode is frequently observed in complexes with central ions of a relatively high oxidation number and may proceed through intramolecular, as well as intermolecular, pathways.

Flash photolysis of these systems most frequently involves the spectral and kinetic investigations of ligand or solvent radicals and metal fragments including a reduced metal ion. There may be, however, difficulties with the detection of some radicals, especially when only spectral properties are observed, because not all radicals absorb more strongly than the substrate irradiated. In such cases a combination of flash and chemical scavenging methods facilitates the identification of transient species. For example, halogen radicals, especially $Cl\cdot$, absorb only in the deep UV, whereas dihalogen radicals, $X_2^-\cdot$, absorb in the near UV. Similarly, the generation of $N_3\cdot$ radical in the photoredox process may be observed in the presence of I^- ions as the transient absorption characteristic of $I_2^-\cdot$.

The identification of metal fragments may also be difficult due to their weak and generally unknown spectral properties, though the nature of the metal fragment is frequently easy to infer from strictly chemical information.

(b) Photooxidation of transition-metal central ion

The outward electron transfer due to CTTL or CTTS transitions is expected to lead to oxidation of the metal or the complex as a unit, accompanied by the reduction of ligand or solvent. The former case is achieved through an intramolecular mechanism, whereas the intermolecular reaction path may lead to a reduced solvent radical, or more frequently to solvated electron production.

Ligand reduction has been found, or rather inferred, from flash results for only a few complexes.

The generation of a solvated (hydrated) electron was detected by flash spectroscopy and chemical scavenging in numerous complexes, especially cyanides of transition metals. The general prerequisites for solvated electron production in photolysis of coordination compounds were formulated by Waltz et al. [84] as follows: (a) the flash source should contain the appropriate wavelength to irradiate the CT band, (2) the complex should have a reasonably stable one-electron higher oxidation state of the same stoichiometry and (3) the complex should not have a stable one-electron lower oxidation state of the same stoichiometry. These prerequisites are generally fulfilled although some exceptions may be found especially for cationic complexes.

Some discussion has been generated as to the excited state responsible for such a reaction mode (cf. e.g. [4]). It was suggested to be a charge transfer to solvent (CTTS) transition reached either by direct excitation or by internal conversion from higher excited states. However, many data also suggest the involvement of charge transfer to ligand (CTTL) excitations. In any case, a radial redistribution of the electron charge leading to an increase of electron density at the periphery of the complex seems to be necessary for photochemical generation of hydrated electrons.

(iv) Photoreactions of ligands

Structural changes in ligands are frequently observed as a result of ligand centered excitation, although charge-transfer transitions may also be involved. The chemical pathways following flash photolysis are divided in this article into two types: cleavage of a metal—ligand bond and scission of an intraligand bond. The net reaction observed in the former case can be photosubstitution (photoaquation) or linkage isomerization.

Cleavage of an intraligand bond has been found to produce a stable molecule and an unstable metal fragment (cf. references cited in Section D(v) (a)).

(v) Reactions with radicals

Besides the photochemical studies, flash photolysis was employed to follow reactions between transition metal complexes and radicals generated upon flash. They are mainly of two types: redox processes and radical complex formation. In the former group either oxidation of the metal central ion or its reduction was observed. In these studies discrimination between outer-sphere and inner-sphere mechanisms could be made on the basis of the effect of the ligand on the reaction rates (cf. references cited in Section D(vi) (a)).

Radical complexes with transition metal ions are observed due to their higher stability compared to free radicals and thus the kinetics of their formation and decay have been studied.

D. DESCRIPTIVE FLASH PHOTOLYSIS

(i) Excited states studies

Chromium(III) complexes. The LF excited states of some chromium(III) complexes, such as: $K_3[Cr(NCS)_6]$, $NH_4[Cr(NCS)_4(NH_3)_2]$, $[Cr(acac)_3]$ and $[Cr(exan)_3]$, were investigated by Ohno and Kato [85,86] using a flash technique at low temperature (down to 77 K). Transient species with strong absorption bands in the visible and near ultraviolet (about 18.5 and 27 kK) were observed within a μs time scale. They were found to decay at the same rate as the phosphorescence for the chromium complexes. Therefore the transient spectra were assumed to originate from the lowest excited doublet states (^2E_g) produced from the photochemically generated quartet states ($^4T_{2g}$) through inter system crossing. The transient absorption bands were proposed to be charge transfer in origin and the decay rates of the $^4T_{2g}$ and ^2E_g states were estimated, being of the order 10^{10} s^{-1} and 10^5 s^{-1}, respectively. The competing photolysis of $^4T_{2g}$ excited state, leading to the release of one thiocyanate ligand was also reported in the case of $K_3[Cr(NCS)_6]$ and $NH_4[Cr(NCS)_4(NH_3)_2]$ complexes [86].

$[Mo(CN)_8]^{4-}$. The bleaching in absorption observed for octacyanomolybdate(IV) within μs upon flashing at room temperature was proposed to origi-

nate from a ligand—field excited state [87] though this conclusion needs further support.

[Re$_2$X$_8$]$^{2-}$(X = Cl$^-$, Br$^-$). Laser flash photolysis studies of [Re$_2$Cl$_8$]$^{2-}$ have revealed the presence of a short-lived transient (lifetime of 134 ns in CH$_3$CN and 73 ns in CH$_2$Cl$_2$) upon 337 and 615 nm irradiation [88]. The transient absorption was observed between 360—460 nm with λ_{max} at 390 nm. From the kinetic data the transient was reported to be an electronic excited state of [Re$_2$Cl$_8$]$^{2-}$, most probably that corresponding to $\sigma^2\ \pi^4\ \delta^1\ (\delta^*)^1$ configuration. The 390-band was assigned to an e_u(Cl) → δ charge-transfer transition. On irradiation at 337 nm only 80% of the excitation energy was internally converted into the δ-antibonding state, the remaining 20% of the upper excited state was proposed to undergo non-radiative decay to a halide-bridge intermediate leading to the photocleavage of the Re—Re bond.

The analogous transient of [Re$_2$Br$_8$]$^{2-}$ (lifetime of 51 ns in CH$_2$Cl$_2$) was found to exhibit two e_u → δ charge-transfer bands, at 490 and 555 nm [88].

[Ru(bipy)$_3$]$^{2+}$. The use of laser flash spectroscopy to study tris(2,2'-bipyridine)ruthenium(II) has revealed the transient spectrum (λ_{max} 360 nm), generated within the time resolution of the lasser pulse (60 ns) [89,90]. The spectrum was identical for water and acetonitrile solutions at 530, 353 or 265 nm excitation and was thus identified as the (^{3}CT)[Ru(bipy)$_3$]$^{2+}$ excited state. The quantum yield for the triplet state formation was determined (Φ_T = 0.5) [89]. The transient absorption was assigned as a triplet—triplet transition. The kinetics of the absorption decay were characterized and the first order rate constant was identical to that for decay of transient emission [89, 91,92]. In the presence of oxygen the bimolecular rate constant ($3.3 \cdot 10^9$ M^{-1} s^{-1}) was consistent with that from quenching experiments [89,93,94].

[Co(NH$_3$)$_5$Cl]$^{2+}$. Flash photolysis and scavenging experiments have prompted Caspari et al. [95] to assume that a reactive transient detected in the 320—360 nm region at μs resolution time in chloropentaamminecobalt(III) solution is most likely a metastable charge-transfer triplet excited state of [Co(NH$_3$)$_5$Cl]$^{2+}$ generated from an initial singlet excited state through an intersystem crossing process.

UO$_2$$^{2+}$. At ns resolution time, with the use of a ruby frequency doubled laser (347.1 nm), as well as on the μs time scale with conventional flash apparatus, transient absorption in the range 450—650 nm, (λ_{max} ca. 590 nm), was observed in uranyl perchlorate or nitrate solution [96]. The kinetic studies and quenching experiments have prompted the assumption that the short-lived ($t_{1/2}$ ca. 1.05 μs) transient spectrum is due to the excited state of the UO$_2$$^{2+}$ ion, which was reported to be the precursor of the photochemical reaction, as well as of the fluorescence.

(ii) Photosubstitution and related reactions

(a) Photodissociation

This reaction mode has been studied by flash photolysis, mainly in the case of carbonyl or mixed carbonyl—arene complexes.

[Ni(CO)$_4$]. An early investigation [97] using a high intensity UV flash revealed that gaseous tetracarbonylnickel decomposes according to the reaction scheme

$$[\mathrm{Ni(CO)_4}] \xrightarrow{h\nu} [\mathrm{Ni(CO)_3}] + \mathrm{CO} \tag{1}$$

$$[\mathrm{Ni(CO)_3}] \xrightarrow{h\nu} [\mathrm{Ni(CO)_2}] + \mathrm{CO} \tag{2}$$

$$[\mathrm{Ni(CO)_2}] \rightarrow \mathrm{Ni^0} + 2\,\mathrm{CO} \tag{3}$$

The decomposition was strongly inhibited by adding carbon monoxide because of the reverse reactions of (1) and (2). In contrast to the other observations, it has been reported that flash photolysis of tetracarbonylnickel yields an appreciable amount of elemental nickel [97].

[Fe(CO)$_5$]. In this case elemental iron was also found to be produced upon flashing [98], and moreover Fe, or in the presence of oxygen, FeO radicals, were detected within the ms time range [99].

[M(CO)$_6$] (M = Cr, Mo, W). More recent studies were performed for hexacarbonyls, in particular for [Cr(CO)$_6$]. In this case transient absorption, with a maximum near 500 nm, was attributed to pentacarbonylchromium [Cr(CO)$_5$] [100—102]. There are some discrepancies regarding the detailed mechanism of the photodissociation. Nasielski et al. [101] reported the presence of two transient species absorbing in the visible region. The first (λ_{max} 483 nm) did not react with CO, but instead generated, with a half-life of 6 ms, the second transient (λ_{max} 447 nm). The latter slowly recombined with CO and under these conditions had a half-life of 25 s. These species were assigned to the C_{4v} and D_{3h} (or C_{2v}) forms of [Cr(CO)$_5$], respectively. However, the existence of the D_{3h} form has been doubted by some authors [103,104] and it was also reported that the decay kinetics and absorption spectra were not reproducible [105].

In recent flash photolysis work, performed in μs and ns resolution time, Kelly et al. [102,106] observed only one transient spectrum which could be assigned to [Cr(CO)$_5$], and other transient absorptions were reported to originate from trace impurities. Pentacarbonylchromium was found to be generated immediately after flash in the photodissociation reaction

$$[\mathrm{Cr(CO)_6}] \xrightarrow{h\nu} [\mathrm{Cr(CO)_5}] + \mathrm{CO} \tag{4}$$

It showed a broad absorption in the visible range (centered at 503 nm) and a lifetime $\tau > 200$ μs. In a solution saturated with CO the species, which had a half-life of 25 μs, reverted to [Cr(CO)$_6$]

$$[\mathrm{Cr(CO)_5}] + \mathrm{CO} \rightarrow [\mathrm{Cr(CO)_6}] \tag{5}$$

The structure of the pentacarbonylchromium generated upon flash photolysis has not been defined due to a shift in its spectrum compared with that of the C_{4v} form of the [Cr(CO)$_5$] found earlier [102].

Samoilova et al. [99], using an intense flash source with ca. 0.1 ms time resolution, found transient absorption which they attributed to the metal radicals Cr, Mo and W (and possibly Cr_2 and Mo_2) for undiluted hexacarbonyls of these metals. Dilution with argon suppressed the transient absorption intensity. The transients, generated in mixtures of hexacarbonyls with O_2, H_2 as well as D_2, were also investigated and the radicals CrO, CrH, CrD, WO and possibly MoO, were characterized spectrally and kinetically [99].

$[Fe(C_4H_4)(CO)_3]$. In the case of mixed arene—carbonyl complexes the photodissociation of the carbonyl group has been observed [3], but a dissociation of ligands other than CO can also occur. Mass spectrometry measurements of tricarbonylcyclobutadieneiron, $[Fe(C_4H_4)(CO)_3]$, flashed in the vapour phase, gave evidence for the dissociation reaction [81]

$$[Fe(C_4H_4)(CO)_3] \xrightarrow{h\nu} [Fe(CO)_3] + {}^{\bullet}C_4H_4 \qquad (6)$$

rapidly followed by

$${}^{\bullet}C_4H_4 \rightarrow 2\ C_2H_2 \qquad (7)$$

and

$$2\ {}^{\bullet}C_4H_4 \rightarrow C_6H_6 + C_2H_2 \qquad (8)$$

The formation of the $[Fe(CO)_3]$ species was also demonstrated by e.p.r. spectroscopy of photolyzed tricarbonylcyclobutadieneiron at low temperature [81].

$[M_2(CO)_8(phen)]$ ($M = Mn, Re$). For dimeric metal—metal bonded carbonyl complexes a somewhat different reaction pathway was found. Continuous photolysis has revealed homolytic M—M cleavage upon irradiation of the low-lying CTTM band [107]. In flash experiments the dimeric species $[M_2(CO)_{10}]$ as well as $[M_2(CO)_6L_2]$ (L = phen or biquin) were observed in good yield. They were assumed to be formed in photoinduced cross-coupling reactions. Attempts to induce the cross-coupling of metal radicals by flash photolyzing $[Re_2(CO)_8(biquin)]$ were unsuccessful [107].

$[NiL(H_2O)_2]^{2+}$. Photodissociation of coordinated water has been revealed in laser photolysis of the nickel(II) complex with the quadridentate ligand *N,N'*-bis(2-aminoethyl)-1,2-propanediamine, $(NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$ (L)) [108,109]. This complex is known to exist in aqueous solution as an equilibrium mixture of low-spin planar ($^1A_{1g}$) and high-spin octahedral ($^3A_{2g}$) forms

$$[NiL]^{2+} + 2\ H_2O \rightleftharpoons trans\text{-}[NiL(H_2O)_2]^{2+} \qquad (9)$$

The octahedral species predominates at room temperature. After photolysis with 1.06 μm radiation from a neodymium laser source the immediate (within 30 ns) increase in absorption of the planar form (at 440 nm) was observed [108]. Since the octahedral complex absorbs at the laser wavelength the octahedral—planar interconversion was supposed to follow the electronic transition $^3A_{2g} \rightarrow {}^3T_{2g}$. The photochemical process is accompanied by a temperaturejump perturbation, which however is about 50 times weaker than the photochemical one with 1.06 μm radiation [109]. The rapid rise in concentration of the planar form was reported to be followed by a return to almost the original level. A relaxation time of about 0.3 μs was reported and interpreted as a two stage mechanism

$$[NiL]^{2+} + H_2O \rightleftharpoons [NiL(H_2O)]^{2+} \tag{10}$$

$$[NiL(H_2O)]^{2+} + H_2O \rightleftharpoons [NiL(H_2O)_2]^{2+} \tag{11}$$

Similar effects were observed in aqueous solutions of nickel(II) complex with triethylenetetramine [108].

(b) Photoaquation

Cyanide complexes. Flash photolytic investigations of photoaquation pathways include a considerable number of cyanide complexes, of which hexacyanoferrate(II) ion, has received most attention.

[Fe(CN)$_6$]$^{4-}$. In this case the primary reaction

$$[Fe(CN)_6]^{4-} \xrightarrow[H_2O]{h\nu} [Fe(CN)_5(H_2O)]^{3-} + CN^- \tag{12}$$

inferred from steady state illumination [3,4] has been confirmed in flash experiments [40,110—113]. In μs [40] as well as in ns [110—113] resolution times the same transient spectrum was observed in the range 370—525 nm, with a maximum at about 450 nm (pH $\geqslant$ 3.8) or 420 nm (pH $\leqslant$ 2.0) [113]. This was attributed to $[Fe(CN)_5(H_2O)]^{3-}$ complex which was reported to be generated within $\leqslant$1 ns and stable on the time scale of the flash observation. The pH dependence of the transient spectrum was attributed to the participation of the protonated species $H[Fe(CN)_6]^{3-}$. The photoaquation was reported to be the sole reaction mode in the long wavelength region ($\lambda > 313$ nm), whereas at more energetic radiation it is accompanied by hydrated electron production [110—113] (cf. pp. 167, 168). The precursor $^1T_{1g}$ state which was suggested to yield the aquation, might be accessible directly by absorption at $\lambda > 313$ nm, or generated from higher excited states ($^1T_{1u}$, or $^1T_{2g}$) through radiationless transitions [113].

[Fe(CN)$_5$NO]$^{2-}$. As above, similar low intensity transient absorption (λ_{max} about 450 nm shifted to about 420 nm at low pH values) was found for nitrosylpentacyanoferrate(II) in preliminary flash experiments performed in our laboratory [114]. It was accompanied by more prominent transient spectra due to redox products (cf. p. 166). The photoaquation reaction was proposed to involve the NO$^+$ ligand

$$[Fe(CN)_5NO]^{2-} \xrightarrow[H_2O]{h\nu} [Fe(CN)_5(H_2O)]^{3-} + NO^+ \tag{13}$$

Thus this pathway suggested earlier on the basis of continuous illumination studies, [3,4,115—123] has been further supported.

[Mo(CN)$_8$]$^{4-}$. Among the pathways suggested for LF photochemistry of

octacyanomolybdate(IV), the photoaquation reaction eqn. (14)

$$[Mo(CN)_8]^{4-} \xrightarrow[H_2O]{h\nu} [Mo(CN)_7(H_2O)]^{3-} + CN^- \tag{14}$$

has been the most strongly supported [3,4,124]. In flash photolysis studies, completed by scavenging experiments [87,125], a long-lived transient absorption with maximum at 534 nm was attributed to the heptacyanoaquomolybdate(IV) complex. It was reported to be formed, at the expense of the excited LF state, in the aquation reaction competing with isomerization. Further, it was proposed to decay to $[Mo(CN)_8]^{4-}$ through anation and to $[MoO(OH)(CN)_4]^{3-}$ through successive decompositions. A full scheme is presented in Fig. 1.

$[Co(CN)_6]^{3-}$. Photoaquation of the hexacyanocobaltate(III) complex eqn. (15)

$$[Co(CN)_6]^{3-} \xrightarrow[H_2O]{h\nu} [Co(CN)_5(H_2O)]^{2-} + CN^- \tag{15}$$

was recognized long ago and has been investigated in detail with steady illumination [3,4,6,126—128]. The system is relatively simple to study because the $[Co(CN)_5(H_2O)]^{2-}$ complex is the sole and terminal product at irradiations with wavelengths longer than 250 nm involving ligand field transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$. The dissociative decay of the excited LF state was proposed [129], involving a pentacoordinated $[Co(CN)_5]^{2-}$, as the reactive intermediate. Another acceptable pathway involves interchange of an inner sphere CN^- ligand and a water molecule in the outer sphere of the photoexcited $[Co(CN)_6]^{3-}$, this may be outlined as

$$\{[Co(CN)_6]^{3-} \cdot (H_2O)_n\} \xrightarrow{h\nu} {}^*\{[Co(CN)_6]^{3-} \cdot (H_2O)_n\} \tag{16}$$

$${}^*\{[Co(CN)_6]^{3-} \cdot (H_2O)_n\} \xrightarrow{k} \{[Co(CN)_5(H_2O)]^{2-} \cdot (CN^-)(H_2O)_{n-1}\} \tag{17}$$

To distinguish between the two mechanisms, the flash photolytic and scavenging techniques have been used [130]. No intermediates could be detected in flash photolyzed $[Co(CN)_6]^{3-}$ solutions, with the formation of $[Co(CN)_5(H_2O)]^{2-}$ occurring within the resolution time of the flash (50 μs). Moreover, in the presence of NaN_3, flash photolysis of $[Co(CN)_6]^{3-}$ did not yield any detectable $[Co(CN)_5N_3]^{3-}$. On the basis of these experiments the dissociative pathway for the photoaquation of hexacyanocobaltate(III) has been excluded [130].

$[Co(CN)_5X]^{3-}$ (where $X = Cl^-, Br^-, I^-, N_3^-$). For mixed acidopentacyanocobaltate(III) complexes of the type $[Co(CN)_5X]^{3-}$ the photoaquation of coordinated ligand X

$$[Co(CN)_5X]^{3-} \xrightarrow[H_2O]{h\nu} [Co(CN)_5(H_2O)]^{2-} + X^- \tag{18}$$

was found in steady state irradiation [3,4,131]. In flash photolysis experiments no transient absorption attributable to the aquation product could be observed for the $[Co(CN)_5I]^{3+}$ complex [132]. Similar results were obtained for flash photolyzed solutions of azidopentacyanocobaltate(III), [Co-

$(CN)_5N_3]^{3-}$: the only process observed was the photochemical decomposition of the substrate [43,132]. However, the yields of $[Co(CN)_5(H_2O)]^{2-}$ produced from flash photolysis of $[Co(CN)_5N_3]^{3-}$ were determined from changes in substrate concentration and from the concentrations of redox products formed [43,132]. Photoaquation of the azide ligand was the only process reported to result from irradiation of the lower ligand—field absorption band (λ_{max} at 360 nm) [132].

Complexes with acido ligands, excluding cyanide. The other group for which photoaquation has been extensively studied with flash technique is that of mixed acido—ammine or acido—amine complexes of cobalt(III) and rhodium(III).

$[Co(NH_3)_5X]^{2+}$ ($X = Br^-, NCS^-, N_3^-, CH_3COO^-$). Two different photoaquation mechanisms were found in the case of acidopentaamminecobalt(III) complexes: the acido ligand aquation was detected in bromide and isothiocyanate complexes [133,134]

$$[Co(NH_3)_5X]^{2+} \xrightarrow[H_2O]{h\nu} [Co(NH_3)_5(H_2O)]^{3+} + X^- \qquad (19)$$

for $X = Br^-, NCS^-$
whereas the ammonia ligand aquation was reported in the case of azido and acetato compounds [134—136]

$$[Co(NH_3)_5X]^{2+} \xrightarrow[H_2O]{h\nu} [Co(NH_3)_4(H_2O)X]^{2+} + NH_3 \qquad (20)$$

for $X = N_3^-$ and CH_3COO^-

In all cases no transient species responsible for photoaquation were found on flashing and the pathway was inferred from chemical analysis of the products. Quantitative conclusions could, however, be drawn from the differences between the change in substrate concentration and that of redox product formation upon flash.

In the case of acetato complex the photoaquation was found to be limited to ligand—field excitation [135], whereas for azido complex [134] it was reported to predominate over the whole spectral region studied (530—210 nm). Two mechanisms were considered to be most plausible: (1) the thermally equilibrated photoactive CTTM state may have some Co—NH_3 bonds considerably lengthened and its electronic relaxation would be coupled with aquation, or (2) the CTTM excited state can relax to populate a photoactive LF state [134].

$[Rh(NH_3)_5X]^{2+}$ (where $X = Cl^-, Br^-, I^-, N_3^-$). For analogous acidopentaamminerhodium(III) complexes, and for *trans*-$[Rh(NH_3)_4I_2]^{2+}$ similar combined continuous and flash studies were performed by Kelly and Endicott [41,132, 137]. In the flash technique appropriate cut-off filters were used to irradiate the complexes in their ligand field absorption bands. Such irradiation did not give rise to $X_2^- \cdot$ radical transients, indicating that there was no contribution from photoredox processes. Both continuous and flash results revealed two

different photoaquation processes: (1) halide aquation (most important for $[Rh(NH_3)_5Cl]^{2+}$) and (2) *trans*-ammonia aquation (most important for $[Rh(NH_3)_5I]^{2+}$). It was proposed that the combination of halide and *trans*-ammonia aquation obtained from LF excitation of $[Rh(NH_3)_5Br]^{2+}$ resulted from the competitive population, decomposition and deactivation of two different triplet states [137]. In flash photolysis of $[Rh(NH_3)_5I]^{2+}$ no transient was observed [41] and the spectral changes observed upon flashing were consistent with photoaquation of $[Rh(NH_3)_5I]^{2+}$ and production of *trans*-$[Rh(NH_3)_4(H_2O)I]^{2+}$ as an immediate (within $\tau < 50$ μs) photolysis product. It was suggested that the LF excited state is five-coordinate, pyramidal with I^- apical [137].

In the case of azide complex, Ferraudi and Endicott [132] reported that LF excitation leads largely to N_3^- aquation. On the other hand, Basolo and co-workers [138] were not able to detect azide ions in the photolyte, although the formation of $[Rh(NH_3)_5(H_2O)]^{3+}$ was found to be increased as the exciting light wavelength was increased. The generation of $[Rh(NH_3)_5(H_2O)]^{3+}$ was then proposed to proceed as in a redox process

$$[Rh(NH_3)_5N_3]^{2+} \xrightarrow{h\nu} [Rh(NH_3)_5]^{2+} + N_3\cdot \tag{21}$$

$$[Rh(NH_3)_5]^{2+} + H_2O + \text{oxidant} \rightarrow [Rh(NH_3)_5(H_2O)]^{3+} + \\ + \text{reduced product} \tag{22}$$

$[Co(NH_3)_4CO_3]^+$ and $[Co(en)_2CO_3]^+$. Flash photolysis of the carbonato—ammine and carbonato—amine complexes of cobalt(III) with bidentate carbonate, has revealed, besides the transient absorption caused by photoredox reaction, a long-lived tail absorption in the 300-nm region which decayed through pH-dependent first-order kinetics. The comparison of the behaviour with that of an intermediate in the acid-catalyzed aquation, as well as complementary scavenging experiments, led Hoffman and co-workers [139,140] to identify the transient species as aquocarbonato complexes of Co(III), *cis*-$[Co(NH_3)_4(CO_3H)(H_2O)]^{2+}$ and *cis*-$[Co(en)_2(CO_3H)(H_2O)]^{2+}$, or products of their base hydrolysis. Further thermal aquation of the aquocarbonato complexes has led to the diaquo final products: *cis*-$[Co(NH_3)_4(H_2O)_2]^{3+}$ and *cis*-$[Co(en)_2(H_2O)_2]^{3+}$. The discussion of the excited states involved and mechanistic details is presented later (cf. p. 161).

$[Co(HEDTA)X]^-$ (where $X = Cl^-, Br^-, NO_2^-$). Continuous, as well as flash studies, of ethylenediaminetetraacetate complexes of Co(III) of the type $[Co(HEDTA)X]^-$ have revealed the photoaquation of ligand X following LF and CTTM excitation. It was inferred that the reactive states have triplet multiplicity [141—143]. In these studies the flash method was used to follow transient changes in $[Ru(bipy)_3]^{2+}$ absorbance during sensitized photoreactions of $[Co(HEDTA)X]^-$.

Some flash experiments have also been performed for acido, ammine or mixed acido—ammine complexes of chromium(III), iron(III), ruthenium(III) and platinum(IV).

trans-$[Cr(NCS)_4(NH_3)_2]^-$ *and* $[Cr(NCS)_6]^{3-}$. In the case of chromium(III) isothiocyanate complexes, sharp transient spectra were observed upon flash in ketone solvents, S [86]. They were tentatively assigned to complexes formed between NCS^- ion and the solvent, which is in line with the photochemically accelerated aquations or rather solvations

$$trans\text{-}[Cr(NCS)_4(NH_3)_2]^- \xrightarrow[S]{h\nu} [Cr(NCS)_3(S)(NH_3)_2] + NCS^- \tag{23}$$

$$[Cr(NCS)_6]^{3-} \xrightarrow[S]{h\nu} [Cr(NCS)_5(S)]^{2-} + NCS^- \tag{24}$$

$[Fe(ox)_n]^{3-2n}$ *(where n = 3,2 or 1).* For tris- and bisoxalato systems evidence has been found from flash photolysis studies that photoaquation

$$[Fe(ox)_3]^{3-} \xrightarrow[H_2O]{h\nu} [Fe(ox)_2(H_2O)_2]^- + ox^{2-} \tag{25}$$

competes effectively with photoredox as a primary process [144] (cf. pp. 154—156). The relatively slow absorbance changes occurring at $t > 200$ μs after flash in the 310—500 nm region were reported to be due to the decomposition of Fe(II) oxalato complexes (cf. eqns. 68 and 69) as well as to the anation

$$[Fe(ox)_2(H_2O)_2]^- + ox^{2-} \rightarrow [Fe(ox)_3]^{3-} + 2\,H_2O \tag{26}$$

In contrast to the tris- and bisoxalatoferrate(III) ions, for the monoxalatoiron(III) complex, photoaquation was found not to be a significant primary process [145].

$[Ru(NH_3)_6]^{3+}$ *and* $[Ru(NH_3)_5Cl]^{2+}$. It has been demonstrated by flash and continuous photolysis studies [44] that the ruthenium(III) complexes are largely unreactive when their UV absorption bands are irradiated. The single reaction that could be unequivocally established in both cases was a low yield ($\Phi < 0.1$) photoinduced aquation of the ammine ligand.

trans-$[Pt(NH_3)_4X_2]^{2+}$ *(X = Br⁻ and NCS⁻).* The mixed acido—ammine complexes of platinum(IV) were reported [3,146] to provide examples of photoaquation occurring as the net reaction of the complex, even though a redox process is involved. Based on spectral evidence of ion pairing as well as transient species found in flash experiments [146] the overall reaction was suggested to be eqn. (27)

$$trans\text{-}[Pt(NH_3)_4X_2]^{2+} \cdots\cdot X^- \xrightarrow[H_2O]{h\nu} trans\text{-}[Pt(NH_3)_4X(OH)]^{2+} + \\ + X_2^- \cdot + H \tag{27}$$

$[PtCl_6]^{2-}$. For hexachloroplatinate(IV) complex the fall in concentration resulting from flash was found to be much greater than that from the redox products formation [147]. Analysis of spectral changes in flashed solutions have led to identification of the photoaquation product as $[PtCl_5(OH)]^{2-}$, formed in the reaction

$$[PtCl_6]^{2-} \xrightarrow[H_2O]{h\nu} [PtCl_5(OH)]^{2-} + H^+ + Cl^- \tag{28}$$

The ratio of quantum yields for reduction and aquation (estimated as 1 : 10) was reported to represent the fraction of the excited $[PtCl_6]^{2-}$ ions in which energy transfer from the CTTM state, generated by irradiation, to excited triplet state, reacting towards aquation, is inefficient [147].

(c) Photosubstitution

Other flash results are available which suggest direct substitution of ligands other than solvent molecules. This suggestion comes from studies on photolysis of hexacyanoferrate(III), $[Fe(CN)_6]^{3-}$, solutions containing azide ions [148]. The direct substitution reaction

$$[Fe(CN)_6]^{3-} + N_3^- \xrightarrow{h\nu} [Fe(CN)_5N_3]^{3-} + CN^- \qquad (29)$$

was reported to proceed upon flashing. However, due to the ms time resolution of the apparatus used initial photoaquation cannot be excluded. The decay of the azidopentacyanoferrate(III) as a function of pH, ionic strength and concentration of CN^- or N_3^- was followed using kinetic spectrophotometry. This has led to the rather peculiar conclusion that azidopentacyanoferrate(III) obtained photochemically retains the photoexcitation which is followed by the dark process, reverse of eqn. 29, to yield excited hexacyanoferrate(III) with a lifetime of the order of seconds.

(d) Photoisomerization

Geometrical photoisomerization has been supposedly observed in flash photolyzed solutions of cyanide complexes of nickel(II) and molybdenum(IV).

$[Ni(CN)_4]^{2-}$. The labile tetracyanonickelate(II) ion was found in steady irradiation to be insensitive to LF or CT excitations [3,4,149]. However, in flash photolysis experiments a transient absorption has been observed [3,146, 150]. Considering the fact that the excited state of the tetracyanonickelate(II) complex may have its stable conformation in a distorted tetrahedral structure, as suggested by Ballhausen et al. [151], the transient species observed upon flash may originate from the steric rearrangement. However, photoaquation products cannot be excluded as well since the $[Ni(CN)_4]^{2-}$—CN^- exchange is, thermally, very rapid.

$[Mo(CN)_8]^{4-}$. In this case a long-lived (minutes) absorption (λ_{max} = 495 nm) whose decay was not affected by the concentration of CN^- ions, was assigned to the unstable, antiprismatic form of octacyanomolybdate(IV) [87, 125]. The photoisomerization process was reported to proceed in competition with photoaquation (cf. pp. 142, 143). The scheme, involving both the pathways as well as the secondary thermal reaction leading to the final product, $[Mo(CN)_4O(OH)]^{3-}$, is presented in Fig. 1.

(iii) Photoreduction of transition-metal central ion

Halide complexes

Among the numerous photoredox processes following CTTM excitation

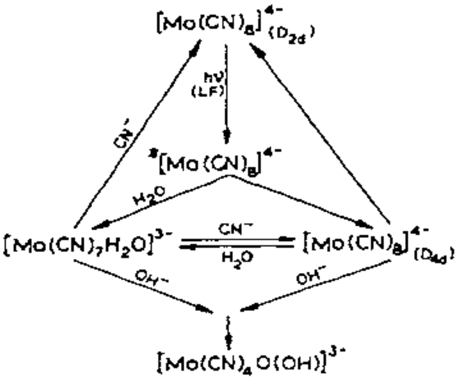


Fig. 1. Photochemical and secondary thermal reactions in octacyanomolybdate(IV) solutions on flashing in a LF region (taken from ref. 87).

the most extensively studied by flash photolysis are those of halide complexes. The main features of these investigations are summarized in Table 1. In the case of halide complexes the photoreduction path was found for chromium(VI), iron(III), cobalt(III), rhodium(III), platinum(IV), mercury(II) and uranium(IV) compounds. These data, especially the recent results, are sufficiently concordant and consistent with the pathway expected for CTTM photochemistry: halogen radicals, detected mainly as dihalogen ones, were observed in most cases. Unfortunately it appears that metal fragments commonly escape direct observation.

The spectra of dihalogen radicals are characterized by intense bands at 380, 364 and 340 nm for $I_2^- \cdot$, $Br_2^- \cdot$ and $Cl_2^- \cdot$, respectively [16,152—155]. In addition to main bands each radical shows some weaker absorption at shorter wavelengths, possibly consisting of several overlapping bands [16]. The radicals can be detected with μs time resolution and decay by pH independent second-order kinetics with rate constants of $9 \cdot 10^9$, $2\text{-}6 \cdot 10^9$ and $4 \cdot 10^9$ M^{-1} s^{-1}, respectively [16,152—158].

Due to photooxidation of halide ions occurring upon irradiation with far UV [159], the flash source must have wavelengths shorter than 270 nm filtered off, in order to detect the formation of $X \cdot$ radicals from complex photoredox decomposition.

The detailed mechanisms proposed for individual complexes are described below.

CrO_2Cl_2. The photochemistry of chromyl chloride has been investigated in the gas phase and two transient absorptions have been assigned to the CrO_2Cl and CrO_2 radicals [160]. The CrO_2 species was reported to arise from the photoexcited CrO_2Cl radical in the reaction sequence

$$CrO_2Cl_2 \xrightarrow{h\nu} {}^*CrO_2Cl_2 \rightarrow CrO_2Cl \xrightarrow{h\nu} {}^*CrO_2Cl \rightarrow CrO_2 \qquad (30)$$

Both transients reached their maximum concentration within the flash lifetime and decayed independently of each other. Addition of inert gas lowered

TABLE 1

Transient species from photoredox decomposition of halide complexes, detected by flash photolysis technique

Substrate irradiated	Transient species	References
CrO_2Cl_2	CrO_2Cl (s), CrO_2 (s), $Cl\cdot$ (i)	160
$[FeCl]^{2+}$	$Cl_2^-\cdot$ (ss)	161
$[FeBr]^{2+}$	$Br_2^-\cdot$ (ss)	161
$[Ru(NH_3)_5Cl]^{2+}$	none (s)	44
$[Co(NH_3)_5Cl]^{2+}$	$NH_2Cl^-\cdot$ or $NH_3Cl\cdot$ (ss)	95, 152
$[Co(NH_3)_5Br]^{2+}$	$Br_2^-\cdot$ (ss)	133, 143, 157, 163
$[Co(NH_3)_5I]^{2+}$	$I_2^-\cdot$ (ss)	157, 163
$[Co(CN)_5I]^{3-}$	$I_2^-\cdot$ (ss)	152
$[Co(HEDTA)Cl]^-$	$[Co^{II}(Y\cdot)]^-$ (i)	141—143, 152
$[Co(HEDTA)Br]^-$	$[Co^{II}(Y\cdot)]^-$ (i)	141—143, 152
$[Co(N_4)Cl_2]^+$	$Cl_2^-\cdot$ (ss)	95, 157
$[Co(N_4)Br_2]^+$	$Br_2^-\cdot$ (ss)	157
$[Rh(NH_3)_5Cl]^{2+}$	$Cl_2^-\cdot$ (ss)	168
$[Rh(NH_3)_5Br]^{2+}$	$Br_2^-\cdot$ (ss)	168
$[Rh(NH_3)_5I]^{2+}$	$I_2^-\cdot$ (ss), $[Rh(NH_3)_4]^{2+}$ (i)	41
$[PtCl_6]^{2-}$	$Cl_2^-\cdot$ (ss), $[PtCl_4]^-$ (s)	147
$[PtBr_6]^{2-}$	transient oxidizing species other than $Br\cdot$ or e_{aq}^- and unstable form of $[PtBr_4]^{2-}$ (i)	163
$[PtI_6]^{2-}$	non-planar $[PtI_4]^{\cdot -}$ (i)	163
trans-$[Pt(NH_3)_4Br_2]^{2+}$	$Br_2^-\cdot$ (ss), $H\cdot$	3, 146
$HgCl_2$	$Cl_2^-\cdot$ (ss)	156
$[HgCl_4]^{2-}$	$Cl_2^-\cdot$ (ss)	156
$HgBr_2$	$Br_2^-\cdot$ (ss)	156
$[HgBr_4]^{2-}$	$Br_2^-\cdot$ (ss)	156
HgI_2	not identified transient (λ_{max} = 330 nm)	156
$[HgI_4]^{2-}$	$I_2^-\cdot$ (ss)	156
UI_4	atomic U (s)	172, 173

s = spectral detection, i = inferred from flash data, ss = spectral detection after chemical scavenging, $[Co^{II}(Y\cdot)]^-$ = methyleneethylenediaminetriacetate radical coordinated to the reduced metal.

the initial concentrations of both intermediates, as well as the extent of the photolytic decomposition.

$[FeCl]^{2+}$ and $[FeBr]^{2+}$. Deaerated solutions containing the halogen—iron(III) complexes were flash photolyzed with unfiltered light as well as with filtered light having no contribution from wavelengths <270 nm [161]. In both cases the same transient spectra were observed resembling those of radical anions $Cl_2^-\cdot$ and $Br_2^-\cdot$. This was consistent with the photoredox reaction eqn. (31)

$$[FeX]^{2+} \xrightarrow{h\nu} Fe^{2+} + X\cdot \tag{31}$$

$$X\cdot + X^- \rightleftharpoons X_2^-\cdot \tag{32}$$

although in continuous irradiation of iron(III) chloride the primary photooxidation of OH^- ions was also proposed [162]. Flash photolysis of halogen—iron(III) complexes has been used as a source of radical anions for kinetic studies [161].

$[Ru(NH_3)_5Cl]^{2+}$. Flash and continuous photolysis of pentaamminechlororuthenium(III) complex have demonstrated that irradiation of CTTM absorption bands does not result in detectable photoredox processes ($\Phi < 0.1$) [44]. The relative photochemical inertness of this ruthenium(III) complex has been accounted for by the relatively small distortion expected of the CTTM states, with a t_{2g}^6 electronic configuration. In addition it may be expected that the CTTM states are lower in energy than the LF excited states in the $[Ru^{III}(NH_3)_5X]^{2+}$ complexes [44].

$[Co(NH_3)_5X]^{2+}$ ($X = Cl^-, Br^-, I^-$). Irradiation of pentaamminehalogenocobalt(III) complexes in their intense CTTM bands results in a number of possible processes (cf. p. 144) the most predominant of which is photoreduction with formation of Co^{2+} and an oxidized ligand free radical from one electron transfer. Some flash photolytic studies have helped to distinguish between alternative mechanisms. Penkett and Adamson [163] reported the formation of halogen atom transients from bromo- and iodo-derivatives on flashing, in either a quartz or a Pyrex cell, according to the reaction (33)

$$[Co(NH_3)_5X]^{2+} \xrightarrow{h\nu} Co^{2+} + 5\ NH_3 + X\cdot \qquad (33)$$

(where $X = Br^-, I^-$). This reaction pathway was more recently confirmed by several flash and continuous photolytic studies [133,143,157,164,165]. Thus, the alternative oxidation of the ammonia ligand in the primary chemical act, that would be suggested by the lack of bromine among the final products, was excluded by flash experiments.

On the other hand flash photolysis, product analysis and chemical scavenging studies carried out by Endicott and co-workers [95,166] showed that the oxidized radical, resulting from the photoreduction of pentaamminechlorocobalt(III) complex, is largely nitrogeneous. There were no transients observed. However in the presence of free Cl^- a transient species was detected that could not be identified as $Cl_2^-\cdot$ but rather as $NH_2Cl^-\cdot$ or $NH_3Cl\cdot$. Characteristics of the immediate cobalt(II) species were not defined; a more detailed discussion on the photoredox behaviour may be found in the recent articles of Endicott et al. [152,164,165].

$[Co(CN)_5I]^{3-}$. It was found that flash irradiation of the ligand field absorption band of pentacyanoiodocobalt(III) did not produce $I_2^-\cdot$, whereas irradiation of CT region (254—360 nm) resulted in the formation of appreciable I_2^- [132].

$[Co(HEDTA)X]^-$ ($X = Cl^-, Br^-$). The flash photolysis of halogenoethylenediaminetetraacetate complexes of cobalt(III) in the presence of $[Ru(bipy)_3]^{2+}$ ions has revealed the nearly diffusion-controlled oxidation of the ruthenium(II) complex by primary radicals [141—143,152]. These were presumed to be *N*-methyleneethylenediaminetriacetate which remained coordinated to the re-

duced metal after the initial photoreaction (cf. Table 1). The reactive excited states were inferred to have triplet spin multiplicity and the carboxylate to cobalt charge-transfer excited state to have a lower dissociation energy than the X^- to cobalt excited state [141—143].

$[Co(N_4)X_2]^+$ (where N_4 represents a cyclic tetradentate nitrogen donor ligand: 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene or its amine analogs; $X = Cl^-, Br^-$). The formation of dihalogen radicals was observed in the presence of halide anions and kinetics of their decay were studied in detail [95,157].

$[Rh(NH_3)_5X]^{2+}$ ($X = Cl^-, Br^-, I^-$). In the case of chloro and bromo derivatives the formation of $Cl_2^- \cdot$ and $Br_2^- \cdot$ radicals, respectively, in flash photolysis has been briefly mentioned [168], whereas pentaamminciodorhodium(III) complex was studied in more detail by Kelly and Endicott [41]. The charge-transfer excitation of this complex was reported to lead to oxidation of coordinated I^- and formation of a transient $[Rh(NH_3)_4]^{2+}$ species according to the reaction

$$[Rh(NH_3)_5I]^{2+} \xrightarrow[H^+]{h\nu(CTTM)} [Rh(NH_3)_4]^{2+} + NH_4^+ + I\cdot \qquad (34)$$

Flash photolysis and ^{131}I tracer studies indicated that the redox yield is ~0.2 at 254 nm. It was concluded that internal conversion from charge-transfer to ligand—field excited-state manifolds is relatively inefficient, compared to product formation and deexcitation [41].

trans-$[Rh(NH_3)_4I_2]^+$. Flash photolysis of CTTM bands ($\lambda < 270$ nm) has provided evidence for photoredox processes in these spectral regions [41]. The pattern of products and yields in this case was reported to be consistent with the mechanistic model for the photochemistry of $[Rh(NH_3)_5I]^{2+}$.

$[PtX_6]^{2-}$ ($X = Cl^-, Br^-, I^-$). Wright and Laurence [147] observed a transient absorption with a maximum at 410 nm generated in solutions of hexachloroplatinate(IV) upon flash irradiation, involving both LF and CT bands. The absorption decayed with a lifetime of about 0.1 s, by a second order process. A comparison of these data with those obtained from pulse radiolysis experiments [169] allowed the transient spectrum to be attributed to a platinum(III) complex which disproportionated by second-order decay (eqn. 37). Moreover, the transient absorption due to $Cl_2 \cdot$ radical was detected in the presence of an excess of Cl^- ions upon flashing with light having $\lambda < 230$ nm filtered off. The sequence of reactions, (35)—(38), in photoreduction of $[PtCl_6]^{2-}$ in the CTTM bands was thus proposed [147]

$$[PtCl_6]^{2-} \xrightarrow{h\nu(CTTM)} [PtCl_5]^{2-} + Cl\cdot \qquad (35)$$

$$[PtCl_5]^{2-} \rightarrow [PtCl_4]^- + Cl^- \qquad (36)$$

$$Pt(III) + Pt(III) \rightarrow Pt(II) + Pt(IV) \qquad (37)$$

$$Cl\cdot + Cl^- \rightarrow Cl_2^- \cdot \qquad (38)$$

In the case of $[PtBr_6]^{2-}$ complex a short lived oxidizing species was observed in degassed solution upon flashing, but no indications of any bromine atoms or free electrons were found [163]. A two-electron intramolecular photoredox process was thus proposed (eqn. 39)

$$[PtBr_6]^{2-} \xrightarrow{h\nu} [PtBr_4]^{2-} + Br_2 \tag{39}$$

The tetrabromoplatinate(II) generated photolytically was further thought to remain in an unstable geometry (e.g. trigonal pyramid) long enough to serve as a chain-carrier for the exchange. The experimental evidence, however, is not yet sufficient to wholely confirm these suggestions.

For hexaiodoplatinate(IV) a 0.1 s half-life transient absorbing at 410 nm was observed which was supposed to be the non-planar $[PtI_4]^{2-}$ species [163]. The spectral and kinetic properties of the species [169] could also lead to the assumption that it is a platinum(III) transient which is responsible for this absorption. Moreover, one would expect photoaquation of the complex found in continuous studies [4,170] to be perceptible in flash experiments as well.

trans-$[Pt(NH_3)_4Br_2]^{2+}$. In solutions containing an excess of bromide ions, $Br_2^- \cdot$ radicals were found to be generated along with hydrogen atoms and products of aquation [3,146]. Photoredox of the complex was proposed to lead to aquation as the net reaction (cf. eqn. (27) on p. 146) although competitive mechanisms cannot, as yet, be excluded.

HgX_2 *and* $[HgX_4]^{2-}$ ($X = Cl^-, Br^-, I^-$). Aqueous solutions of the mercury(II) halides undergo redox photolysis on irradiation with the first CT band. Using flash photolysis technique with suitable filters to eliminate absorption by uncomplexed halide ions, Langmuir and Hayon [156] observed the corresponding radical anions $Cl_2^- \cdot$, $Br_2^- \cdot$, $I_2^- \cdot$ in all cases, except HgI_2 which gave rise to an intermediate with a maximum at 330 nm that was not identified. Two possibilities were considered for the primary photochemical act leading to the formation of $X_2^- \cdot$ radicals. (1) The intermolecular transfer of an electron from a water molecule to give an OH radical

$$\{[HgX_4]^{2-} \cdot H_2O\} \xrightarrow{h\nu} [HgX_4]^{3-} + H^+ + OH \cdot \tag{40}$$

$$\text{or } \{HgX_2 \cdot H_2O\} \xrightarrow{h\nu} [HgX_2]^- + H^+ + OH \cdot \tag{41}$$

followed by rapid thermal reactions

$$OH \cdot + X^- \rightarrow OH^- + X \cdot \tag{42}$$

$$X \cdot + X^- \rightarrow X_2^- \cdot \tag{43}$$

(2) The intramolecular transfer of an electron from one of the ligands to the central ion of the complex

$$[HgX_4]^{2-} \xrightarrow{h\nu} [Hg^{(+)}X_4^{(3-)}]^{2-} \tag{44}$$

$$\text{or } HgX_2 \xrightarrow{h\nu} Hg^{(+)}X_2^{(-)} \tag{45}$$

followed either by direct formation of $X_2^- \cdot$, or by a simple homolytic rupture of a mercury—halogen bond and reaction (43). The first mechanism had to be discarded due to the lack of pH dependence of the initial $X_2^- \cdot$ radical concentration, whereas reaction (42) is known to be pH dependent. Moreover, mechanism (2) is consistent with a partial CTTM character of the exciting bands [4]. It was not possible to distinguish between the simple homolytic rupture and concerted departure of the two atoms. The latter case was also thought to occur upon flash photolysis of permanganate ion [171] and halide complexes of platinum(IV) [163] (cf. eqn. 39).

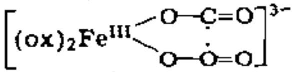
UI_4. Atomic uranium was identified as the product of flash photolysis of uranium tetraiodide vapour at a temperature of about 600°C [172,173]. The flash photolysis of UI_4 and $U(BH_4)_4$ was proposed as a new source of atomic uranium for absorption spectroscopy and other applications.

Oxalato complexes

Another group studied extensively using flash photolysis is the oxalato complexes of iron(III), cobalt(III) and uranium(IV); the main transients revealed are gathered in Table 2. In this case, however, in spite of numerous investigations the detailed mechanisms of the photoredox primary act, as well as secondary reactions, are still not completely defined.

TABLE 2

Transient species found in flash photolyzed solutions of oxalato complexes

Substrate irradiated	Transient species	References
$[Fe(ox)_3]^{3-}$	$ox^- \cdot$ (s,e)	73, 144, 171, 178, 179
	$CO_2^- \cdot$ (s,e)	73, 144, 179
	unidentified metastable state (s)	178
	 (e)	73, 179
	$[(ox)_2Fe^{II}(CO_2\cdot)]^{3-}$ (s)	73, 179
$[Fe(ox)]^+$	$ox^- \cdot$ (s)	145
	$[Fe^{II}(ox^- \cdot)]^+$ (s)	145
	$[Fe(ox)]$ (s)	145
$[Co(ox)_3]^{3-}$	$ox^- \cdot$ (s)	180,181
	$[(ox)_2Co^{II}(ox^- \cdot)]^{3-}$ (s)	180,181
	$[(ox)_2Co^{II}(ox^- \cdot)_2]^{4-}$ (s)	180
	e^-_{aq} (i)	180
	$[(ox)_2Co^{II}(ox^- \cdot)(H_2O)]^{3-}$(s)	181
	$[(ox)_3Co^{II}(ox^- \cdot)]^{5-}$ (s)	181
$[Co(NH_3)_5(ox)]^+$	$[(NH_3)_5Co—COO]^+$ (s)	64, 184
$[Co(NH_3)_4(ox)]^+$	$[(NH_3)_4Co—COO]^+$ (s)	64, 184
$[Co(en)_2(ox)]^+$	$[(en)_2Co—COO]^+$ (s)	64, 184
$[Cr(ox)_3]^{3-}$	none (s)	178
$UO_2^{2+}—ox^{2-}$	transient species not identified (s,e)	171, 178

e = electrochemical detection, s = spectral data, i = inferred from flash data.

$[Fe(ox)_3]^{3-}$. Mechanism of photoredox decomposition based on continuous photolysis [3,4,174—177] involved initial excitation, followed by dissociation, to give a ferrous oxalate molecule and an oxalate radical anion. The oxalate radical was reported to react with another ferrioxalate ion or itself

$$[Fe(ox)_3]^{3-} \xrightarrow{h\nu} {}^*[Fe(ox)_3]^{3-} \tag{46}$$

$$ {}^*[Fe(ox)_3]^{3-} \rightarrow [Fe(ox)_2]^{2-} + ox^- \cdot \tag{47}$$

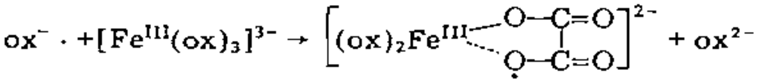
$$ox^- \cdot + [Fe(ox)_3]^{3-} \rightarrow [Fe(ox)_2]^{2-} + 2\ CO_2 + ox^{2-} \tag{48}$$

$$2\ ox^- \cdot \rightarrow 2\ CO_2 + ox^{2-} \tag{49}$$

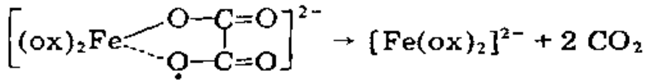
Flash experiments made as early as 1959 by Parker and Hatchard [178] revealed a long lived transient species absorbing at about 420 nm which decayed with a first order rate constant of ca. 200 s^{-1}. These observations, plus the fact that the quantum yield of iron(II) production exceeded unity, were consistent with the general reaction scheme proposed earlier. However, the first order, i.e. ferrioxalate independent, decay of the transient was assumed to preclude the bimolecular reaction between $ox^- \cdot$ radical and ferrioxalate as the rate controlling step. The reaction scheme was then modified as follows

$$ {}^*[Fe(ox)_3]^{3-} \rightarrow \text{(metastable state)} \tag{50}$$

$$\text{(metastable state)} \rightarrow [Fe^{II}(ox)_2]^{2-} + ox^- \cdot \tag{51}$$



$$ox^- \cdot + [Fe^{III}(ox)_3]^{3-} \rightarrow \left[(ox)_2Fe^{III}\begin{matrix} O\text{—}C{=}O \\ | \\ \dot{O}\text{—}C{=}O \end{matrix}\right]^{2-} + ox^{2-} \tag{52}$$



$$\left[(ox)_2Fe\begin{matrix} O\text{—}C{=}O \\ | \\ \dot{O}\text{—}C{=}O \end{matrix}\right]^{2-} \rightarrow [Fe(ox)_2]^{2-} + 2\ CO_2 \tag{53}$$

As possible structures for the metastable state those of free radical, a quartet state of the original complex or a ferrooxalate ion attached to an oxalate radical were proposed [178].

In recent flash studies some earlier results have been confirmed; however, the system was found to be more complicated then previously thought. A new short-lived transient was detected by Cooper and DeGraff [144] at $\lambda \leqslant 300$ nm in both acid and neutral solutions of ferrioxalate and assigned to either the $CO_2^- \cdot$ or $ox^- \cdot$ radical. This radical was assumed to be generated in photoredox process (47) or in photoreaction

$$[Fe(ox)_3]^{3-} \xrightarrow{h\nu} [Fe(ox)_2]^- + 2\ CO_2^- \cdot \tag{54}$$

The latter suggestion is interesting but as yet has not found further support in other studies. The $CO_2^- \cdot$ or $ox^- \cdot$ radical was reported to be responsible for the secondary reduction of Fe(III) according to the reaction

$$ox^- \cdot (\text{or } CO_2^- \cdot) + [Fe(ox)_3]^{3-} \rightarrow 2\ (\text{or } 1)\ CO_2 + [Fe(ox)_3]^{4-} \tag{55}$$

The slower absorbance changes occurring at $t > 200\ \mu s$ after flashing in the

310—500 nm region, supposed earlier to be due to the oxalate radical, were assigned by Cooper and DeGraff [144] to the decomposition of ferrous oxalate complex

$$[Fe(ox)_3]^{4-} \rightleftharpoons [Fe(ox)_2]^{2-} + ox^{2-} \tag{56}$$

and the anation of the photoaquation product (cf. p. 146).

Flash photolysis of trisoxalatoferrate(III) complex was also followed using electrochemical methods. Paszyc and Norrish [171] observed the formation of a reduced species recording a photovoltaic effect occurring in the system upon flashing. A more detailed study was carried out recently by Perone and co-workers [73,179] who adapted electroanalytical measurement techniques to study transient species generated upon flashing. The current—voltage profile obtained immediately after irradiation qualitatively described the presence of photolytic intermediates. The disappearance of these intermediates and product formation were followed using time-delay potentiostatic electrolysis. The electrochemical monitoring was compared with digitally simulated data, as well as with simultaneous photometric monitoring at 430 nm. Although the data did not allow an explicit assignment of all the intermediate species, the spectroscopic and electrochemical characteristics have revealed that only some of the species may be followed spectrophotometrically. Thus the proposed mechanism is still more complicated: it is thought to involve two competing initial photolytic processes ((57) and (58)) followed by a sequence of secondary reactions (eqns. (59)—(63))

$$2[Fe(ox)_3]^{3-} \xrightarrow{h\nu} 2[Fe(ox)_2]^{2-} + 2\,CO_2 + ox^{2-} \tag{57}$$

$$[Fe(ox)_3]^{3-} \xrightarrow{h\nu} A \tag{58}$$

$$A \xrightarrow{k_1} B + Y \tag{59}$$

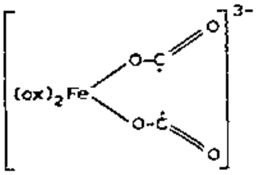
$$Y + [Fe(ox)_3]^{3-} \xrightarrow{fast} B \tag{60}$$

$$B + [Fe(ox)_3]^{3-} \xrightarrow{k_2} C \tag{61}$$

$$B \xrightarrow{k_3} C \tag{62}$$

$$C \xrightarrow{k_4} [Fe(ox)_2]^{2-} \tag{63}$$

The oxidizable (at 0.1 V vs. sce) iron(III) diradical species A of suggested structure



was reported to disappear by a rapid first-order reaction (59) ($k_1 = 2.8 \times 10^3$ s^{-1}). The rate of disappearance of the second intermediate was dependent on the iron(III) oxalate concentration, and was supposed to be due to reactions

(61) and (62) in which the non-oxidizable transient B was assumed to be a species containing one $CO_2^- \cdot$ radical acting as a bidentate ligand allowing delocalization of the odd electron. The reactive intermediate, Y, that disappeared in a very rapid step not being observed electrochemically or photometrically, was presumed to be a free $CO_2^- \cdot$ radical. The third step in the mechanism (eqns. (62) and (63)) produced the final product, dioxalatoferrate(II), through a non-oxidizable species C whose spectrum was very similar to that of $[Fe(ox)_2]^{2-}$ and was assigned to a carbonate or bicarbonate complex. Of the three consecutive steps, only the reactions of the second intermediate, B, could be followed photometrically, the initial and final reactions were monitored electrochemically. The reaction sequence proceeded to completion in less than 1 s [73,179].

It should be noted, however, that some results of this interesting electrochemical flash study are in conflict with other measurements, especially the second order decay of the intermediate absorbing at 430 nm which contradicts earlier data [178].

[Fe(ox)]⁺. The photochemistry of the monoxalatoiron(III) ion in aqueous perchloric acid with and without excess Fe^{3+} was studied by kinetic spectroscopy [145]. Deaerated solutions of $[Fe(ox)]^+$ flash irradiated in the charge-transfer spectral region displayed absorbance changes which were characterized by the time scale on which they occured. The initial decay, complete within 50 μs, was reported to be controlled by the rate of photolysis and to be due to the primary photoredox and thermal reactions of the resulting $ox^- \cdot$ free radical with $[Fe(ox)]^+$, Fe^{3+} or itself (eqn. (49))

$$[Fe(ox)]^+ \xrightarrow{h\nu} [Fe^{II}—OCOCO_2 \cdot]^+ \qquad (64)$$

$$[Fe^{II}—OCOCO_2 \cdot]^+ \rightarrow Fe^{2+} + ox^- \cdot \qquad (65)$$

$$ox^- \cdot + [Fe(ox)]^+ \rightarrow [Fe(ox)] + 2\ CO_2 \qquad (66)$$

$$ox^- \cdot + Fe^{3+} \rightarrow Fe^{2+} + 2\ CO_2 \qquad (67)$$

Subsequent absorbance changes were found to result from decomposition of the product of reaction (66)

$$[Fe(ox)] + [Fe(ox)]^+ \rightarrow Fe^{2+} + ox^{2-} + [Fe(ox)]^+ \qquad (68)$$

$$[Fe(ox)] + Fe^{3+} \rightarrow Fe^{2+} + ox^{2-} + Fe^{3+} \qquad (69)$$

Quantitative kinetic values were reported for the various reactions. The possibility of another decay of metal fragment $[Fe^{II}—OCOCO_2 \cdot]^+$ leading to ferrous ions and non radical products was also considered.

[Co(ox)₃]³⁻. The photolysis of cobalt(III) oxalate complexes has received relatively little attention. A survey of the literature on the photoreduction of $[Co(ox)_3]^{3-}$ revealed a tendency to assume a similar, if not identical decomposition mechanism as for $[Fe(ox)_3]^{3-}$. Although most of the data seems to confirm this assumption, there is no clear proof that the same reactive species are present. A preliminary experiment made by Parker and Hatchard [178]

revealed the existence of three stages upon flash: an immediate rise in absorption (at 313 nm), a rapid decrease and a slow decrease.

Recently De Jaegere and co-workers [180] and Hoffman and co-workers [181] considerably expanded upon this study. In the first work the experiments with complete immediate conversion of the initially present trisoxalatocobaltate(III) with one flash discharge revealed two transient species: one (Y) absorbing within 330—600 nm (λ_{max} about 390 and 480 nm) and another (X) absorbing at $\lambda < 420$ nm. Both were reported to decay in a monomolecular process, with rate constants $k_X = 20\ s^{-1}$ and $k_Y = 87\ s^{-1}$. Evidence was found for the photochemical generation of X at the expense of Y. The thermal decomposition of Y was said to yield $ox^- \cdot$ radicals which then reacted fast with $[Co(ox)_3]^{3-}$ and/or with themselves. The complete mechanism suggested was as follows

$$[Co(ox)_3]^{3-} \xrightarrow{h\nu} Y \tag{70}$$

$$Y \begin{array}{l} \xrightarrow{h\nu} X \\ \longrightarrow Co^{2+} + ox^- \cdot \end{array} \tag{71}$$

$$ox^- \cdot + [Co(ox)_3]^{3-} \rightarrow [Co(ox)_2]^{2-} + 2\ CO_2 + ox^{2-} \tag{72}$$

$$2\ ox^- \cdot \rightarrow ox^{2-} + 2\ CO_2 \tag{73}$$

From numerous possible structures considered for Y a bidentate oxalate radical coordinated to the Co(II) center $[(ox)_2Co^{II}(C_2O_4^- \cdot)]^{3-}$, was assumed to be the most probable. A diradical metal fragment, $[(ox)Co^{II}(C_2O_4^- \cdot)_2]^{2-}$, has been proposed for X, which would be generated in the photochemical reaction of Y, along with solvated electron production. The latter product has also been suggested for photolysis of trisoxalatocobaltate(III) by Shagisultanova et al. [182,183].

On the other hand, Hoffman and co-workers [181] found only one intermediate, I, absorbing weakly in the 360-nm region, which was seen as arising from charge transfer to metal followed by rapid spin relaxation of the resulting Co(II) center. The intermediate, thought to involve a bidentate oxalate radical ion coordinated to the high spin Co(II), $[(ox)_2Co^{II}(C_2O_4^- \cdot)]^{3-}$, was assumed to be in rapid equilibrium with a minor component, intermediate II, in which the oxalate radical is monodentate, with water occupying the sixth coordination site, $[(ox)_2Co^{II}(C_2O_4^- \cdot)(H_2O)]^{3-}$. The latter species was designated as the direct precursor of free $ox^- \cdot$ radicals. The decay of intermediate I was found to be first-order ($k = 58\ s^{-1}$) and accelerated by acid and oxygen, but retarded by added oxalate. The latter reaction was accompanied by a significant increase in absorption and changes in spectrum, which were assigned to the third intermediate, III, related to II by substitution of a monodentate ox^{2-} for H_2O in the sixth coordination site. The details of the mechanism proposed are presented in Fig. 2.

Comparing the recent flash photolysis studies [180,181] of trisoxalatocobaltate(III) it is interesting to note that though the essentially identical prim-

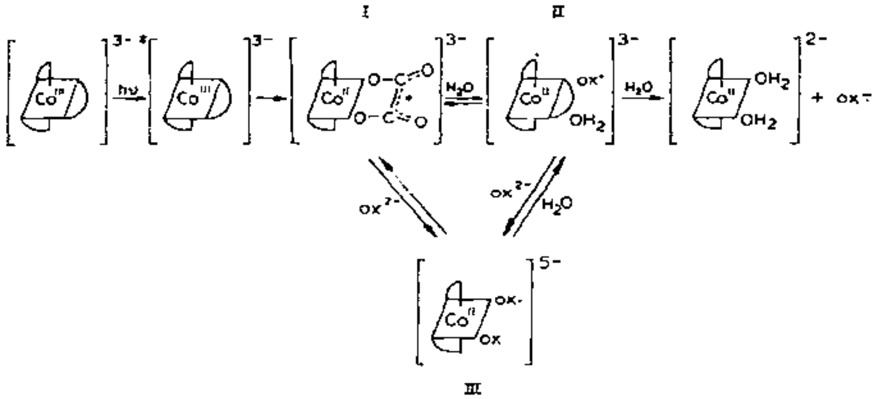


Fig. 2. Transient species observed in flash photolyzed solutions of trisoxalatocobaltate(III) according to Hoffman and co-workers [181].

ary act is proposed to follow CTTM excitation there are considerable discrepancies between the kinetic and spectral results, and consequently between the conclusions of both investigations.

$[Co(NH_3)_5(ox)]^+$, $[Co(NH_3)_4(ox)]^+$ and $[Co(en)_2(ox)]^+$. Flash photolysis of these complexes [64,184] has revealed two distinguishable transient species absorbing at $\lambda < 340$ nm. A short-lived species, which appeared within the lifetime of the flash and decayed through first order kinetics, was not identified. A long-lived transient was assigned as the C-bonded formato complex. The excited state initially populated by the absorption of radiation was supposed to undergo radiationless transition to at least two other electronic states: a charge-transfer excited state which produces the direct primary yield of CO^{2+} and the accompanying oxalate radical, and a ligand excited state which gives rise to the formation of a C-bonded complex (for detailed scheme see p. 171).

$[Cr(ox)_3]^{3-}$. No transient species were detected upon flashing this species; This has led to the conclusion that the excited state lifetime is shorter than the flash duration (15 μs) [178].

UO_2^{2+}—ox^{2-} system. Uranyl oxalate was reported to produce a long-lived intermediate on flashing. Its decay depended on the presence of excess oxalic acid, as well as oxygen [178]. Moreover, the photovoltaic effect has been investigated using flash photolysis [171]. Unfortunately these results did not provide a basis for a definite interpretation of the reaction mechanism.

Isothiocyanato complexes

In the case of isothiocyanato complexes of chromium(III), cobalt(III) and rhodium(III) which have been studied flash photolytically, UV radiation gives rise to a transient absorption with λ_{max} about 480 nm. This was found to be due to $(NCS)_2^- \cdot$ radicals [155,185—187]. The thiocyanate radical, NCS ·, possibly generated in the primary photochemical act, could not be observed directly. Concerning the metal fragments produced along with thiocyanate radicals, contrasting conclusions have been drawn for chromium(III) and the other complexes.

For the cobalt(III) complexes: $[Co(NH_3)_5NCS]^{2+}$, $[Co(CN)_5NCS]^{3-}$ and $[Co(CN)_5SCN]^{3-}$ and for rhodium(III), $[Rh(NH_3)_5NCS]^{2+}$, cobalt(II) or rhodium(II) species were found among the products. Moreover, no transient absorbance changes were detected when free NCS^- was carefully excluded from the sample solution. A transient absorbance at about 480 nm [132,134,152] developed only in the presence of free NCS^-. This behaviour would be expected for the reactions

$$[Co(NH_3)_5NCS]^{2+} \xrightarrow[H^+]{h\nu} Co^{2+} + 5\,NH_4^+ + NCS\cdot \qquad (74)$$

$$NCS\cdot + NCS^- \rightleftharpoons (NCS)_2^-\cdot \qquad (75)$$

$$2\,(NCS)_2^-\cdot \rightarrow (NCS)_2 + 2\,NCS^- \qquad (76)$$

$$(NCS)_2 + H_2O \rightarrow \text{hydrolysis products} \qquad (77)$$

A similar reaction pathway was also proposed for $[Rh(NH_3)_5NCS]^{2+}$ [152], $[Co(CN)_5NCS]^{3-}$ [132] and $[Co(CN)_5SCN]^{3-}$ [132].

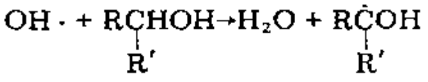
To account for enhanced yields of Co^{2+} observed in glycerol media on irradiation of $[Co(NH_3)_5NCS]^{2+}$ in the deep UV, the intermolecular mechanism involving $OH\cdot$ radicals has also been proposed [134]

$$[Co(NH_3)_5NCS]^{2+} \xrightarrow[H_2O]{h\nu} \{Co(NH_3)_5NCS^+, H_2O^+\} \qquad (78)$$

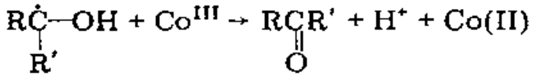
$$\{Co(NH_3)_5NCS^+, H_2O^+\} \rightarrow \begin{cases} [Co(NH_3)_5NCS]^{2+} \\ Co^{2+} + 5\,NH_4^+ + NCS^- + H_2O^+\cdot \end{cases} \qquad (79)$$

$$H_2O^+\cdot \rightleftharpoons OH\cdot + H^+ \qquad (80)$$

$$OH\cdot + NCS^- + H^+ \rightarrow H_2O + NCS\cdot \qquad (81)$$

 (82)

$$OH\cdot + R\underset{R'}{\underset{|}{C}}HOH \rightarrow H_2O + R\underset{R'}{\underset{|}{\dot{C}}}OH \qquad (82)$$

 (83)

$$R\underset{R'}{\underset{|}{\dot{C}}}{-}OH + Co^{III} \rightarrow R\underset{O}{\underset{\|}{C}}R' + H^+ + Co(II) \qquad (83)$$

(where $R\underset{R'}{\underset{|}{C}}HOH$ = glycerol)

On the other hand, in the case of the chromium(III) complexes, $[Cr(NCS)_6]^{3-}$ and $[Cr(NH_3)_2(NCS)_4]^-$, Cr(II) could not be detected among the products of deaerated solutions [86]. Instead, a short-lived species absorbing at 735 nm was observed and was attributed to solvated electron production (cf. pp. 168, 169). Moreover, the $(NCS)_2^-\cdot$ radicals were identified in solutions when no excess of NCS^- ions were added, suggesting the concerted departure of two thiocyanate ligands, according to the reaction

$$[\mathrm{Cr^{III}(NCS)_6}]^{3-} \xrightarrow{h\nu} [\mathrm{Cr^{III}(NCS)_4}]^{-} + (\mathrm{NCS})_2^{-}\cdot + e^{-}_{\mathrm{solv}} \qquad (84)$$

However, the last suggestion is not adequately confirmed, because $\mathrm{NCS^-}$ ions were found to be produced efficiently in the system due to photosolvation (cf. p. 146).

Azide complexes

Photoreduction of the transition metal central ion was reported to lead, in the case of azide complexes, to $\mathrm{N_3}\cdot$ radicals, which could not be observed directly in flash experiments. An indirect detection method consists of recording the fate of the strongly absorbing $\mathrm{I_2^-}\cdot$ radical probe generated in the reactions [16,132,136,188]

$$\mathrm{N_3}\cdot + \mathrm{I^-} \rightarrow \mathrm{N_3^-} + \mathrm{I}\cdot \qquad (85)$$

$$\mathrm{I}\cdot + \mathrm{I^-} \rightleftharpoons \mathrm{I_2^-}\cdot \qquad (86)$$

The investigation, however, may be complicated by formation of iodo-complexes.

A further, serious difficulty in the study of the photoredox path comes from a very efficient electronic relaxation from higher CT to lower LF or intra ligand (IL) excited states, leading to predominating photoaquation or ligand reaction paths. Such a tendency increases in the series: Co(III), Ru(III) and Ir(III). Thus no $\mathrm{I_2^-}\cdot$ transients were observed in the presence of $\mathrm{I^-}$ for $[\mathrm{Rh(NH_3)_5N_3}]^{2+}$ [43] or $[\mathrm{Ir(NH_3)_5N_3}]^{2+}$ [189] solutions. For $[\mathrm{Rh(NH_3)_5N_3}]^{2+}$, however, the production of $\mathrm{N_3}\cdot$ radical was postulated as responsible for the generation of $[\mathrm{Rh(NH_3)_5(H_2O)}]^{3+}$ (cf. p. 145) [138].

On the other hand, for cobalt(III) azide complexes, $[\mathrm{Co(NH_3)_5N_3}]^{2+}$ and $[\mathrm{Co(CN)_5N_3}]^{3-}$, transient absorption due to $\mathrm{I_2^-}\cdot$ radical has been detected [43,132,163]. Moreover, cobalt(II) ions were found among the products.

For azidopentaamminecobalt(III) complex the photooxidation path of azide ligand

$$[\mathrm{Co(NH_3)_5N_3}]^{2+} \xrightarrow[\mathrm{H^+}]{h\nu} \mathrm{N_3}\cdot + \mathrm{Co^{2+}} + 5\,\mathrm{NH_4^+} \qquad (87)$$

was thought to be accompanied by the intermolecular photooxidation of the water upon irradiation in the deep UV, according to equations similar to (78)—(83) [134].

In the case of azidopentacyanocobaltate(III) a photoredox reaction yielding azide radical and Co(II) species

$$[\mathrm{Co(CN)_5N_3}]^{3-} \xrightarrow{h\nu} \mathrm{N_3}\cdot + [\mathrm{Co(CN)_5}]^{3-} \qquad (88)$$

was found to follow from irradiation of the CTTM band ($\lambda_{\max}$ 281 nm), whereas at irradiation of the lower energy LF band ($\lambda_{\max}$ 360 nm) only azide aquation was observed (cf. p. 144). In the presence of $\mathrm{I^-}$, the $[\mathrm{Co(CN)_5I}]^{3-}$ complex was additionally reported [43,132].

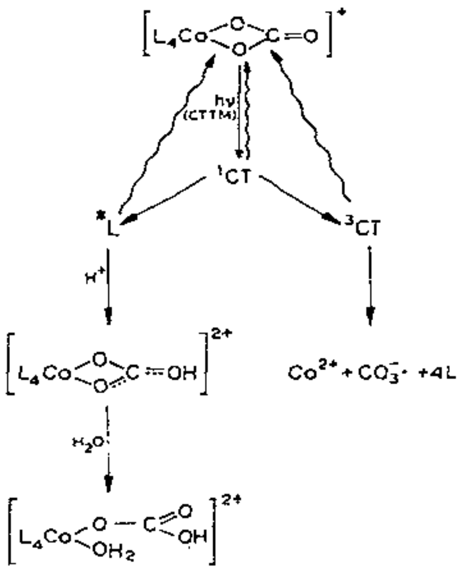


Fig. 3. Photochemistry of $[CoL_4CO_3]^+$ complexes including redox and ligand photoreaction paths; L = NH_3 or $\frac{1}{2}$ en (taken from refs. 139 and 191).

Carbonate complexes of cobalt(III)

Flash photolysis of mixed carbonatoamminecobalt(III) complexes in aqueous solution has been reported to generate the carbonate radical, $CO_3^- \cdot$, which is characterized by its absorption spectrum with λ_{max} = 600 nm and second-order kinetics [139,140,185,190,191]. Flash photolysis of $[Co(NH_3)_4CO_3]^+$ was proposed as a convenient photochemical source of $CO_3^- \cdot$ radicals. The radical was also found to be generated from $[Co(NH_3)_5CO_3]^+$ and, to a lesser extent, from $[Co(en)_2CO_3]^+$ [139,191]. Scavenging studies have led to the conclusion that at pH 7 the radical must exist in its acidic form, $CO_3H \cdot$, with a $pK_a = 9.6$ [140].

Photochemical excitation of bidentate carbonate complexes in the intense CTTM band was said to produce the charge-transfer singlet state (^{1}CT) which generated through intersystem crossing, the charge-transfer triplet state (^{3}CT) and competitively a ligand excited state (L^*) [139]. The ^{3}CT state was thought to be the precursor of the oxidation—reduction products; protonation of the carbonate ligand in the L^* state was considered to cause ring opening and aquation (cf. pp. 145 and 169). The detailed scheme proposed is shown in Fig. 3. The lifetime of the intermediate Co(II)—$CO_3^- \cdot$ species was found to be shorter than the instrumental time resolution so that rapid aquation of the species would release the $CO_3^- \cdot$ radical into bulk solution before detection.

Carboxylatopentaamminecobalt(III) complexes

Many acidopentaamminecobalt(III) complexes upon irradiation in their intense CTTM band generate Co^{2+} and a free radical derived from a one-electron oxidation of the acido ligand

$$[Co^{III}(NH_3)_5X]^{2+} \xrightarrow[CTTM]{h\nu} Co^{2+} + 5\ NH_3 + X\cdot \qquad (89)$$

Hoffman and co-workers [192] also found that in the case of carboxylatopentaamminecobalt(III) complexes the photoreduction may be simply described as

$$[Co^{III}(NH_3)_5O_2CR]^{2+} \xrightarrow[CTTM]{h\nu} Co^{2+} + 5\ NH_3 + CO_2 + R\cdot \qquad (90)$$

although it has not been established whether the precursor radical, $RCO_2\cdot$, is actually released into solution.

[Co(NH$_3$)$_5$O$_2$CH]$^{2+}$. In this case a very similar reaction mode, as shown in Fig. 3 for carbonatoamminecobalt(III), has been proposed. The excited ^{1}CT state generated directly by irradiation in the CTTM band passes to a dissociative ^{3}CT state yielding Co^{2+}, H atoms and CO_2 and to an excited state that is largely ligand localized, yielding the C-bonded isomer (see also p. 170) [184, 193]. The reaction pathway was based on the results of the 254-nm continuous photolysis and flash-scavenging experiments. On flashing, two transient species have been observed: one short-lived, which was not identified, and the other, long-lived, which was assumed to be a C-bonded formato complex.

[Co(NH$_3$)$_5$O$_2$CCH$_3$]$^{2+}$. No transient species were detected upon flashing in deoxygenated solutions of pentaammineacetatocobalt(III), whereas in the presence of oxygen a transient decay with second order kinetics was observed [135]. There was apparently no reaction of O_2 with the excited state or radical precursor since $\Phi_{Co^{2+}}$ and Φ_{CO_2} are unaffected by O_2. The results were interpreted as the primary process

$$[Co(NH_3)_5O_2CCH_3]^{2+} \xrightarrow[H^+]{h\nu} Co^{2+} + 5\ NH_4^+ + CH_3COO\cdot \qquad (91)$$

followed by immediate decarboxylation

$$CH_3COO\cdot \rightarrow CH_3\cdot + CO_2 \qquad (92)$$

In the presence of oxygen the $CH_3\cdot$ radical was reported to oxidize to the $CH_3O_2\cdot$ radical

$$CH_3\cdot + O_2 \rightarrow CH_3O_2\cdot \qquad (93)$$

which was assumed to be responsible for the transient spectrum. The photochemical generation of $CH_3\cdot$ radical has also been confirmed in e.s.r. studies [192] and has been employed in synthesis of macrocyclic complexes containing Co(III)—alkyl bonds [194]. An electron transfer from the acetate ligand to metal center was found only as a result of irradiation of the CTTM band, whereas LF band irradiation was reported to yield $[Co(NH_3)_4(H_2O)O_2CCH_3]^{2+}$ (cf. p. 144). No evidence of primary acetate aquation or the oxidation of ammonia ligand has been found [135].

[Co(NH$_3$)$_5$O$_2$CR]$^{2+}$. Recently a number of carboxylatopentaamminecobalt-

(III) complexes of the type $[Co(NH_3)_5O_2CR]^{2+}$ have been studied using flash photolysis and radical scavenging techniques [192]. The results were consistent with the general scheme proposed (eqn. (90)) although not in all cases could the transient spectrum be unequivocally assigned to the proper radical. The transient absorption (λ_{max} at 360 nm, shifted to 320 nm in acidic medium) for the malonato complex recorded after 50 μs was consistent with the spectral properties of $CH_2CO_2^- \cdot$ or $CH_2CO_2H \cdot$ radicals [195]. The flash photolysis of the phenylacetato complex gave rise to the characteristic absorption spectrum of the benzyl ($PhCH_2\cdot$) radical with λ_{max} at 303 and 315 nm which decayed through second-order kinetics [196—199]. On the other hand, the flash photolysis of a number of other complexes (R = $-(CH_2)_2CO_2H$, $-(CH_2)_3CO_2H$, $-CH{=}CHCO_2H$ (*cis* and *trans*), $-C{\equiv}CCO_2H$, and $-C_6H_{10}CO_2H$) resulted only in weak tail absorption at $\lambda < 320$ nm, consistent with the unstructured spectra known for β- and γ-carboxy radicals [192,195].

Ammine and amine complexes

Only a few flash photolysis studies dealing with photoreduction of ammine or amine complexes have been performed and no general conclusions can be drawn from them, especially since considerable number of the complexes studied appeared to be photoredox inactive.

$[Ru(NH_3)_6]^{3+}$. No evidence was obtained for generation of a radical from the photooxidation of the ammonia ligand coordinated to ruthenium(III). No transient absorption appeared between 250—550 nm upon flashing [44]. Some weakly absorbing transients observed upon flashing in the deep UV, in the presence of halogen ions, were attributed to ion-pair (or outer sphere) charge transfer absorptions [44].

EDTA complexes: $[M(EDTA)]^-$ (M = Co(III), Rh(III)), $[M(HEDTA)(H_2O)]$ (M = Cr(III), Fe(III)) and $[M(H_2EDTA)(H_2O)]$ (M = Ni(II), Cu(II)). The photoredox behaviour of these metal—ethylenediaminetetraacetate complexes, studied by Natarajan and Endicott [141—143,200], has been revealed as divergent. The chromium(III), nickel(II) and copper(II) complexes were found to be essentially inert ($\Phi_{redox} < 10^{-4}$) to excitation wavelengths $\geqslant$214 nm. The rhodium(III) complex appeared to be moderately photosensitive ($\Phi \sim 0.1$ at 254 nm) but the results were difficult to interpret. The cobalt(III) and iron(III) complexes were reported to be reasonably photosensitive but exhibited conflicting behaviour.

For $[Co(EDTA)]^-$ no transient could be detected unless Br^- ions were present in the flashed solution; then $Br_2^- \cdot$ radical was observed. The fate of the primary generated intermediate was also followed through transient oxidation of $[Ru(bipy)_3]^{2+}$. A similar reaction pathway, as in the case of $[Co(HEDTA)X]^-$ complexes, was then proposed involving *N*-methyleneethylenediaminetriacetate radical coordinated to Co(II) as an intermediate species (cf. pp. 150, 151 and 173).

In the case of $[Fe(HEDTA)(H_2O)]$ the UV flash excitation gave rise to highly absorbing (at about 420 nm) metastable species (lifetime (20—200 ms) which decayed by reacting with the substrate. On the other hand, flash photolysis of the Fe(III) complex did not result in oxidation of Br^- or $[Ru(bipy)_3]^{2+}$. The results obtained so far do not give any elucidation of the reaction mechanism.

Other complexes

$[Co(HEDTA)NO_2]^-$. Natarajan and Endicott [141,142,200] found in this case the same behaviour as for the other complexes of the type $[Co(HEDTA)X]^-$ (cf. pp. 150,151) i.e. *N*-methyleneethylenediaminetriacetate radical coordinated to the reduced metal was generated upon flash photolysis.

Ferrocene. In contrast to steady state studies (cf. e.g. [4]) flash photolysis of gaseous ferrocene [201] was reported to yield cyclopentadienyl radicals and atomic iron.

$[Mo(CN)_8]^{3-}$. Octacyanomolybdate(V) ion is the only cyanide complex for which the photoreduction of the central atom and oxidation of cyanide ligand were substantiated by flash photolysis [124,125,202,203]. The transient absorption over the range 400—650 nm was monitored and was identified using scavenging techniques and e.p.r. measurements in the glassy state. The three short-lived transient species were assigned as: CN · radical (absorbing strongly at $\lambda < 450$ nm), the $[Mo(CN)_7(H_2O)]^{3-}$ complex ($\lambda_{max} = 532$ nm), and antiprismatic isomer of $[Mo(CN)_8]^{4-}$ ($\lambda_{max} \approx 500$ nm). Moreover, the relatively long-lived transient ($\lambda_{max} \approx 435$ nm) assigned to dicyanogen radical, $(CN)_2^- \cdot$ [204], was reported to be generated in thermal processes [202].

The results are consistent with an intramolecular primary redox process following CTTM excitation [3,124,205,206], but are incompatible with an alternatively proposed mechanism suggesting primary aquation or heterolytic bond fission [4]. The decay of the cyanogen radical in deaerated solutions was

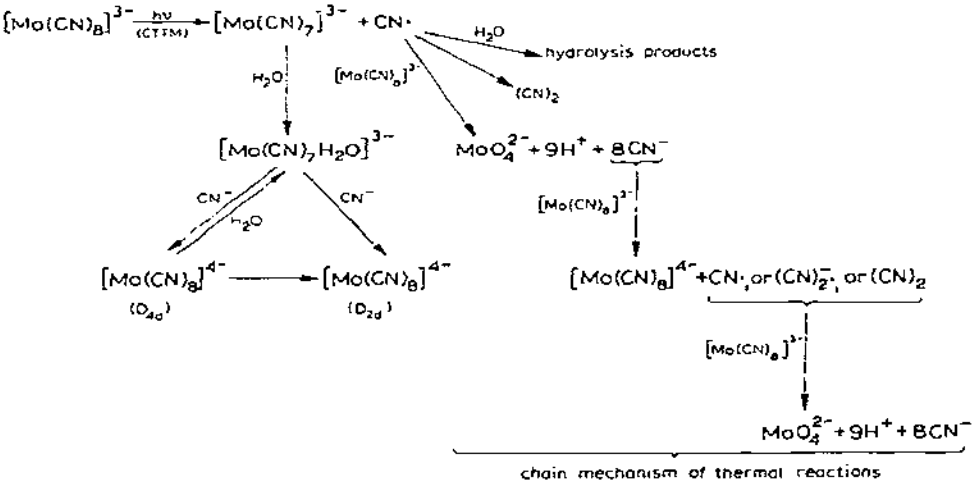


Fig. 4. Photoreduction and secondary thermal reactions in flash photolyzed solutions of octacyanomolybdate(V) (data from refs. 124, 125, 202 and 203).

reported to proceed through recombination, hydrolysis or reaction with the substrate [87,124,203,207,208]. The latter process was found to be responsible for initiating the chain mechanism of the secondary thermal reactions. The results of $[Mo(CN)_8]^{3-}$ photolysis are summarized in Fig. 4.

Complexes of cerium(IV). Solutions of cerium(IV) nitrate, sulfate, perchlorate and acetate were studied extensively by the flash technique and consequently photoreduction of cerium(IV) to cerium(III) has been generally accepted. There are, however, discrepancies as to the radical species formed in the primary act.

A characteristic well resolved spectrum with λ_{max} at 335, 595, 640 and 675 nm of the $NO_3\cdot$ radical was obtained on flashing ceric ammonium nitrate dissolved in concentrated HNO_3. This has prompted the assumption of an intramolecular oxidation—reduction reaction between one of the nitrate ligands and the central Ce(IV) atom [20,209]

$$Ce^{IV}\ NO_3^- \xrightarrow{h\nu} Ce(III) + NO_3\cdot \tag{94}$$

However, later flash and scavenging studies [210,211] showed that the main primary photolytic process in both sulfate and nitrate solutions was a charge transfer from the hydration sphere to the Ce(IV) ion

$$Ce(IV)\cdot H_2O \xrightarrow{h\nu} Ce(III) + OH\cdot + H^+ \tag{95}$$

followed by reactions

$$OH\cdot + HNO_3 \rightarrow NO_3\cdot + H_2O \tag{96}$$

$$OH\cdot + HSO_4^- \rightarrow HSO_4\cdot + OH^- \tag{97}$$

$HSO_4\cdot$ radical was characterized by absorption between 350—550 nm (with a maximum at 455 nm) and second-order decay.

Ceric ammonium nitrate photolyzed in glacial acetic acid with wavelengths between 280—405 nm, under both flash and steady irradiation conditions, yielded Ce(III) and a variety of organic species ascribable to redox decomposition products of acetic acid [212]. An intramolecular oxidation—reduction between the acetate ligand strongly coupled to the Ce(IV) atom was suggested. This would then be followed by reaction of the acetate radical with the medium. The primary process did not involve the nitrate ligands.

(iv) Photooxidation of transition-metal central ion

(a) Intramolecular mechanism

Such a reaction pathway was reported to proceed in some complexes of iron(II) and ruthenium(II) with organic ligands or NO^+ for which the CTTL band was found to be of low energy.

Fe^{2+}—thionine and Fe^{2+}—methylene blue. Oxidation of ferrous ions and the reduction of a dye is observed frequently when such solutions are irradiated. These systems have also been studied hy flash photolysis [213,214]. In

the case of Fe^{2+}—thionine two intermediate species were revealed on the ms and μs time scales and were assigned to the metastable excited state of thionine (assumed to be the triplet state) and to the semithionine radical, respectively. Quenching of the excited state of the dyestuff was thought to be mainly responsible for the Fe^{2+} oxidation. On the other hand, Havemann et al. [215,216] found that Fe^{2+} and thionine form a complex which is actually the species responsible for the photochemical reaction, whereas Ainsworth [217] suggested that both free thionine and the Fe^{2+}—thionine complex are photoactive.

Similar behaviour was reported for the Fe^{2+}—methylene blue system [213, 217].

[Fe(CN)$_5$NO]$^{2-}$. Product analysis in steady state irradiations ($\lambda \leq$ 300 nm) of pentacyanonitrosylferrate(II) has revealed production of nitric oxide and Fe(III) complexes [3,4]. The primary photooxidation of the central atom and the reduction of the NO$^+$ ligand

$$[\mathrm{Fe(CN)_5NO}]^{2-} \xrightarrow{h\nu} [\mathrm{Fe^{III}(CN)_5}]^{2-} + \mathrm{NO} \qquad (98)$$

was proposed to result from homolytic cleavage of the metal—ligand σ bond upon CTTL excitation (eqn. 98). This interpretation has recently received a good deal of confirmatory evidence from steady state studies [123,218,219] as well from our preliminary flash experiments [114]. In the latter case, a strong absorption at wavelengths shorter than 450 nm (with λ_{max} about 340 and 400 nm) was detected within the flash lifetime (20 μs). Since the spectral properties agreed with those of [Fe(CN)$_5$(H$_2$O)]$^{2-}$ [220] the addition of a water molecule to the pentacyanoferrate(III) species is expected to occur within this time, or an alternative associative mechanism may be involved. The [Fe(CN)$_5$(H$_2$O)]$^{2-}$ species was also found to be formed within the ms time range in thermal processes and was accompanied by the decay of a minor product, [Fe(CN)$_5$(H$_2$O)]$^{3-}$ (cf. p. 142). More detailed studies are in progress [114].

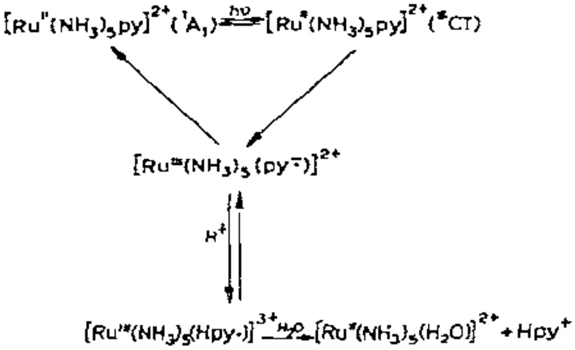


Fig. 5. Photoxidation and secondary thermal reactions of [Ru(NH$_3$)$_5$py]$^{2+}$ according to Natarajan and Endicott [221].

$[Ru(NH_3)_5L]^{2+}$ (L = py, NCC_6H_5) and $[M(LL)_3]^{2+}$ (M = Ru(II), Fe(II), LL = bipy, phen). Flash photolysis of numerous ruthenium(II) and iron(II) complexes with organic ligands has revealed a transient bleaching of the CTTL absorption of the substrate [221]. The transient spectra could not be detected due to strong substrate absorptions and low transient yields (approximately 10^{-3} for $[M(LL)_3]^{2+}$ complexes). The extent of bleaching was found comparable for all the systems but lifetimes for Ru(II) intermediate species exceeded by about four times those for Fe(II). To accomodate the similar behaviour of these various complexes a redox mechanism was proposed which involved a reduced ligand radical anion coordinated to an oxidized central atom [221]. Such a mechanism, exemplified in Fig. 5, received further support from continuous photolysis [222] and pulse radiolysis [223] studies. However, for $[Ru(bipy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ this photodecomposition is very small. Consequently these two complexes can often serve as efficient triplet energy sensitizers [221].

(b) Hydrated electron production

The detection of hydrated electron generated in flash photolysis of transition metal complexes is a relatively simple task due to its advantageous spectral properties: an appreciable absorption ($\epsilon_{max} = 1.85 \cdot 10^4$ dm^3 mol^{-1} cm^{-1}) occurs at long wavelengths (λ_{max} = 715 nm) where complex absorption does not frequently occur. In the absence of effective scavengers the spectrum of e^-_{aq} may be detected with μs resolution equipment. Moreover, the numerous reactions of e^-_{aq} are well established, especially in extensive pulse radiolysis investigations, and the use of electron scavengers is commonly adapted for quantitative studies. The properties and reactions of the hydrated electron are widely described in a number of works and reviews (cf. e.g. [224—227]).

Cyanide complexes. Of the complexes which photochemically generate e^-_{aq} the cyanides are the most common. The best known and effective e^-_{aq} producer is hexacyanoferrate(II).

$[Fe(CN)_6]^{4-}$. The generation of hydrated electrons in flash photolysis of hexacyanoferrate(II) was detected by Matheson et al. in 1963 [228]. The diffuse band, centered at about 680 nm, was identified by the use of nitrous oxide, oxygen, nitrate or hydrogen ions as scavengers. This discovery was further developed in a number of flash photolytic and scavenging studies. The spectrum of e^-_{aq} obtained from photooxidation of $[Fe(CN)_6]^{4-}$ was reinvestigated and found to resemble precisely that from pulse radiolysis investigations [110,111,229]. Hexacyanoferrate(III) was found to be produced, along with a hydrated electron, according to the following equation [40,230—247]

$$[Fe(CN)_6]^{4-} \xrightarrow[H_2O]{h\nu} [Fe(CN)_6]^{3-} + e^-_{aq} \qquad (99)$$

The possible process leading to H atom production was excluded [232—234] unless the protonated species, $H[Fe(CN)_6]^{3-}$ was involved. In the latter case the photoredox generation of H atoms was also considered [233,238]

$$H[Fe(CN)_6]^{3-} \xrightarrow{h\nu} [Fe(CN)_6]^{3-} + H \qquad (100)$$

In the presence of N_2O scavenger the molar ratio of $[Fe(CN)_6]^{3-}$ to nitrogen was found to be 1.6 : 1, instead of 2 : 1 [237]. The latter ratio would be expected from eqn. (99) followed by eqn. (101)

$$e^-_{aq} + N_2O + H_2O \rightarrow N_2 + OH\cdot + OH^- \qquad (101)$$

and the oxidation of a second molecule of the complex with the OH · radical. The overall reaction may be described by eqn. (102)

$$2[ML_n]^x + N_2O + H_2O \xrightarrow{h\nu} 2[ML_n]^{x+1} + 2\,OH^- + N_2 \qquad (102)$$

As minor products, aquopentacyanocomplexes of Fe(II) and Fe(III) were also reported and said to be generated in primary or secondary processes [40,110, 113,239–241].

The fate of an electron separated from its parent ion has been the subject of much discussion: secondary geminate recombination has been considered [112,225,230,232,233,242] and numerous scavenging processes were studied in detail [230,234,243–245].

Quantum yields of hydrated electron production were measured repeatedly and found to be strongly dependent on the wavelength of radiation as follows: 0.89 (for 214 and 228 nm), 0.65 (254 nm), 0.52 (265 nm), 0.13 (289 nm) and 0.0 ($\lambda \geqslant 337$ nm) [110,112,230,232,233,237,245–247]. The considerably high yield from $[Fe(CN)_6]^{4-}$ was employed to generate photochemically e^-_{aq} in this system for other studies [248–252].

The excited state responsible for the production of e^-_{aq} from hexacyanoferrate(II) has been widely discussed [110,112,113,246,247]. Flash photolysis measurements as a function of the flash intensity were used to analyze the process of hydrated electron formation and in the case of $[Fe(CN)_6]^{4-}$ it was found to be monophotonic [253].

[Ru(CN)₆]⁴⁻. The transient species obtained on flashing with wavelengths ⩽300 nm was identified as a hydrated electron produced by CT excitation [237]. Although the presence of $[Ru(CN)_6]^{3-}$ was not ascertained, it was inferred that the system fitted the general reaction scheme

$$[ML_n]^x \xrightarrow{h\nu} [ML_n]^{x+1} + e^-_{aq} \qquad (103)$$

The quantum yield of e^-_{aq} generation was found to be 0.36 [237].

[Mo(CN)₈]⁴⁻. In this case the same reaction path (eqn. (103)) was reported for $\lambda < 300$ nm (84,237], but the substrate was found to be a relatively good electron scavenger ($k \sim 5 \cdot 10^8\ M^{-1}\ s^{-1}$) and the quantum yield consequently low (0.28) [237]. The formation of $[Mo(CN)_8]^{3-}$ was, however, not confirmed, presumably due to its immediate photoreduction with a quantum yield reported to exceed by 5–15 times that of the photoelectron production from $[Mo(CN)_8]^{4-}$ [4,124,254,255] (cf. p. 164).

[W(CN)₈]⁴⁻. The same problems were found for octacyanotungstate(IV) [84,237] where secondary photolysis of $[W(CN)_8]^{3-}$ [4,256,257] presumably

makes its detection difficult (eqn. 103). The quantum yield of hydrated electron production in this case was found to be comparable with that for $[Ru(CN)_6]^{4-}$ (0.34) [237].

Other acido complexes. $[Cr(NCS)_6]^{3-}$. A short lived transient absorption (a few μs) observed in a deaerated ethanol solution of hexaisothiocyanatochromium(III) at 735 nm was assigned to e^-_{aq} production [86]. In this case, however, the oxidized species was reported not to be the central metal ion, but an isothiocyanate ligand, forming $(NCS)_2^- \cdot$ radical (cf. eqn. (84) on p. 160).

$[Co(ox)_3]^{3-}$. The hydrated electron was inferred to be produced in the secondary photochemical reaction of trisoxalatocobalt(III) [180] (cf. eqns. (70—73) and discussion on p. 157). This, however, needs to be better substantiated.

$[IrCl_6]^{3-}$. For hexachloroiridium(III) the quantum yield of e^-_{aq} production according to eqn. (103) was found to be only 0.03 [237] presumably due to the very efficient electron scavenging ability ($k = 2 \cdot 10^{10}$ M^{-1} s^{-1}) of $[IrCl_6]^{2-}$ [227]. The spectral changes observed were consistent with the presence of $[IrCl_6]^{2-}$ and $[IrCl_5(H_2O)]^-$ (or $[IrCl_5(OH)]^{2-}$). The aquo (or hydroxo) species, produced in the subsequent photolysis of $[IrCl_6]^{2-}$ was found to be more abundant. The ratio of the total Ir(IV) to N_2 produced was close to 2 : 1 which is consistent with eqn. (102) [237].

Amino and aquocomplexes. There has been some discussion concerning the possibility of photoelectron production from a positive ion which seemed rather implausible due to electrostatic effects [4,159]. In fact, the flash photolysis of $[Ru(bipy)_3]^{2+}$, which satisfies the general prerequisites (cf. p. 137), produces no transient characteristic of e^-_{aq}, nor was reaction with N_2O observed [258].

On the other hand, Basco et al. [259] recently found that hydrated electrons were produced with a quantum yield of almost unity when low valence state hydrated ions Co^+, Ni^+, Zn^+ and Cd^+ were photolysed in their CTTS band centered at about 300 nm. The ions were assumed to be present as simple aquocomplexes, but they might well be treated as solvated ion-electron pairs. The experiments used a double flash photolysis method [260] whereby the first flash photolyzed SO_4^{2-} ions with light of $\lambda < 220$ nm to produce hydrated electrons which then reacted with Co^{2+}, Ni^{2+}, Zn^{2+} or Cd^{2+} ions present in concentrations of 10^{-5} to 10^{-6} M. The short-lived monovalent ions so formed were photolysed 10—300 μs later by a second flash of restricted wavelength.

The aquocomplex of Cu^+ studied under these conditions did not show any detectable absorption changes at 633 nm [261], whereas Ag^0 and Tl^0 revealed e^-_{aq} production [261]. Some evidence has also been reported in favour of a photoelectron production from the aquocomplex of iron(II) [4] but there is lack of direct confirmation of this suggestion in flash experiments.

(v) Photoreactions of ligands

(a) Cleavage of metal—ligand bond

Intra-ligand excitation of some cobalt(III) complexes was reported to result in M—L bond cleavage followed by aquation or linkage isomerization.

The first case was found with the carbonato complexes $[Co(NH_3)_4CO_3]^+$ and $[Co(en)_2CO_3]^+$ [139] which have already been discussed (cf. pp. 145 and 161).

The second case was detected in formatopentaamminecobalt(III) [184, 193]. Furthermore the photochemical behaviour of $[Co(HEDTA)NO_2]^-$ [141—143] might also be interpreted in this reactivity pattern.

$[Co(NH_3)_5O_2CH]^{2+}$. A long-lived transient absorption in the range 260—300 nm with λ_{max} at 268 nm decaying by first order kinetics (k within 4—10 $\cdot 10^{-4}$ s^{-1}) was assigned to the C-bonded formato isomer of the substrate $[Co(NH_3)_5CO_2H]^{2+}$ [184,193]. It was thought to be generated from a ligand localised excited state populated through higher energy CT singlet by radiationless transitions. A more detailed scheme suggested by Hoffman and co-workers [184,193] is presented in Fig. 6.

$[Co(HEDTA)NO_2]^-$. The spectral changes observed on irradiating this complex with visible light has prompted Natarajan and Endicott [141—143] to assume that nitro→nitrito photoisomerization is the predominant reaction resulting from LF excitation of $[Co(HEDTA)NO_2]^-$. Only minor photoaquation was observed (cf. p. 145). The relatively small redox yields (cf. p. 164) resulting from these excitations seemed to indicate that linkage isomerization is in-

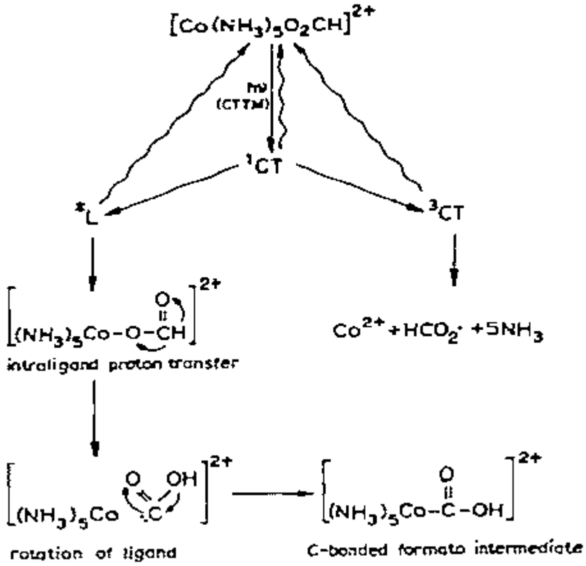


Fig. 6. Photoreduction and photoreaction of ligand in flash photolyzed solutions of $[Co(NH_3)_5O_2CH]^{2+}$ (taken from ref. 193).

dependent of the formation of NO_2. On the other hand, the source of the isomerization was not completely elucidated due to the existence of low energy ligand centered electronic excited states.

(b) Scission of intraligand bond

Heterolytic scission of the C—C or N—N bond was found in some cobalt(III) oxalate complexes as well as in some azide complexes of rhodium(III) and iridium(III), respectively.

$[Co(NH_3)_5(ox)]^+$, $[Co(NH_3)_4(ox)]^+$ and $[Co(en)_2(ox)]^+$. A long-lived (seconds) transient detected for oxalatopentaamminecobalt(III) was found identical with that for formatopentaamminecobalt(III) and was similarly assigned to a C-bonded formatopentaamminecobalt(III) complex [64,184]. A similar transient observed in bidentate oxalato complexes absorbing between 200—500 nm (λ_{max} at 421, 320, 262 and <200 nm) was assumed to have the formula $[Co(NH_3)_4(H_2O)CO_2]^+$ or $[Co(en)_2(H_2O)CO_2]^+$ with C-bonded formato ligand. These complexes were thought to be formed from ligand-centered excited state generated through radiationless transition from the precursor ^1CT according to Fig. 7 (cf. also p. 158).

$[M(NH_3)_5N_3]^{2+}$ (M = Rh(III), Ir(III)). Basolo and co-workers [138,189, 262] discovered that UV excitation of azidopentaamminerhodium(III) as well as azidopentaammineiridium(III), leads to N^-—N_2 cleavage of the coordinated azide, generating a metal coordinated nitrene intermediate.

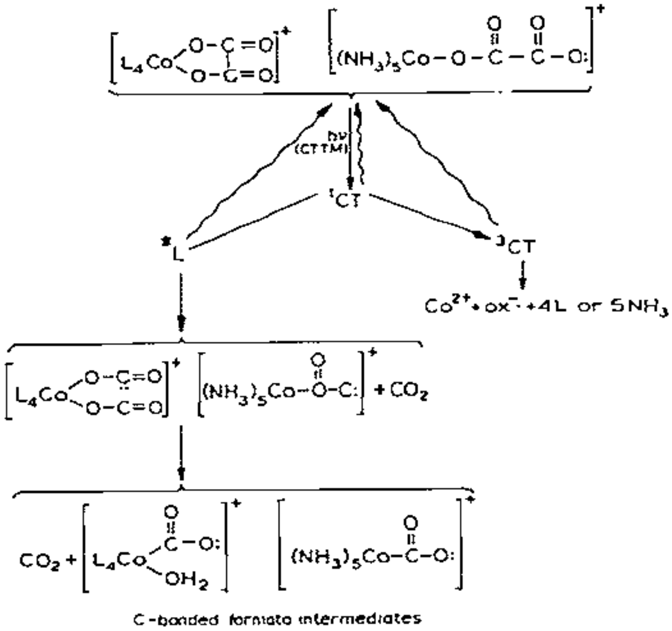


Fig. 7. Photochemical reaction, including photoredox and ligand photoreaction paths, for monooxalato complexes of Co(III), taken from refs. 64 and 184; L = NH_3 or $\frac{1}{2}$ en.

In the case of cobalt(III) azido complexes flash photolysis has not established the formation of nitrene intermediates in $[Co(NH_3)_5N_3]^{2+}$ and *trans*-$[Co(N_4)(N_3)_2]^+$, whereas some evidence was found for photochemical generation of nitrene as a minor process in the case of $[Co(CN)_5N_3]^{3-}$ [43,132].

Flash photolysis of aqueous solutions containing $[Rh(NH_3)_5N_3]^{2+}$, or *trans*-$[Rh(NH_3)_4(N_3)_2]^+$, was found to produce various absorbing transients which, however, appeared to be the products of the reaction of nitrene complexes with the solution species, rather than nitrenes themselves [43]. The nitrene complexes were assumed to be responsible for momentary bleaching of the substrate in the near UV spectrum (duration about 300 μs). Regeneration of absorbance in this region was supposed to be associated with the reactions of the primary photoproducts $[Rh(NH_3)_5N]^{2+}$ and $[Rh(NH_3)_5NH]^{3+}$ and their several successors. Within a pH 3—7 these species were reported to dimerize and form two new transients, which absorbed strongly between 500 and 600 nm (with λ_{max} at 510 nm for one and 570 nm for the other). Dimerization was found to proceed in competition with the reaction of the photoproducts with Cl^- or I^-. The detailed reaction scheme for $[Rh(NH_3)_5N_3]^{2+}$ derived from flash photolysis results [43] is presented in Fig. 8. The $[Rh(NH_3)_4(N_3)_2]^+$ complex was found to behave in a qualitatively similar manner [43].

In azidopentaammineiridium(III) solutions only one intermediate species, I, was detected on flashing. This was attributed to the product of the reaction of coordinated nitrene and the solvent (λ_{max} 400 nm, half-life about 17 ms) [189,262]. For solutions containing hydrochloric acid the photolysis was found to yield exclusively $[Ir(NH_3)_5NH_2Cl]^{3+}$. The quantum yields were wavelength dependent and appreciable even for excitation in the LF range of the spectrum.

The detailed reaction scheme is compared with that for the rhodium complex in Fig. 8. The differences lie in the fate of the primary photoproducts.

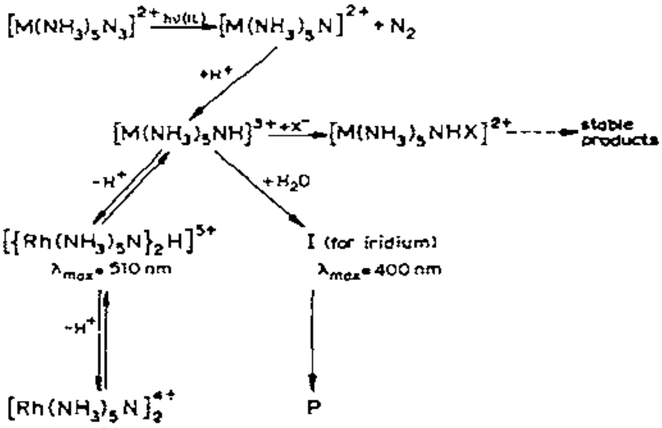


Fig. 8. Photoreactions of azide ligand in rhodium(III) and iridium(III) complexes, (data from refs. 43, 132, 138, 189 and 262); M = Rh(III) or Ir(III), X = Cl^-, ClO_4^- or I^-.

For example the dimerization of the nitrene intermediate was not recognized as an adequate explanation for the iridium system, although the kinetic behaviour of the transients is essentially the same. The differences may be attributed to an increased stability of nitrene intermediates in the order Co(III) < Rh(III) < Ir(III) [189].

The N^-—N_2 cleavage found for the azido complexes was interpreted in terms of a model where a lower energy azido ligand excited state is the reactive level [138,189,262]. The other possibilities involving CTTL excited states were also considered [152].

(vi) Reactions with radicals

(a) Oxidation of transition-metal ions

The most widely studied radical species have been dihalogen anions $X_2^- \cdot$ among which $Cl_2^- \cdot$ and $Br_2^- \cdot$ were found to be powerful oxidants.

Aquocomplexes of manganese(II). Oxidation of the aquocation of Mn(II) to Mn(III) by the radical ion $Br_2^- \cdot$ was initiated by flash photolysis of NaBr

$$Mn_{aq}^{2+} + Br_2^- \cdot \rightarrow Mn_{aq}^{3+} + 2\ Br^- \qquad (104)$$

The process occurred by an inner-sphere mechanism with a second-order rate constant of $1.4 \cdot 10^6\ M^{-1}\ s^{-1}$ [263,264].

Complexes of iron(II). Aquo- and halogen complexes of iron(II) were found to be oxidized to iron(III) species by radical anions $Cl_2^- \cdot$ and $Br_2^- \cdot$ [161,263]. The reaction product between the ions $Br_2^- \cdot$ and Fe^{2+} was the $[FeBr]^{2+}$ complex. The reaction was reported to proceed by an inner-sphere substitution path with a rate constant of $3.6 \cdot 10^6\ M^{-1}\ s^{-1}$ at 25°C. On the other hand the reaction between the ions $Cl_2^- \cdot$ and Fe^{2+} proceeded by two paths: inner-sphere substitution with a rate constant of $4.0 \cdot 10^6\ M^{-1}\ s^{-1}$, and outer-sphere substitution with a rate constant of $1.0 \cdot 10^7\ M^{-1}\ s^{-1}$ [161].

$[Ru(bipy)_3]^{2+}$. It was found that the $[Ru(bipy)_3]^{2+}$ sensitized redox decomposition of $[Co(NH_3)_5Br]^{2+}$ results in the formation of Co^{2+} and $[Ru(bipy)_3]^{3+}$ in the ratio of about 1 : 1 [133,143,258]. The fate of $Br_2^- \cdot$ radicals generated in flash photolysis of the Co(III) complex (cf. p. 150) was followed. It was found that increasing the $[Ru(bipy)_3]^{2+}$ concentration accelerated the decay of $Br_2^- \cdot$, although it had no influence on initial radical yield. It was thus concluded that there were $Br_2^- \cdot$ radicals which were responsible for the oxidation of Ru(II) species according to eqn. (105) [133,143]

$$Br_2^- \cdot + [Ru(bipy)_3]^{2+} \overset{k}{\rightleftharpoons} \{[Ru(bipy)_3]^{3+} \cdot Br^-\} + Br^- \qquad (105)$$

with $k = 3 \cdot 10^9\ M^{-1}\ s^{-1}$.

$[Ru(bipy)_3]^{2+}$ was also reported to be oxidized, in nearly diffusion-controlled reaction, [141—143,200] by *N*-methyleneethylenediaminetriacetate radicals generated on flashing $[Co(EDTA)]^-$ or $[Co(HEDTA)X]^-$ complexes (cf. pp. 150,151 and 163).

It must be noticed, however, that the opinions on the quenching mechanism of the luminescent excited state of $[Ru(bipy)_3]^{2+}$ are divergent (for a more detailed discussion cf. refs. 265, 266).

Cobalt(I) and cobalt(II) complexes. An aquo complex of Co(II) was found to increase the rate of the disappearance of $Br_2^- \cdot$, but the rate was independent of the Co^{2+} concentration in the presence of N_2O [263]. The results were interpreted in terms of two successive reactions

$$Co_{aq}^{2+} + e_{aq}^- \rightarrow Co_{aq}^+ \tag{106}$$

$$Co_{aq}^+ + Br_2^- \cdot \xrightarrow{k} Co_{aq}^{2+} + 2\ Br^- \tag{107}$$

with $k = 1.0 \cdot 10^{10}\ M^{-1}\ s^{-1}$. No reaction between Co^{2+} and $Br_2^- \cdot$ was observed [252]. On the other hand reaction with Co^{2+} was detected in the case of $Cl_2^- \cdot$ radicals generated by flash photolysis of solutions containing Cl_3^- [267]. The oxidation reaction

$$Co_{aq}^{2+} + Cl_2^- \cdot \rightarrow Co_{aq}^{3+} + 2\ Cl^- \tag{108}$$

was found to proceed with a rate constant of $1.4 \cdot 10^6\ M^{-1}\ s^{-1}$, and to be inner sphere-substitution controlled. The initial product was reported to be $[CoCl]^{2+}$ which was not labile on the time scale of the oxidation reaction [267].

$[Co(N_4)]^{2+}$ was found to be oxidized to a Co(III) complex by $Cl_2^- \cdot$, $Br_2^- \cdot$ as well as $I_2^- \cdot$ radicals at nearly diffusion-controlled rates. It was concluded that $I_2^- \cdot$ is a stronger oxidant than I_2 or I_3^- [151].

(b) Reduction of metal ions

The reduction of iron(III), ruthenium(III), cobalt(III) and rhodium(III) complexes was reported to proceed with various radicals generated by flash photolysis. The reaction with dihalogen radical anions was studied, but only in the case of $I_2^- \cdot$ in the presence of $[Ru(NH_3)_6]^{3+}$ [44] and $[Co(NH_3)_5I]^{2+}$ [157], were some reducing properties postulated.

Several cobalt(III) complexes: $[Co(NH_3)_5Br]^{2+}$, $[Co(EDTA)]^-$, $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_5O_2CCH_2OH]^{2+}$, were found to be reduced to Co(II) species by $(CH_3)_2COH \cdot$ radicals, whereas $CH_2OH \cdot$ was inactive [143,192]. Similarly, $CO_2^- \cdot$ (or $HCO_2 \cdot$) radicals were reported to reduce Co(III) to Co(II) in the $[Co(NH_3)_5PNB]^{2+}$ complex [223].

The rhodium(III) complex, $[Rh(NH_3)_5(H_2O)]^{3+}$ was found to decrease the $I_2^- \cdot$ lifetime, probably due to a redox reaction [41].

Aquo- and oxalatocomplexes of iron(III) were reported to be reduced by oxalate radicals, $C_2O_4^- \cdot$ in the flash photolyzed solutions [73,144,145,178, 179] (cf. pp. 154—156)

$$Fe(III) + C_2O_4^- \cdot \rightarrow Fe(II) + 2\ CO_2 \tag{109}$$

(c) Radical complex formation

Some radicals are known to form radical complexes with metal ions which are relatively stable when compared to free radicals. Most of these studies involved $HO_2 \cdot$ radicals which undergo complexation (eqn. (110))

$$M^{n+} + HO_2\cdot \rightleftharpoons [M{-}HO_2]^{n+} \tag{110}$$

with metal ions, usually in their highest oxidation state e.g. Ti(IV), Zr(IV), Ce(III), V(V), Th(IV), U(VI), Mo(VI) and Cu(II) [268,269 and references cited therein]. The complexation reaction in the case of cupric ions was studied recently using flash photolysis and e.p.r. techniques [269]. $HO_2\cdot$ radicals were generated by flashing hydrogen peroxide inside the e.p.r. cavity

$$H_2O_2 \xrightarrow{h\nu} 2\ OH\cdot \tag{111}$$

$$OH\cdot + H_2O_2 \rightarrow HO_2\cdot + H_2O \tag{112}$$

Thorium(IV) was used as a spin trap for $HO_2\cdot$ radicals and decay kinetics of the long-lived Th-$HO_2\cdot$ complex formed were studied in the presence of Cu^{2+} ions. It was concluded that the reaction between Cu^{2+} and $HO_2\cdot$ proceeds through complex formation (eqns. (113—115))

$$Cu^{2+} + HO_2\cdot \rightleftharpoons [Cu{-}HO_2\cdot]^{2+} \tag{113}$$

$$[Cu{-}HO_2\cdot]^{2+} \rightarrow Cu^+ + H^+ + O_2 \tag{114}$$

$$Cu^+ + HO_2\cdot \xrightarrow{H^+} Cu^{2+} + H_2O_2 \tag{115}$$

for which the stability constant was $5.1 \cdot 10^7\ M^{-1}$, and its rate of decomposition (eqn. (114)) 30 s^{-1} [269].

Similarly, the increase in stability of flavosemiquinone radicals, generated by flash photolysis of riboflavine [270] was observed in the presence of Zn^{2+} and Cd^{2+} [271]. It was concluded that complexation reaction (eqn. (116))

$$Fl^- + Cd^{2+} \rightleftharpoons [CdFl\cdot]^+ \tag{116}$$

is followed by a slow process

$$2[CdFl\cdot]^+ \rightarrow \text{products} \tag{117}$$

For Zn^{2+} ions similar behaviour was reported. Kinetic and spectral characteristics of the complexes were given [271].

E. CONCLUDING REMARKS

It is encouraging to note that there has been a significant increase in the number of flash photolysis studies with transition metal coordination compounds during the past few years. We have made an attempt to collect all of the available data on this subject and to reiterate major points of discussion and interpretation. With a few exceptions we have avoided adding our own opinions or conclusions.

Clearly the application of the flash technique to the photochemistry of coordination compounds has led to many important achievements. However, mechanistic conclusions must be drawn with great caution, in particular when only one detection method has been used. More useful results have been obtained from flash photolysis by means of two or more detection techniques. The most valuable data were gathered when flash experiments had been complemented by scavenging, pulse radiolysis, sensitization, photoluminescence or other studies giving information about the short-lived species generated upon excitation.

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