Coordination Chemistry Reviews, 61 (1985) 1–53
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

PHOTOCATALYTIC SYSTEMS WITH LIGHT-SENSITIVE COORDINATION COMPOUNDS AND POSSIBILITIES OF THEIR SPECTROSCOPIC SENSITIZATION—AN OVERVIEW

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(Received 3 January 1984)

CONTENTS

0010-8545/85/$18.55

ABBREVIATIONS

A	substrate
B	product
bpy	2,2′-bipyridine
Bu	butyl
C	catalyst
C′	modified catalyst
Ch	chromophoric ligand
CT	charge transfer
CTLM	charge transfer, ligand to metal
CTML	charge transfer, metal to ligand
CTTL	charge transfer to ligand (CTML)
CTTM	charge transfer to metal (CTLM)
CTTS	charge transfer to solvent
d	electron with an azimuthal quantum number of 2 (however, see k_d)
dmg	dimethylglyoximate
en	ethylenediamine or 1,2-diaminoethane
htc$^-$	bis(2-hydroxymethyl)dithiocarbamate
h	Planck's constant
$h\nu$	excitation by irradiation with photons of frequency ν
IL	inner ligand
IPCT	ion-pair charge transfer
irr	irradiation
IT	intervalence transfer
k_{cat}	specific rate constant for the catalysed thermal reaction
k	specific rate constant
k_d	specific rate constant for the formation of an encounter complex
K	coordination compound
K_{IP}	ion-pair formation constant
L	ligand
LF	ligand field
M	metal
Me	methyl
napht	naphthyl
NBD	norbornadiene
NDMA	*p*-nitrosodimethylaniline
OTf	triflate or trifluoromethanesulfonate
Ph	phenyl
phen	1,10-phenanthroline

prod	product
Py	pyridine
Q	quadricyclene
R	alkyl
S	sensitizer
sens	sensitization
stat	static
tmp	2,4,6-trimethylpyridine
TPP	meso-tetraphenylporphyrin
X	ligand
γ	number of moles formed during photoreaction
η (or η_{prod})	efficiency
λ	wavelength
ν	frequency
π	pi electrons or energy levels (based on molecular orbital diagram)
σ	sigma electrons or energy levels (based on molecular orbital considerations)
Σ	summation (to allow for more general situations where more than one path exists)
ϕ_p	product quantum yield

A. INTRODUCTION

The photochemistry of both coordination compounds and organometallics have been definitively discussed in a number of excellent books [1] and reviews [2]. The aim of this review is to bring into focus the intriguing areas of photocatalysis and photosensitization, which have not been extensively reviewed in English, for professional chemists and advanced students of chemistry who are not currently working in the field of inorganic photochemistry. Photochemical reactions of coordination compounds are even more fascinating than organic photoreactions because of the possibility of generating a more diverse number of electronically excited states which are characterized by different kinds of electron density distributions. Under certain circumstances it is possible to obtain more or less distinct excited states of the inner ligand (IL), ligand field (LF) and charge transfer (CT) type by varying the wavelength (λ) of irradiation. These states, which are obtained by photophysical processes, may be regarded as isomers of the appropriate ground state coordination compound if they are starting points for photochemical reactions (Fig. 1), and they are designated IL, LF, and CT isomers, respectively, in this review. The charge transfer processes can be further subdivided into charge transfer from metal to ligand (CTTL or CTML), from ligand to metal (CTTM or CTLM), from the complex to the solvent (CTTS), intervalence transfer (IT), and ion-pair (IPCT) types. As anticipated from the nature of the excited states, CT excitation often leads to photoredox reactions, whereas excitation of LF states often initiates photodissociation and photosubstitution processes.

The few unambiguous examples of IL photoreactions quoted in the literature show unusual photoreactions of coordinated ligands which occur without the participation of the central metal atom. However, irradiation of coordination compounds may lead to the population of more than one kind of excited state, or the excited state may be in thermal equilibrium with an excited state of another type. Therefore, competitive photoreactions must be considered which depend on the energy-level schemes of the appropriate coordination compounds and the band shapes of their electronic spectra, as well as on the bandwidth of the light source. As is also the case in organic photochemistry, excitation to a given excited state or energy level does not always result in a chemical reaction starting from this state; that is, a radiationless cascade down to an excited state of lower energy, or complete deactivation back to the ground state may occur before any chemical reaction begins. The product quantum yield, ϕ_p, which is the number of product molecules relative to that predicted from the number of photons of excitation, is a quantitative measure of such a situation.

The often unusual reactivity of the various excited states of coordination compounds has been demonstrated by a number of rather surprising reactions which are completely unexpected when compared to normal thermal reaction pathways. Several examples, chosen arbitrarily from the literature

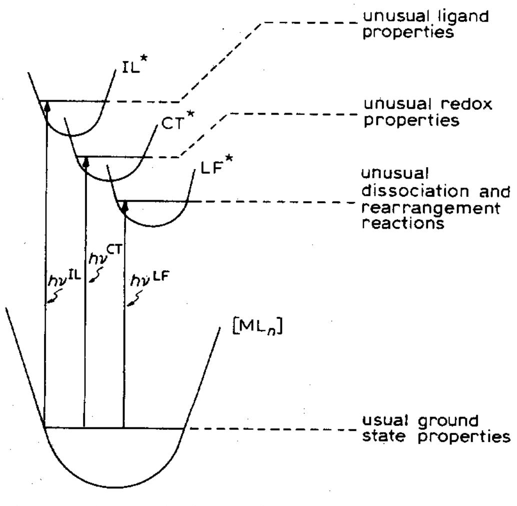
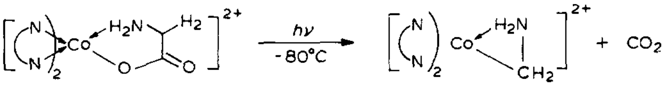


Fig. 1. Electronically excited states of coordination compounds in relation to their photochemical behaviour.

demonstrate some really surprising results of photochemical reaction pathways caused by the photophysical generation of LF, IL, and CT excited states (LF, IL, and CT isomers, respectively).

Poznyak et al. [3–5] showed that low-temperature LF excitation of cobalt(III) mixed-ligand complexes with amino acid ligands leads to the formation of a new class of thermally stable Co–C- σ-bonded η^2-aminomethylene complexes characterized, according to X-ray crystal structure investigation [6], by the formation of a very uncommon three-membered chelate ring (1)

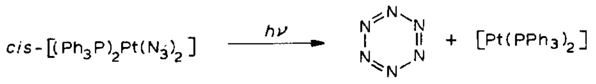


(1)

(N N = en, phen or bpy)

The few known examples of photoreactions caused by IL excitations include the interesting results obtained by Vogler [7,8], who showed that a loss of ligating properties of the amine ligands can be produced by an IL(π–π^*) excitation leading to considerable reduction of the electron density at the nitrogen lone pair [7]. Another example is the *trans–cis* isomerization of *trans*-4-stilbenecarboxylic acid coordinated to either iridium(III) or ruthenium(III). The isomerization is accomplished by the IL excitation of the stilbene ligand [8]. This coordinated-ligand isomerization reaction is unambiguously attributed to IL excitation, since CT excitation of the appropriate *trans*-4-stilbenecarboxylatocobalt(III) complexes leads to very interesting photoredox reactions [9]. A further illustration of IL photochemistry [7] is the photochemical behaviour of *cis*-dichlorobis(1-naphthylamine)platinum(II) upon irradiation in the 250 nm region. This photoreaction leads to formation of the free 1-naphthylamine ligand with relatively high values of the quantum yield ($\phi = 0.1$). Irradiation of the naphthylamine ligand is known to produce an excited state with decreased base strength compared with the ground state; thus, the reaction appears to be the result of an IL isomer. Furthermore, *d–d* excitation in the 435 nm region of the platinum(II) complex does not show any 1-naphthylamine release. Together, these results provide evidence that the photoreaction is initiated exclusively by IL excitation. Thus under certain circumstances it is possible to change a ligand to a non-ligand by excitation of its IL states.

Among the considerable number of surprising CT-generated photoredox reactions of coordination compounds, one of the most spectacular is the following, also described by Vogler et al. [10], in which a two-electron reduction of *cis*-diazido-bis(triphenylphosphine)platinum(II) leads to the formation of an intermediate tentatively assigned to hexazine or hexazabenzene (2)



(2)

These remarkable and sometimes rather unexpected results are due to the generation of highly reactive, short-lived, electronically excited states which are characterized by a high excess energy of about 100 kcal mol^{-1}. Most advantageously, these highly reactive IL-, LF- and CT-isomeric forms of appropriate ground state compounds can be achieved at very low temperatures and can lead to the formation of coordinatively unsaturated species, free ligands, or a change of formal oxidation numbers, even when these are not expected from classical thermal chemistry. Such species provide the basis for unique and interesting photocatalytic and photoassisted reactions.

B. PHOTOCATALYTIC REACTIONS OF LIGHT-SENSITIVE COORDINATION COMPOUNDS

Some confusion surrounds the definition of photocatalysis. Historically, any photoreaction has been regarded as photocatalytic [11], and a number of reactions described in the literature as photoinitiated, light-initiated, light-accelerated, photoenhanced, photosensitized, truly photocatalysed, etc. very often deal with the same aspects [12–15]. In an attempt to overcome this confusion, the present authors have provoked some discussion very recently on this problem [16,17]. Considering the comments made by Mirbach [18] and Carassiti [19], it is suggested that the following terms be used to distinguish between the different light-induced reactions which lead to the catalysed conversion of diverse substrates:

(a) Photoinduced catalytic reactions

$$A \xrightarrow{h\nu} C \tag{3}$$

$$S \xrightarrow{[C]} P \tag{4}$$

The term photoinduced catalytic reaction implies the photochemical generation of a catalyst C from a thermally stable and catalytically inactive precursor A. Although A is a coordination compound in this case, the catalyst C can be a coordinatively unsaturated complex species, a free ligand, a complex (and/or a ligand) with a changed formal oxidation number, or any other highly reactive species formed in the course of reaction (3). Unlike the formation of the catalyst C, which is a photochemical reaction, the transformation of the substrate S into the product P, catalysed by C, is an exclusively thermal process. The catalyst C is not consumed in the course of reaction (4). Hence, the overall quantum yield for the formation of the product P may exceed unity. However, very often the catalyst formed in the photoreaction (3) undergoes side reactions which lead to consumption of the catalyst ("poisoning"). Therefore, depending on the initial quantum yield for the formation of the catalyst and the turnover number, i.e. the number of cycles initiated by the catalyst, the overall quantum yield may not necessarily be > 1.

In an extreme case, the catalyst will be consumed in the course of reaction (4), leading to a stoichiometric catalytic process, as discussed by Basolo and Pearson [20]. However, such reactions are typically better described as photoassisted (see below). Although light is required to generate the catalyst, all subsequent reactions are purely thermal processes. As a consequence, products are also formed after the light source is removed. Hence, the overall quantum yield is time-dependent and is affected by the substrate concentration and other factors (see eqn. (36) of ref. 21).

(b) Photoassisted reactions

$$\mathrm{A} \xrightarrow{h\nu} \mathrm{C} \tag{5}$$

$$\mathrm{C} + \mathrm{S} \xrightarrow{h\nu \text{ or } kT} \mathrm{P} + \mathrm{A} \tag{6}$$

In this type of reaction a catalytically inactive precursor is transformed into a photoassistor C (otherwise known as a "pseudo-catalyst" [18]) by the absorption of light (5). C then may bring about the transformation of the substrate S into the product P while C itself is converted back to the precursor A. Thus, A is not consumed in this process; however, a new photon is required to start the next cycle. The photoassistor C can react with the substrate S either by thermal or by further photochemical activation. In either case the overall product yield is not catalytic with respect to the number of incident photons. Hence, the overall quantum yield is always < 1 for this type of reaction.

Unlike photoinduced catalytic reactions, photoassisted reactions do not proceed without continuous irradiation. Synonymous with the term "photoassisted reactions" are others such as "photoenhancement" proposed by Alexander and Roundhill [22], or "photoactivated", as used by Strohmeier and Weigelt [23].

Alexander and Roundhill also give a very clear experimental distinction between photoinduced catalytic reactions and photoassisted reactions, based on the catalytic decomposition of hydrogen peroxide by the light-induced activation of dirhenium decacarbonyl. Figure 2 provides an illustration of both photoinduced catalytic and photoassisted reactions.

(c) Sensitized photoreactions

$$\mathrm{A} \xrightarrow{h\nu} \mathrm{A}^* \tag{7}$$

$$A^* + S \rightarrow A + S^* \tag{8a}$$

$$A^* + S \rightarrow A^+ + S^- \tag{8b}$$

$$A^* + S \rightarrow A^- + S^+ \tag{8c}$$

$$S^*(S^+, S^-) \rightarrow P \tag{9}$$

In a sensitized photoreaction a sensitizer A, which is catalytically inactive in its electronic ground state, absorbs the incident light quanta to give an electronically excited molecule A* (7). A* may transfer its excitation energy to a substrate S (8a) which then will form the product (9). The sensitization also may proceed as an electron transfer process (8b,c). In either case, activation of the substrate is mediated by the photoactive sensitizer. However, unlike the photoassistor in a photoassisted reaction, the sensitizer is active only in its electronically excited state. Owing to several deactivation processes the overall quantum yield for the formation of the product is < 1. No reaction is observed after irradiation is stopped.

(d) Catalysed photoreactions

$$S \xrightarrow{h\nu} S^* \tag{10}$$

$$S^* \xrightarrow[{[C]}]{} P \tag{11}$$

In this type of reaction a catalyst reacts with the excited state of a substrate molecule, which is then transformed into the product. Unlike the examples (a)–(c) discussed previously, the light is absorbed by the substrate; no activation of the catalyst is necessary. Catalysed photoreactions have been discussed in detail by Wubbels [15] very recently and are not considered in this review.

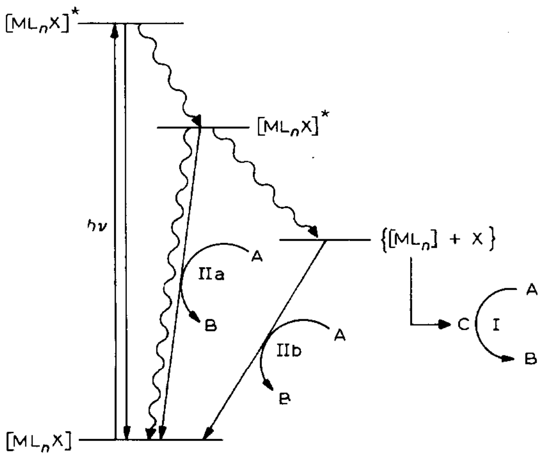


Fig. 2. Simplified Jablonski diagram of photoinduced catalytic (I) and photoassisted (II) reactions.

Mirbach [18] suggested the use of the term "photocatalysis" as a general expression to indicate that both light and a catalyst are necessary to influence a reaction. This may be particularly useful in these cases where the actual mechanism is not known. In the next two sections are presented some examples of photoinduced catalytic and photoassisted reactions which illustrate in detail the concepts of photogeneration of catalysts and photoassistance with metal complexes, respectively. The examples have been taken from the literature and include some results obtained by the present authors. However, these considerations are limited as follows:

(i) Since both photoinduced catalytic and photoassisted reactions based on light-sensitive organometallics (especially metal carbonyls) have been reviewed excellently very recently [13,24,25,14], preference has been given to systems based on light-sensitive Werner-type complexes.

(ii) Reflections on data from the literature primarily deal with results published since about 1977, because earlier results were reviewed in detail elsewhere [12].

(iii) Special applications, as discussed in Section C, have been described only if there are no special reviews dealing with the topic.

(iv) These considerations are limited to reactions in homogeneous phases.

(i) Examples of photoinduced catalytic reactions

The photocatalytic system shown in Fig. 3, which is based on the well-known light sensitivity of octacyanomolybdate(IV) [26–28] has been developed [29]. This photoreaction leads to the generation of cyanide, which is able to catalyse thermally the formation of heterocyclic 1,2-endioles from the appropriate heterocyclic carb-2-aldehydes [30]. The photocatalytic system octacyanomolybdate(IV)/heterocyclic carb-2-aldehyde is in complete accord with the concept of photogeneration of a catalyst [1]. By LF excitation, octacyanomolybdate(IV) photodecomposes with quantum yields higher than unity, with the formation of oxohydroxotetracyanomolybdate(IV)

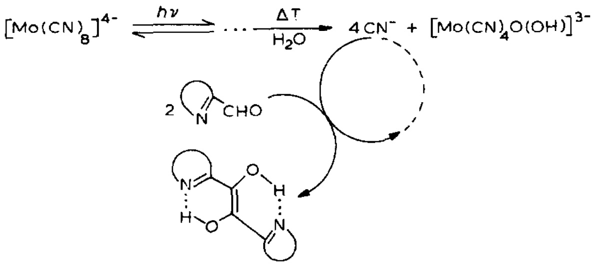
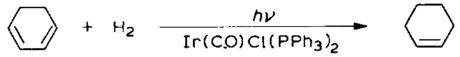


Fig. 3. The photocatalytic system $[Mo(CN)_8]^{4-}$/heterocyclic carb-2-aldehyde [29].

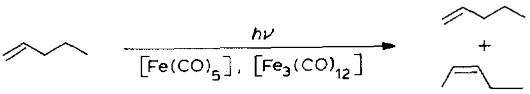
$[Mo(CN)_4O(OH)]^{3-}$ and free cyanide in weakly alkaline aqueous solutions [26]. In the case of CT excitation a much more complicated mechanism must be considered [31]; however, this also leads to free cyanide with high efficiency. Free cyanide is the real catalyst generated photochemically and it is able to promote the strongly cyanide-catalysed formation of heterocyclic 1,2-endioles. This photocatalytic cycle is of some interest because it is related to the formation of strong reductants and chelate-formers [32] as well as pseudo-indigo dyes (heterocyclic 1,2-endioles) [30,33] starting from rather redox-inert, weak or non-chelating and colourless substrates (heterocyclic carb-2-aldehydes). This reaction is also of some interest in applications and is discussed in some detail in Section C(iii). Unfortunately, the photocatalytic system octacyanomolybdate(IV)/heterocyclic aldehyde works only slightly better than stoichiometrically, based on the ratio between the concentration of free cyanide formed photochemically and the concentration of heterocyclic 1,2-endioles obtained catalytically. Preliminary results show turnover numbers of $\leqslant 10$ [34].

However, a number of photocatalytic processes are characterized by comparably high turnover numbers caused mainly by light-induced chain reactions and mediated by light-sensitive Werner-type complexes and organometallics. Some photocatalytic systems, based on light-sensitive coordination compounds and characterized by high turnover numbers, are described in detail (see Section C(iii)) by reason of their possible applied interest. One of the first examples of photoinduced catalytic reactions with high turnover numbers and initiated by light-sensitive coordination compounds was proposed by Strohmeier and Steigerwald [35]. It concerns the photocatalytic hydrogenation of cyclic olefins such as cyclohexadiene to the appropriate saturated and/or partially unsaturated species (12) in the presence of the light-sensitive Vaska complex $[Ir(CO)Cl(PPh_3)_2]$.



(12)

Despite the fact that the real mechanism of both photochemical and thermal processes of the photocatalytic reaction (12) is still unresolved, the reaction is of some importance because a turnover number of about 10^5 catalytic cycles relative to the concentration of the photocatalyst has been shown in combination with other olefins [36]. A detailed but preliminary discussion of the relationships between product quantum yield value ϕ_p, turnover number, irradiation time, reaction time and concentration of the catalyst has been given by Mitchener and Wrighton [37] to explain the very high catalytic activity of the catalysts generated photochemically from iron carbonyl precursors ($[Fe(CO)_5]$, $[Fe_3(CO)_{12}]$). Upon irradiation with light of high intensity (laser photolysis) it has been shown unambiguously that coordinatively unsaturated species ($[Fe(CO)_4]$, and probably $[Fe(CO)_3]$) are the photogenerated highly active catalysts able to promote the isomerization of alkenes, e.g. reaction (13)



(13)

High turnover numbers and turnover rates ($c_{product}/c_{catalyst}$/min) have been found to result from chemical interactions between the coordinatively unsaturated iron carbonyl derivative and the substrate. These results are important, since they are among the first to deal with detailed mechanistic investigations concerning reaction pathways of photolytically generated catalysts.

Among Werner-type complexes, cobalt(III) ammine compounds and other cobalt(III) complexes are of interest with regard to photoinduced catalytic reactions with turnover effects. Nakashima and Kida [38] developed the following photocatalytic cycle based on the photoreactions of tris(ethylenediamine)cobalt(III) compounds and other cobalt(III) ammines in the presence of bis(2-hydroxymethyl)dithiocarbamate (htc^-). This combination leads to an interesting thermal chain reaction which is responsible for higher product yields than are expected from the number of incident photons. The photocatalytic cycle (Fig. 4) is due to photoredox reactions of ion pairs formed between cobalt(III) ammines and htc^-. Irradiation at 450 nm leads to the formation of cobalt(II) complexes and $htc^{\bullet}$ radicals (14).

$$\left([Co(en)_3]^{3+}, htc^-\right) \xrightarrow{h\nu} [Co(en)_3]^{2+} + htc^{\bullet} \tag{14}$$

Although the authors discuss the photoreaction (14) in terms of its initiation by *d–d* excitation, it seems that the reaction pathway is a further example of a photoreaction initiated by the excitation of an ion-pair charge-transfer state, which has not been frequently observed so far [39–45]. Since the photochemically formed tris-(ethylenediamine)cobalt(II) is kinetically labile, it promotes thermal ligand substitution reactions in the presence of an excess of the htc^- ligand (15)

$$[Co(en)_3]^{2+} + 3\ htc^- \rightarrow [Co(htc)_3]^- + 3\ en \tag{15}$$

The tris(dithiocarbamato)cobalt(II) complex $[Co(htc)_3]^-$ itself is able to reduce more tris(ethylenediamine)cobalt(III) thermally (16)

$$[Co(en)_3]^{3+} + [Co(htc)_3]^- \rightarrow [Co(en)_3]^{2+} + [Co(htc)_3] \tag{16}$$

Hence, photochemically generated tris(ethylenediamine)cobalt(II) is the thermal catalyst that acts as a chain carrier in a subsequent dark reaction, as described in Fig. 4. The chain reaction caused by $[Co(en)_3]^{2+}$ leads to overall quantum yield values which are higher than unity for the formation of $[Co(htc)_3]$ and the disappearance of $[Co(en)_3]^{3+}$. Similar photocatalytic cycles have been described for cobalt(III) ammine complexes in the presence of 1-(2-pyridylazo)-2-naphthol [46]. The application of this reaction for unconventional photographic materials has been extensively studied [47–51].

The examples of photocatalytic systems given above clearly demonstrate the validity and utility of the concept of photocatalysis characterized by photochemical generation of catalysts that effect chemical substrate transformation preferably at low temperatures in the dark. Some further examples of photoinduced catalytic reactions are given in Section C.

(ii) Examples of photoassisted reactions

A very impressive example of a photoassisted reaction based on the reaction of an electronically excited state of a coordination compound was described by Koryakin et al. in 1976 [52]. It concerns the oxidation of ethanol to acetaldehyde with the simultaneous reduction of H^+ to hydrogen through photoassisted reactions of vanadium(III) complexes (Fig. 5). From Fig. 5, it follows unambiguously that photoassisted reactions proceed only under conditions of continuous irradiation. Irradiation leads to the formation of electronically excited vanadium(III) characterized by a much increased oxidation potential. Excited vanadium(III) is able to oxidize ethanol to the appropriate aldehyde with concurrent formation of a vanadium(II) complex. Continuous irradiation also leads to the electronic excitation of the vanadium(II) complex, which rapidly reduces protons to molecular hydrogen and restores the initial vanadium(III) complex. Hence, the photoassisted cycle can start again. However, contrary to photoinduced catalytic reactions, removal of the light source stops the reaction immediately. Most investigations of photoassisted reactions initiated by excited states of coordination compounds have been carried out with reference to tris(bipyridyl)ruthe-

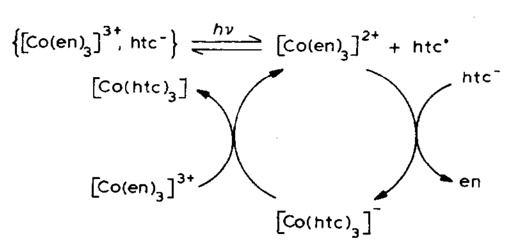


Fig. 4. Photocatalytic cycle of $[Co(htc)_3]$ formation [38] (htc^- = bis(2-hydroxymethyl)dithiocarbamate).

nium(II) and its analogues. Photoassisted reactions of such complexes are of special interest because of their possible application to solar energy conversion. The photophysical and photochemical behaviour of these complexes and their role in photoassisted reactions has been reviewed in detail very recently [53] (see also Section C(iv)).

The next example demonstrates the confusion which exists about the terms photocatalytic reactions and photocatalysis. Arakawa and Sugi [54] described the "photocatalytic" dehydrogenation of 2-propanol using the Wilkinson complex $[Rh(Ph_3P)_3Cl]$. However, there is no doubt that the dehydrogenation is effected by a photoassisted reaction, because the author himself has shown that the reaction described continues only under conditions of continuous radiation. Although the real mechanism is still unresolved, all experimental results seem to indicate that this reaction should be described as a photoassisted reaction.

Another interesting and illustrative example of a photoassisted reaction considered to proceed through the participation of a highly reactive species (but not by interaction with electronically excited states of a complex) has been described by Ledon and Bonnet [55]. This photoassisted cycle deals with the catalysis of the following overall reaction, which is also of some interest for application to solar energy conversion

$$H_3COH + O_2 \underset{\text{reaction}}{\overset{\text{photoassisted}}{\rightarrow}} H_2CO + H_2O_2 \tag{17}$$

Oxoalkoxomolybdenum(V) porphyrin complexes ($[O=Mo(TPP)OCH_3]$) form oxomolybdenum(IV) porphyrin complexes and methoxy radicals by photoinduced homolysis of the $Mo-OCH_3$ bond. In the presence of methanol and oxygen the initial molybdenum(V) complex is restored, with the simultaneous formation of hydrogen peroxide and formaldehyde. The starting molybdenum(V) complex, which is restored during the photoassisted cycle, can be irradiated anew and the cycle starts again, as described in Fig. 6. Photoassisted reactions of this type (in this case coordinative unsaturation and changes in oxidation number of the central metal) operate on the basis of highly reactive species which are in their ground states. The function of

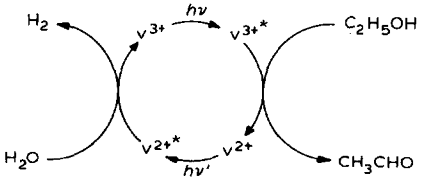


Fig. 5. Reaction pathway of the V^{2+}/V^{3+} photoassisted oxidation of ethanol (simplified scheme).

this photoassisted cycle is to provide a kinetic pathway for the redox reaction. The restoration of the oxoalkoxymolybdenum(V) porphyrin precursor compound completes the cycle.

Another photoassisted reaction, described by Hatano et al. [56], is comparable in some detail with that described above. It also deals with photoassisted reactions of macrocyclic complexes. In the presence of alcohols, the tetra(*p*-sulphophenyl)porphyrincobalt(III) complex ([Co(III)TPPS]) undergoes the photochemical formation of the analogous cobalt(II) complex, with simultaneous oxidation of the alcohols. This photoredox reaction is photoassisted because the photoassistor can be restored by O_2 oxidation of the cobalt(II) complex, as described in Fig. 7. In both the preceding cases the efficiency can be attributed to the high stability of the macrocyclic ligands which are not involved in the light-induced electron transfer processes. Therefore, they can withstand a number of repeated irradiations and photoassisted cycles. This fact is of interest to the modelling of reaction pathways of light-sensitive metalloproteins.

Finally, several other photoassisted and photoinduced catalytic reactions induced by macrocyclic complexes have been described and summarized elsewhere [57–61,227,278].

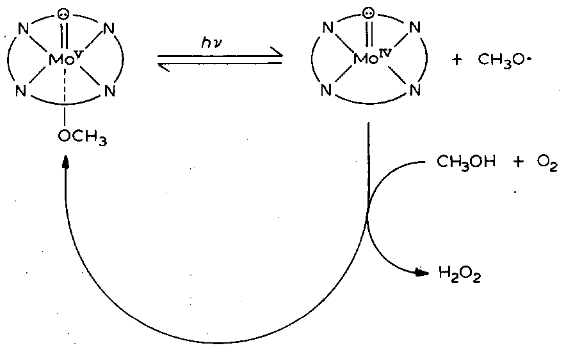


Fig. 6. A simplified scheme of the photoassisted hydrogen peroxide formation mediated by an oxomethoxomolybdenum(V) porphyrin complex [55].

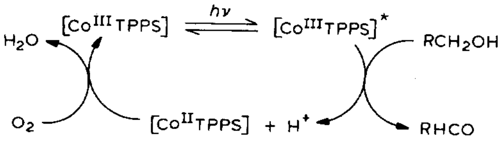


Fig. 7. The photoassisted reaction of [Co(III)TPPS] with alcohols in the presence of oxygen [56] [TPPS = 5,10,15,20-tetra(*p*-sulfophenyl)porphyrin] (simplified scheme).

Benzenethiolatobis(dimethylglyoximato)pyridinecobalt(III) [Co(dmg)$_2$-SPh(Py)] photochemically forms the appropriate cobalt(II) complex [Co(dmg)$_2$Py] with concomitant formation of benzenethiolate radicals (PhS$^\cdot$) by homolytic fission of the cobalt–sulphur bond. Simultaneous hydrogen evolution may be observed when irradiation takes place in the presence of an excess of benzenethiol [62]. Figure 8 shows unambiguously that this light-induced reaction is photoassisted. The photoassisted cycle consists of the light-induced generation of a very reactive species ([Co(dmg)$_2$Py]) which is restored to the initial photoassistor after interaction with the substrate. The present authors [63–66] have proposed a photoassisted cycle which definitely detects the primary photochemical formation of chromium(V) intermediates from chromic acid esters. These short-lived chromium(V) intermediates are able to react in the presence of different aliphatic alcohols with certain cobalt(III), iron(III) and copper(II) complexes to yield the appropriate Co(II), Fe(II), and Cu(I) compounds, respectively, with concomitant restoration of the starting compound (Fig. 9). Unfortunately, the alkoxy radicals formed during homolytic fission of the Cr–OR bond lead to competitive thermal reactions which are well known from the usual mechanism of

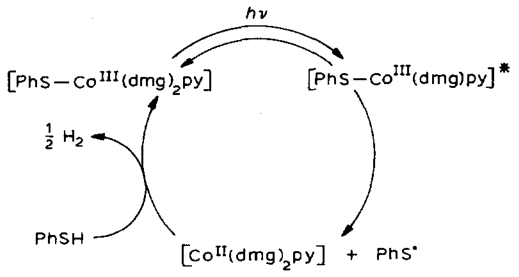


Fig. 8. Photoassisted hydrogen formation from benzenethiol mediated by [Co(dmg)$_2$SPh(Py)] [62].

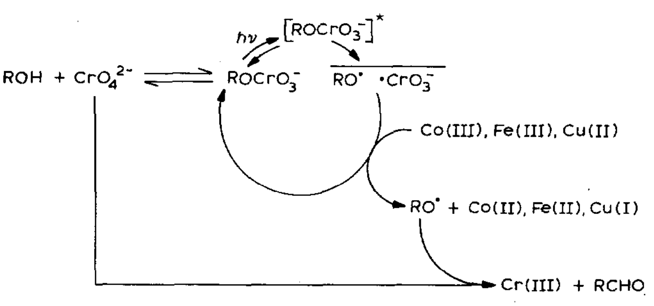


Fig. 9. Photoassisted interaction between chromic acid esters and metal complexes in the presence of aliphatic alcohols [63].

photolysis of chromic acid esters in the absence of the appropriate metal complexes.

Considering the rather unexpected results of both photoinduced catalytic and photoassisted reactions based on light-sensitive coordination compounds, as well as on organometallics, it is not surprising that since the 1970s many studies have dealt with the question of the extensive application of the physical reagent, i.e. light, for several purposes and aims. In the next section are described several of these developments in some detail.

C. APPLICATION OF BOTH PHOTOINDUCED CATALYTIC AND PHOTOASSISTED REACTIONS MEDIATED BY LIGHT-SENSITIVE COMPLEX COMPOUNDS

In this part are discussed diverse aspects of the use of photocatalytic and photoassisted reactions of light-sensitive coordination compounds, in several fields of applied chemistry. These range from the most spectacular investigations, in the field of storage and conversion of solar energy, to unconventional photographic processes.

(i) Photoinduced homogeneous catalysis of olefins

The advantages of using metal complexes for homogeneous catalytic reactions are now widely accepted. However, the most difficult challenge to this type of reaction is the uncertainty often surrounding the true structure of the catalytically active species formed along the reaction pathway, with either organometallic or other metal complexes. Thus, improvements in thermal catalysis are often quite empirical. Furthermore, the elevated temperature conditions often required for thermal reactions can lead to complications caused by thermal deactivation processes and by other competitive reactions. The advantages of both homogeneous photoassisted and photocatalytic complex catalysed reactions compared with the usual thermal reactions are related to the light-controlled formation of intermediates whose structure and composition can in many cases be described in some detail. This is especially important for metal carbonyls [1d, 13], metal hydride complexes [1d, 67], further organometallics [1d, 1e] and other metal complexes [1] where the direct excitation of electronically excited states takes place using monochromatic radiation; these states are known as precursor states of well-defined photochemical reactions.

In this respect metal carbonyls are of special interest since they also allow the formation of catalytically active coordinatively unsaturated species at low temperatures [1d, 13]. Similarly involved are photochemically induced declusterification processes of metal carbonyl cluster compounds as shown in reactions (18) and (19)

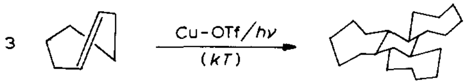
$$[\mathrm{M(CO)}_n] \xrightarrow{h\nu} [\mathrm{M(CO)}_{n-1}] + \mathrm{CO} \xrightarrow{h\nu} [\mathrm{M(CO)}_{n-x}] + x\mathrm{CO} \qquad (18)$$

$$[M_n(CO)_m] \xrightarrow{h\nu} n[M(CO)_{m/n}] \tag{19}$$

Therefore, it is not surprising that metal carbonyls play an important role in photoinduced catalytic processes and photoassisted reactions, as discussed earlier. A considerable number of both photoassisted and photoinduced catalytic reactions are known to be based on light-sensitive metal carbonyls and to lead to various olefin catalyses. Thus, hydrogenation, hydrosilation and other addition reactions, isomerization and interconversion processes, as well as olefin oligomerization reactions, have been described in detail. The exciting field of light-induced homogeneous catalytic reactions of olefins mediated by metal carbonyl compounds and their derivatives has been reviewed very recently by Moggi et al. [69] and will not be described in detail here.

Besides metal carbonyls, rhodium(I), as well as copper(I) complexes are of interest with respect to photocatalytic olefin reactions and have been investigated and reviewed in detail by Salomon [70,14], and in particular for the case of copper(I) photocatalysis by Sykora [71] and Kutal and Grutsch [72]. Among the photocatalytic reactions induced by rhodium(I) and copper(I), rearrangement and oligomerization processes are of special importance, since they lead to a diverse array of novel and unusual reactions. Light-induced copper(I) catalyzed reactions of olefins in most cases are readily distinguished from corresponding thermal processes.

Some recent results not discussed in previous reviews [70–72] clearly show further developments in this field. For instance, Mackor and co-workers have described the photoinduced trimerization of *trans*-cycloheptene mediated by copper(I) triflate (Cu–OTf) (20)



(20)

(Cu–OTf = copper(I) trifluoromethanesulfonate-triflate)

Transition metal-catalysed cyclotrimerization reactions of olefins are very uncommon. Although some details have been established, our understanding of the mechanism of the light-induced trimerization is incomplete. The cyclotrimerization reaction mediated by copper(I) triflate is especially significant, since it is the only example of equal stoichiometry for both light- and thermally induced catalysts [73].

Beside copper(I) triflate reactions, silver(I) triflate light-induced processes are also of increased interest [76]. In the presence of acetonitrile as a solvent, Ag–OTf reacts as a photocatalyst in the conversion of norbornene, as described in Fig. 10. Among copper(I) photoassisted and photoinduced catalytic reactions, the observations of Bolte et al. [77–79] are especially significant since they also demonstrate light-induced dimerization reactions for acyclic olefins and their derivatives. Figure 11 shows the photoassisted cycle leading to cyclobutane derivatives, along with the isomerization of the substrate as a competitive reaction.

In addition to the rhodium(I) salt and rhodium(I) olefin complex light-induced reactions, which were discussed in detail by Salomon [70], rhodium(I) complexes with both phosphine and phosphite ligands also appear to be very attractive as photocatalysts, as has been shown by Faltynek [81]. This observation is especially significant since it demonstrates that low-valent metal phosphine and phosphite complexes give rise to photodissociation reactions similar to those generated by metal carbonyls. Furthermore, Faltynek has discussed some important advantages of metal phosphine complexes, compared with metal carbonyls. When phosphine ligands are labilized by irradiation in the presence of oxygen, a secondary photoreaction readily leads to oxidation of the ligand to the appropriate phosphine oxide [80]. Since phosphorus(V) compounds are weak ligands relative to phos-

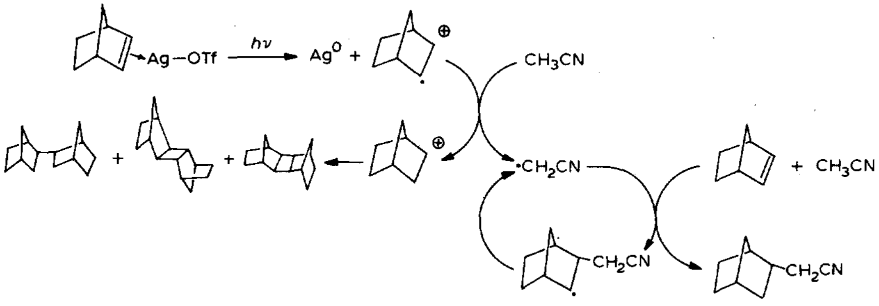


Fig. 10. The photocatalytic reaction of Ag–OTf with norbornene in acetonitrile [76].

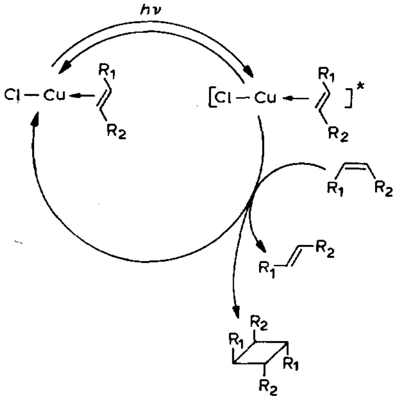


Fig. 11. Copper(I) photoassisted olefin dimerization [77–79].

phines and phosphites, oxidation prevents the back reaction to the catalytically inactive precursor complex. Thus, photolysis leads to high concentrations of coordinatively unsaturated species. However, it appears that further investigations are required to rule out the photochemical interaction between low-valent central metals like rhodium(I) and oxygen.

Faltynek [81] has developed some very interesting photocatalytic hydrosilation reactions of olefinic compounds mediated by rhodium(I) phosphine complexes. He showed that Wilkinson's catalyst $[RhCl(PPh_3)_3]$ and several of its derivatives are very strong hydrosilation photocatalysts. Interestingly, siloxanes have been used as the silyl sources and vinylsiloxanes as the substrates to be silated. Quantum yield values ($\phi^{355} = 21$) and turnover numbers (1450 mol min^{-1}) estimated in the presence of $[RuCl(PBu_3)_3]$ impressively indicate the catalytic efficiency of these complexes. Figure 12 shows the photoinduced catalytic cycle, as proposed by Faltynek. The observations given by Faltynek can be assigned unambiguously to the photoinduced catalytic activity of rhodium(I) complexes, since comparable experiments in the presence of iron pentacarbonyl instead of $[RhCl(PR_3)_3]$ show no photocatalytic reactions. This observation is of some interest since $[Fe(CO)_5]$ has been described as a very reactive mediator in photoassisted hydrosilation reactions [13]. Photoassisted isomerization reactions of olefins have also been described as being mediated by platinum complexes [82]. Despite the possibility of dimerization of the photochemically generated $[PtCl_2(amine)]$ to $[Pt_2Cl_4(amine)_2]$ [83], in the presence of an excess of olefin the coordinatively unsaturated species may react with the olefin rather than form unreactive dimeric bridged complexes. Thus, *trans*-$[PtCl_2(tmp)\text{–}(C_2H_4)]$ (tmp = 2,4,6-trimethylpyridine) is able to react with various olefins such as dichloroethene, pentene and hexene, in a photoassisted cycle which leads to isomerization of the olefins (Fig. 13). This example describes the first *cis–trans* interconversion of olefins with high efficiency mediated by the photoassistance of platinum(II) complexes.

Most of the photocatalytic reactions involving homogeneous complex catalytic processes with unsaturated organic substrates result from the generation of coordinative unsaturation by photodissociation of photolabile

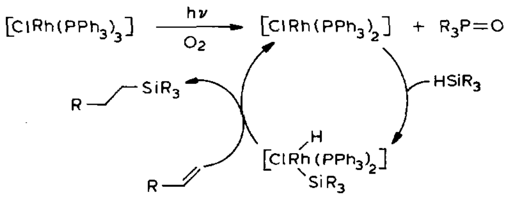


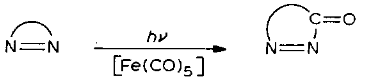
Fig. 12. Simplified scheme of photocatalysed hydrosilation mediated by rhodium(I) phosphine complexes [81].

ligands. However, preliminary results of oxidative photosubstitution reactions involving the light-induced oxidative substitution of chromium hexacarbonyl by tetrachloro-*o*-quinone [84], and the oxidative photosubstitution of metal carbonyls by various ligands which can be deprotonated [85], seem to indicate important new reaction pathways in this field. The preliminary results discussed by Scherer and Jungmann [86] concerning the light-induced oxidative addition of CH_2Cl_2 to $[(Ph_3P)_2Pt(C_2H_4)]$, and of $[Pt(bpy)Cl_2]$ to $CHCl_3$ as described by Vogler and Kunkely [87], seem to support this assumption.

Although several very interesting results of light-induced homogeneous complex catalytic reactions have been described, the main advantage of photocatalysis and photoassistance, which is the generation of highly reactive species otherwise unobtainable under ambient conditions, has not been used industrially as far as the authors know.

(ii) Other photocatalytic organic syntheses

This Section deals with photocatalytic reactions which are not related primarily to olefin reactions, but which involve homogeneous complex catalysis. Preliminary results obtained by Kisch [88] for the light-induced metal-complex-catalysed reactions of heterocyclic compounds illustrate this type of reaction. Kisch showed that iron pentacarbonyl reacts with organic diaza heterocyclic compounds upon irradiation, to yield cyclic diazaone derivatives (21)



(21)

Although the mechanism of this very interesting reaction is not known completely, it seems to offer new reaction pathways for heterocyclic synthetic procedures.

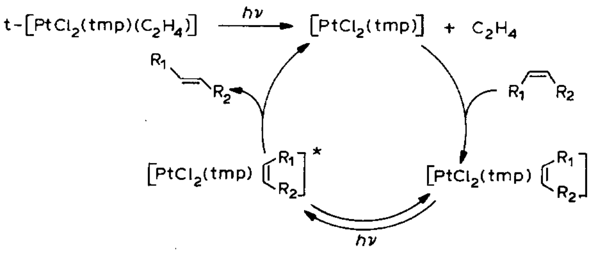
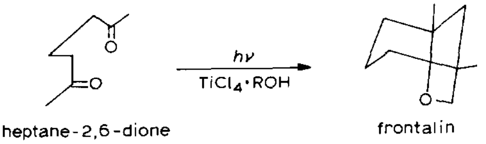


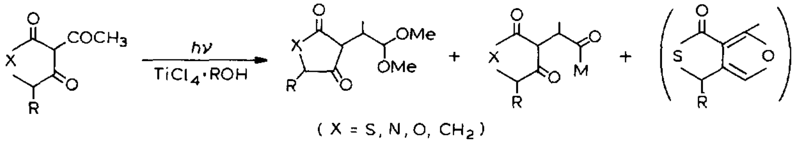
Fig. 13. The photoassisted isomerization of olefins induced by platinum(II) mixed-ligand complexes [82] (tmp = 2,4,6-trimethylpyridine).

A further example with special interest for organic synthesis has been proposed by Sato et al. [89,90]. It deals with $TiCl_4 \cdot ROH$ photoassisted reactions of ketones and other organic compounds in methanol. Although the reaction is not completely understood, some details have been established, and the photoassisted reactions seem to fit the cycle described in Fig. 14. The advantage of this reaction is the very mild thermal conditions required, under which the hydroxyalkylation reactions of heat-sensitive unsaturated ketones occur, as shown below for the case of the very elegant synthesis of the pheromone frontalin from heptane-2,5-dione (22)



(22)

These observations are especially important since they show that it is possible to catalyse a diverse array of novel reactions by the photoassistance of $TiCl_4 \cdot ROH$. Cyclic 1,3-dicarbonyl compounds also undergo photoassisted methanol coupling reactions using electronically excited titanium(IV) [91], thus



(23)

A number of similar photoassisted reactions show the advantage of these processes which are completely distinct from analogous acid catalysed photoreactions using the same substrates [92,275]. Although the mechanistic details of these very attractive light-induced titanium(IV)-mediated reactions are unknown at present, the results are particularly important because they

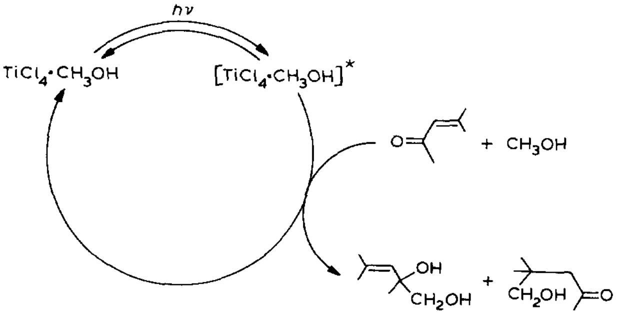


Fig. 14. The $TiCl_4 \cdot ROH$ photoassisted reaction of unsaturated ketones [89,90].

show the applicability of photocatalysts and photoassistors to organic syntheses at ambient temperatures and even lower. Therefore, it is logical to assume that such reactions will become important, especially for the preparation of thermally unstable organic compounds of biological and pharmaceutical importance. Besides unsaturated ketones, Schiff's bases [274], saturated ketones [93], nitriles [274] and alcohols themselves [275] also show $TiCl_4 \cdot ROH$ photoassisted C–C bond formation between substrates and alcohols (preferably methanol), thus generating 1,2-diols or their analogues. The light-induced reactions seem to proceed by the interaction of electronically excited titanium(IV) and ROH, with concomitant formation of titanium(III) and reactive alkoxy and hydroxylalkyl radicals [92].

A very interesting example of an unusual organic synthesis mediated by light-sensitive coordination compounds has been described by Osteryoung and co-workers [94]. Preliminary results seem to indicate a very convenient light-induced generation of the reduced forms of diethylviologene obtained by the photolysis ($\lambda_{irr} > 400$ nm) of several tris(diimine)iron(II) complexes in a room-temperature molten salt mixture consisting of ethylpyridinium bromide and aluminium chloride. Spectroscopic evidence shows the disappearance of the very intense and characteristic Fe(II) diimine charge transfer band with simultaneous appearance of a new band at 680 nm, assigned to reduced viologene forms. Preliminary observations seem to indicate that this very uncommon reaction is due to quenching of excited tris(diimine)iron(II) by ethylpyridinium, combined with the concomitant generation of the appropriate iron(III) complex and the viologene derivative. Although only partially detailed, this result is especially significant because it demonstrates that novel and rather unexpected reaction pathways can be obtained through a change in the photoreaction medium. Furthermore, as far as is known, this is the first example of a photoreaction of a coordination compound performed in molten salts which occurs through the interaction between excited states of complexes and a substrate which is a part of the melt. Unfortunately, no further investigations concerning this special kind of photoassisted reaction have been published.

In summary, it can be stated that light-induced reactions of coordination compounds and organometallics in the presence of appropriate organic substrates lead to some rather surprising syntheses. Such syntheses are valuable for compounds which are sensitive to heat and therefore are difficult, if not impossible, to prepare by the usual organic synthesis technique.

(iii) Photocatalysis and unconventional photographic processes

The search for silver-free photographic materials is of considerable interest for several reasons [95–98], but especially because of the rising silver prices and the general shortage of silver reserves. However, image recording on the basis of light-sensitive silver halides competes strongly with other light-sensitive systems because of the extremely high amplification factors of catalytic image generation induced by the light-generated silver germs and the subsequent chemical development processes. Nevertheless, several unconventional photographic materials have gained importance in special applications [97,98], and it is not surprising that photocatalytic systems based on light-sensitive coordination compounds have been investigated bearing in mind their possible application to unconventional image recording. The results of investigations carried out up to 1977 have been summarized elsewhere [12,99,100]. The reader is referred to earlier sources for details of the classic cyano iron complexes used in the blueprint process and the chromate colloids used in lithography (see also Section C(v) below).

An example of photocatalysis based on Werner-type complexes has been described by Brault et al. [101,102], particular emphasis being placed on its application to unconventional photographic processes. The system uses the light sensitivity of hexamminecobalt(III) compounds combined with the catalytic activity of cobalt(II) sulphide in the presence of $[Co(NH_3)_6]^{3+}$ for the oxidation of certain organic substrates. Exposure of hexamminecobalt(III) leads thereby to cobalt(II); when in the form of an image it is able to react in the presence of a sulphide source, like thiourea or thioacetamide, to generate the catalyst, cobalt(II) sulphide. In the presence of this catalyst, residual $[Co(NH_3)_6]^{3+}$ is able to oxidize the usual organic photographic developers, e.g. *p*-phenylenediamine derivatives, to the appropriate oxidation products. In the presence of photographic colour couplers, dyestuff generation is observed as expected from the normal colour photographic process. The system developed by Brault represents a very interesting example of a really operative photocatalytic system, since the only photochemical reaction involved is the generation of the catalyst, which is then able to catalyse a diverse array of oxidative dye coupling processes, as shown in Fig. 15. The advantage of such photocatalytic systems is based on the photochemically induced conversion of kinetically inert cobalt(III) ammine and amine complexes to labile cobalt(II) compounds. Both the photochemically induced release of ligands and the generation of cobalt(II) have been used for several catalytic image-generating processes [103], which, in general, are comparable with Brault's results.

The present authors also have obtained some results concerning photocatalytic systems, with a view to their application as unconventional photographic materials. The main results concern the photocatalytic formation of heterocyclic 1,2-endioles induced by photochemically generated cyanide [29] as noted above, the photochemical formation of cobalt(II) and oxalate anion radicals from light-sensitive oxalato α-diimine mixed-ligand cobalt(III) complexes [104], and the coupled photoredox system of a chromic acid ester/metal complex [65] (see also Section B). The use of oxalato cobalt(III) mixed-ligand complexes with α-diimine ligands as a photocatalytic system has been studied. Photochemical [105–107] and thermal investigations [272,273], as well as quantum chemical calculations [108–112] concern both the influence of several π-acceptor diimine ligands and different anions in the second coordination sphere on the thermal and photochemical behaviour of the cobalt(III)–oxalate unit. The results of these investigations indicate that the cobalt(III)–oxalate unit, which is responsible for the light sensitivity of oxalato cobalt(III) complexes, can be thermally stabilized by α-diimine ligands, e.g. 1,10-phenanthroline and 2,2′-bipyridine, without appreciably diminishing the photosensitivity. Furthermore, a strong photosensitivity dependence on the anions in the second coordination sphere was found. Photochemical reactions lead to the generation of cobalt(II) with simultaneous formation of oxalate anion radicals in the solid phase. The former can be used in combination with physical development processes for an image-recording procedure, whereas the latter are involved in radical-induced polymerization as an image-forming reaction [104]. It has been demonstrated that appropriate iron(III) oxalate mixed-ligand complexes [113] and their derivatives can also be used as photocatalysts [114] for unconventional photographic materials [115].

The photocatalytic system octacyanomolybdate(IV)/heterocyclic aldehyde (see Fig. 2) is also proposed for image recording purposes, because of the catalytically formed heterocyclic 1,2-endioles. Heterocyclic endioles are strong reducing agents and therefore can be used in physical development processes. Furthermore, these compounds behave like pseudo-indigo dyes which are produced in the presence of a photogenerated catalyst from a colourless substrate (heterocyclic aldehydes). Finally, the photocatalytically obtained dye colours can be intensified by the formation of appropriate metal chelates [29].

No other inorganic coordination compounds can compete successfully

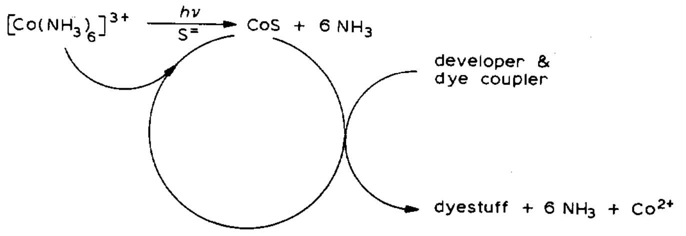


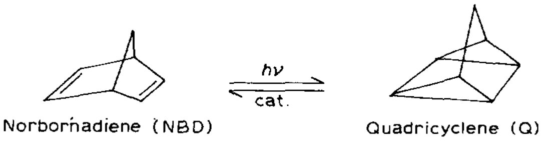
Fig. 15. A photocatalytic image-recording process mediated by light-sensitive cobalt(III) hexammine compounds $[Co(NH_3)_6]^{3+}$ [100,102].

with silver halides at present, and therefore none have found any applications which require significant amplification. However, photocatalytic systems based on light-sensitive coordination compounds or organometallics will have important photographic applications in the future owing to the diverse behaviour mentioned above and elsewhere. The increasing number of patents dealing with such systems supports this suggestion.

(iv) Storage and conversion of solar energy

The search for artificial systems capable of converting solar energy into chemical energy on the basis of both photoassisted and photocatalytic reactions of light-sensitive coordination compounds has been given considerable and quite spectacular attention. Numerous papers deal with this truly fascinating problem. Among these investigations, the exploration of electronically excited tris(diimine)ruthenium(II) complexes is particularly significant, being based on the very peculiar redox properties of their charge-transfer excited states. The main results in terms of the use of these compounds in the chemical conversion of solar energy have been reviewed very recently by several authors [1c,53,116] and will not be discussed here in detail. The use of micellar systems to overcome the very fast back-reactions [10] is particularly noteworthy.

However, some investigations may be distinguished from the ruthenium systems mentioned above (see e.g., refs. 117–120). For instance, Kutal [117] proposed a solar energy storage system based on a copper(I) photoassisted interconversion of norbornadiene (NBD) to quadricyclene (Q). This system is distinguished from the ruthenium(II) polypyridine systems by the storage of kinetically stable energy-rich photoproducts instead of photocatalysed water decomposition. Kutal's idea is based on the well-known light-induced interconversion of NBD to Q. Quadricyclene is characterized by an excess free energy of about 260 cal g^{-1} which is made available through the photochemical interconversion of NBD to Q (24)



(24)

The excess energy of Q can be released by catalysts which convert it back to NBD with concomitant release of heat. However, this photochemical reaction proceeds only by ultraviolet irradiation ($\lambda^{\text{irr}} < 300$ nm); therefore, it is of little interest in solar energy conversion. To overcome the spectral limitation of this interesting reaction, Kutal proposed the use of norbornadiene copper(I) complexes. Cu(I) NBD complexes are characterized by a shift in the absorption spectrum into a region more accessible to solar irradiation. On the basis of these observations, the photoassisted cycle shown in Fig. 16 has been described. The main disadvantage of this cycle is the inadequate spectral sensitivity with respect to the whole solar energy spectrum. However, it should be possible to shift the spectral sensitivity further into the low-energy region. Some preliminary results obtained by Kutal seem to support this assumption.

The advantages and disadvantages of using light-sensitive coordination compounds for solar energy conversion have been discussed in detail elsewhere [53,116,121].

(v) Photopolymerizations

A wide variety of coordination compounds have been investigated in terms of their photoinitiated polymerization reactions. Transition metals which can exist in two or more oxidation states have proven particularly versatile. The range of species found to be suitable includes organic soluble neutral species such as halides, inner chelates, mixed ligand species, carbonyls and organometallics, as well as oxo, cyano, halo, and oxalato anionic and several cationic complexes. Even with all these examples of coordination photopolymerizations, a recent book entitled "Coordination Polymerization" [122] fails to have even a single chapter on such reactions.

Titanium tetrachloride and titanium tetrabromide have been shown to catalyse the polymerization of isobutylene [123]; however, the results are less impressive than with vanadium tetrachloride, and the polymerization mechanism is subject to different interpretations [124–126]. The organometallics tetraneopentyltitanium, dichlorotitanocene, dichlorozirconocene, and diiodozirconocene have all been investigated as polymerization photocatalysts [127]. A titanium tetrachloride/ferrocene "complex" photopolymerizes epichlorohydrin and a titanium tetrachloride/tungsten hexacarbonyl photo-

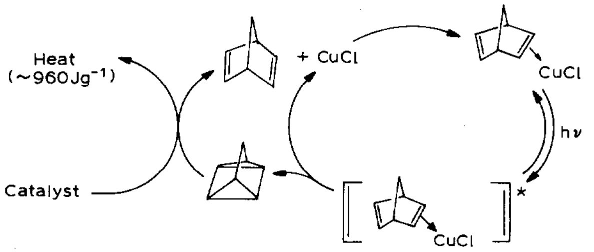


Fig. 16. Photoassisted interconversion of norbornadiene (NBD) to quadricyclene (Q) initiated by copper(I) [117].

catalyses the ring-opening polymerization of cyclopentene, but the mechanisms of these reactions are unknown [128].

Vanadium tetrachloride has proven superior to the titanium halides for photocatalytic polymerization of isobutylene and isobutylene copolymers at low temperatures [123–125,129] with molecular weights for polyisobutylene of one and two million at -40 and $-60°C$, respectively [124c]. VCl_4 provides high-molecular-weight polymers at fairly low temperatures ($-40°C$) compared with the normal Lewis acid catalysts, which require temperatures as low as $-100°C$.

Vanadium chelates, such as chlorobis(2,4-pentanedionato)vanadium(V) [130] and alkoxooxobis(8-quinolinolato)vanadium(V) [131] can initiate free radical polymerizations in the presence of light as follows

$$V^{V}OCl(L)_2 \xrightarrow{h\nu} V^{IV}O(L)_2 + Cl^{\cdot} \tag{25}$$

or

$$V^{V}O(OR)(L')_2 \xrightarrow{h\nu} V^{IV}O(L')_2 + OR^{\cdot} \tag{26}$$

where L and L′ are the anions of acetylacetone (2,4-pentanedione) and 8-quinolinol (8-hydroxyquinoline), respectively. Vanadium chelate-containing polymers can also be used to obtain polymer grafts and cross-linking [132]. The condensation reaction

$$\text{Polymer–OH} + V^{V}O(OH)(L')_2 \rightarrow \text{Polymer–O–}V^{V}O(L')_2 + H_2O \tag{27}$$

forms the vanadium-containing polymer, which can be activated with light, thus

$$\text{Polymer–O–}V^{V}O(L')_2 \xrightarrow{h\nu} \text{Polymer–O}^{\cdot} + V^{IV}O(L')_2 \tag{28}$$

where L′ is again the anion of 8-quinolinol. The radicals can then be used in the formation of block polymers or cross-linking. These photopolymerization reactions of Aliwi and Bamford [132] indicate that metal chelates can effect photopolymerizations, though none of the vanadium chelates approaches the efficiencies of the metal carbonyls noted below. Vanadium(IV) [and chromium(IV)] tetrabis(1-camphenyl) species are also claimed to be polymerization photocatalysts [133]; however, details are not available.

Vanadium(V) on a silica support is thought to provide coordinatively unsaturated vanadium(IV) upon irradiation in a hydrogen atmosphere and coordinatively unsaturated vanadium(III) in a carbon monoxide atmosphere. Similarly, chromate is claimed to be reduced to chromium(V) and -(II), respectively, and molybdate to molybdenum(V) and -(IV), respectively. The coordinatively unsaturated species are claimed to be catalysts for ethylene polymerization [134].

Chromium species have been important in photopolymerization for more than a century. In fact, since 1830 it has been known that dichromate sols of gelatin or albumin become hardened through irradiation (although a polyvinyl alcohol is now widely used). This photochemical reaction has been applied to all major types of printing (relief or letter press, gravure or intaglio, lithography or planography, and porous or screen processes [135]). Agreement on the hardening mechanism is lacking [279], although agreement exists on dichromate photoactivation and on the incorporation of chromium(III) into the hardened product. Studies in this laboratory [136] appear to eliminate the contention [137] of simple alcohol coordination to chromium(III). Holograms using this photochemical procedure [138] are of commercial importance and are seriously rivalled only by silver photographic emulsions at present [139]. Chromate and dichromate have also been patented as photochemical epoxide cross-linking agents [140], and a chromium(III) complex of an azo dye has been patented as an additive which increases the light sensitivity and image density of a photopolymerization composition [141].

Free radical polymerization can be initiated by irradiated arene chromium tricarbonyl and a perhalo compound from which halogen abstraction occurs [142].

$$\text{Arene Cr(CO)}_3 \overset{h\nu}{\rightleftharpoons} [\text{Arene Cr(CO)}_3]^* \rightarrow \text{Arene Cr(CO)}_2 + \text{CO} \qquad (29)$$

$$\text{Arene Cr(CO)}_2 + \text{RX} \rightarrow \text{Arene Cr(CO)}_2\text{X} + \text{R}^\cdot \qquad (30)$$

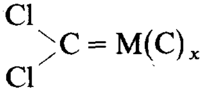
Spectroscopic sensitization by dyes has led to the use of practical lithographic plates using 488 nm light (rather than the ultraviolet light needed for direct activation of the chromium carbonyl entity [143]). Furthermore, these mixed carbonyls can be used to cross-link functionalized polymers via what is tentatively thought to be an oxidative ligand exchange.

The role of molybdenum and tungsten carbonyls in the polymerization of phenylacetylenes has been studied extensively by Masuda and co-workers. $Mo(CO)_6$ is an effective photoinitiator for the polymerization of 1-chloro-2-phenylacetylene [144,280]

$$\text{Mo(CO)}_6 \overset{h\nu}{\rightleftharpoons} [\text{Mo(CO)}_6]^* \rightarrow \text{Mo(CO)}_5 + \text{CO} \qquad (31)$$

$$\text{Mo(CO)}_5 + \text{C}_6\text{H}_5\text{C}{\equiv}\text{CCl} \rightarrow \text{Mo(CO)}_5\text{Cl} + \text{C}_6\text{H}_5\text{C}{\equiv}\text{C}^\cdot \qquad (32)$$

The polymerizations are often quite specific; e.g., $Mo(CO)_6$ photocatalyses the polymerization of 1-chloro-2-phenylacetylene, whereas $Cr(CO)_6$, $W(CO)_6$, $Mn_2(CO)_{10}$ and $Re(CO)_{10}$ do not. On the other hand, $W(CO)_6$ is a better photoinitiator than $Mo(CO)_6$ for the polymerization of phenylacetylene itself [280]. These catalysts often appear to involve halogen abstraction or carbene complexes of the type



$$\mathrm{Cl_2C{=}M(C)}_x$$

[144]. Other radical polymerizations involving irradiation and $W(CO)_6$ have been noted [128,145].

The stereoregularity of ultraviolet-initiated polymerizations with WCl_6 is dependent on the time between mixing and irradiation. The *cis*-polycyclopentene only forms from freshly mixed reagents, whereas a *cis–trans* mixed polymer results if the photopolymerization is delayed. A WCl_4–(cyclopentene) complex has been postulated [146].

Uranyl salts and complexes can photosensitize polymerizations [147], but details are not available.

Manganese chelates can aid photopolymerizations [148]; however, the best quantum yield for a manganese(III) β-diketonate ($\phi_p = 0.015$ at 365 nm) [149a] is appreciably less than that for either manganese or rhenium carbonyl and carbonyl derivatives [150,151]; the ϕ_p values reported for these by Bamford et al. often approach unity [150]. Typically, one radical chain is formed per decomposed carbonyl.

Iron photoactivated polymerizations are best known through the classical inorganic blueprint process [152]

$$\mathrm{Fe(C_2O_4)_3^{3-}} \xrightarrow{h\nu} \mathrm{Fe(C_2O_4)_2^{2-}} + \mathrm{CO_2} + {}^{\cdot}\mathrm{CO_2^-} \qquad (33)$$

$$\mathrm{Fe(C_2O_4)_2^{2-}} + \mathrm{Fe(CN)_6^{3-}} \rightarrow \{\mathrm{Fe_3[Fe(CN)_6]_2}\}_n + \mathrm{C_2O_4^{2-}} \qquad (34)$$

Note that the iron becomes part of the polymer in this case. However, the ferric oxalato chelate can photopolymerize acrylamide [153]; so can the tris(*o*-phenanthroline)iron(III) chelate [154], although the latter has low quantum yields. Vinyl polymerizations have also been reported through the photolysis of ferric chloride [150], an iron(III) porphyrin [155] and ferrocene [156].

Cobalt complexes studied with regard to photopolymerization include the macrocyclic vitamin B_{12} cyanocobalamine [157], the *cis*-aquachlorotetramminecobalt(III) ion [158], other cationic cobalt(III) ammine and amine complexes [159], and the tris(oxalato)cobalt(III) anion [160]. Typically, the complexes have a ligand which can be displaced as a radical, with simultaneous reduction of the cobalt to an oxidation state of II, e.g.

$$\mathrm{Co^{III}L_5X} \xrightarrow{h\nu} \mathrm{Co^{II}} + 5\mathrm{L} + \mathrm{X}^{\cdot} \qquad (35)$$

Nickel chloride interacts at low temperature with methacrylate [161] and acrylonitrile [162] to form complexes which initiate polymerization upon irradiation. Both systems require low-temperature complexation in order to be photoactive. Among the carbonyl studies by Bamford et al. a nickel carbonyltriphenylphosphine complex has been used for photopolymerization [150c].

The photopolymerization reactivity of platinum(II) complexes of the type $PtCl_2$–(olefin)–(diazine) has been studied [163].

Copper(II) amino acid complexes photopolymerize acrylamide at very low quantum yields ($\phi_p \leqslant 5 \times 10^{-3}$) [281], cupric acetate is claimed as a diacetylene oxidative photocoupler [164], copper naphthenate is a component of an epoxyphoto catalyst [165], and several THF-soluble copper and silver salts are cationic photopolymerization initiators for THF [166]. Earlier studies with silver perchlorate [167] and *N*-vinyl carbazole are also cationic photopolymerizations, but the photosensitization mechanism appears uncertain. Photochemical cationic polymerizations of vinyl ethers induced by silver hexafluorophosphate [168] and epoxy cross-linking systems involving photolysis and silver bis(perfluoroalkylsulphonyl)methane [169] have been reported.

Finally, metal 1,8-diazanaphthenates of the first transition series are said to photoinduce polymerization reactions [170], and examples of photocatalytic reactions of non-transition metal complexes have been documented [171].

(vi) Miscellaneous

Photocatalytic reactions also play an important role in biological systems such as light-activated enzyme reactions [172,173].

Some efforts have been made to model those systems using light-sensitive coordination compounds.

Berezin et al. [174] have shown that photochemically generated Fe(II) ions react with protoporphyrin IX to form a peroxidase-like compound with a high catalytic activity. The catalytic activity of the ferric protoporphyrin IX complex was found to be 2.5×10^7 times higher than for aqueous Fe(II) ions. No reaction with porphyrins was observed for Fe(III) ions [175,176].

Peroxidase activity can also be photogenerated from cobalt(III) complexes [177,178]. The photolysis of catalytically inactive cobalt(III) complexes $[Co(NH_3)_5X]^{2+}$ ($X = Cl$, Br, I, NO_2) leads to Co(II) ions which may catalyse the oxidation of 1,2-dihydroxybenzene derivatives by hydrogen peroxide.

The kinetics of the photocatalytic reaction can be described by eqn. (36) [21] where γ is the number of moles of substrate transformed during time t. ϕ is the quantum yield of the initial photoreaction and k_{cat} is a constant related to the catalysed thermal reaction

$$\gamma = \phi k_{\text{cat}} t \tag{36}$$

Equation (36) is valid if the irradiation time is short compared with the reaction time t and if the concentration of the substrate is high and practically unchanged during the reaction.

The photolytically induced peroxidase activity of the Co(II) ion may also be used for unconventional photographic processes. It has been demonstrated that the oxidative coupling of 1,4-diaminobenzene derivatives with couplers known from the conventional photographic process may be achieved by hydrogen peroxide in the presence of Co(II) ions [179].

The oxygenase activity of the cytochrome P450 and its model approach using iron porphyrin complexes have been studied extensively [180]. Recently it has been shown that the oxygenase activity can be induced photochemically by irradiation of μ-oxo-bis[(meso-tetraphenylporphinato)] iron(III), $[(\text{TPP})\text{Fe}]_2\text{O}$ [181] thus

$$(\text{TPP})\text{Fe}{-}\text{O}{-}\text{Fe}(\text{TPP}) \xrightarrow{h\nu} (\text{TPP})\text{Fe}^{\text{II}} + (\text{TPP})\text{Fe}^{\text{IV}}\text{O} \tag{37}$$

Both the $(\text{TPP})\text{Fe}^{\text{II}}$ and the $(\text{TPP})\text{Fe}^{\text{IV}}\text{O}$ complexes are known to be catalytically active, and the oxidation of phosphines, arsines and stibines [181] as well as that of hydrocarbons [182] and olefins [182,183,278] have been studied. The photooxidation of SO_2 by anchored Zn porphyrins has also been noted [277].

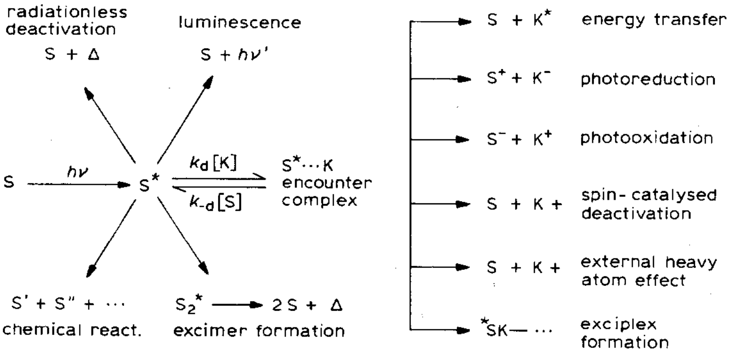
D. SPECTROSCOPIC SENSITIZATION OF PHOTOCATALYTIC SYSTEMS WITH LIGHT-SENSITIVE COORDINATION COMPOUNDS

Under certain circumstances spectroscopic sensitization is required to make photocatalytic and photoassisted reactions practical [184]. Spectroscopic sensitization over the whole spectral region is to be considered as a conditio sine qua non for the storage and conversion of solar energy and for unconventional photographic processes. The spectroscopic behaviour of coordination compounds is frequently characterized by weakly absorbing *d–d* transitions in the visible region and by intensive inner-ligand and charge transfer transitions which mostly are responsible for the catalytically interesting photoredox reactions in the ultraviolet. The principle of spectroscopic sensitization is the conversion of a coordination compound K into the product P by irradiation with light of wavelength λ_{sens}, thus

$$\text{K} + \text{S} \xrightarrow{h\nu_{\text{sens}}} \text{P} + \text{S}' + \ldots \tag{38}$$

However, irradiation with light of energy $h\nu_{\text{sens}}$ in the absence of the sensitizer S leads to no or negligible photoreaction of the complex K, since λ_{sens} is higher than λ_{K}, which is the wavelength responsible for the usual photoreactivity of the coordination compound in the absence of the sensitizer.

Apart from some special details, the same basic models of spectroscopic sensitization described for sensitized organic reactions [185] are valid for coordination compounds. Some reviews concerning the sensitized photoreactions of coordination compounds deal primarily with the exploration of primary photoprocesses for which sensitization as well as quenching experiments are very common [186]. However, sensitizers used in such investigations have not been selected primarily for their spectral sensitivity over the whole spectral region. Most of them fall into the category of well-known organic singlet and triplet sensitizers (donors) with strong absorption preferably in the ultraviolet. Therefore, it is the aim in the following to discuss the general possibilities of spectroscopic sensitization of photocatalytic systems based on light-sensitive coordination compounds over a wide spectroscopic region. A general pathway for spectroscopically sensitized photoreactions can be described by the scheme shown in eqn. (39), where K is a coordination compound and S is a sensitizer. Besides the deactivation processes of the excited sensitizer [shown on the left-hand side of eqn. (39)], interactions with the coordination compound K may occur which lead to further deactivation processes connected with quenching of the excited state [the right-hand side of eqn. (39)].



(39)

Among the quenching processes, energy transfer and electron transfer are particularly interesting. Both processes are true sensitization reactions if they are combined with consecutive chemical reactions of the appropriate coordination compound itself. Radiationless energy transfer may occur either through dipole–dipole interactions based on a Förster mechanism [187] or through exchange interactions [188]. In the case of exchange interactions, the formation of an encounter complex between the sensitizer and the complex compound, with substantial overlap of the electron shells of both partners, must be considered. On the other hand, dipole–dipole interactions may also occur over long distances (up to 50–100 Å). However, as shown in detail elsewhere [184], energy transfer processes are of little interest in long wavelength spectroscopic sensitization because of the strong physical restrictions. Only in the case of triplet–triplet energy transfer has a small shift in the low-energy region been observed [189–191]. On the other hand, sensitization reactions due to electron transfer processes are not limited by such strong restrictions.

Photoinduced electron transfer reactions have been investigated very intensively in the past [192]. The kinetics of such processes can be described by the conceptual approach of Rehm and Weller [193,194], which has recently been confirmed experimentally by Scandola and Balzani [195]. The thermodynamics of light-induced redox reactions between a sensitizer and a coordination compound can be classified according to two different reaction pathways [196] (Fig. 17)

(a) The oxidation potential of the sensitizer is higher than the reduction potential of the complex compound. However, because of strong kinetic barriers, the reaction does not proceed as expected from thermodynamic considerations. Hence, the absorption of photons overcomes the activation barrier and leads therefore to electron transfer processes (Fig. 17a).

(b) The oxidation potential of the sensitizer is lower than the reduction potential of the coordination compound. Therefore, in contrast with (a), the dark reactions cannot proceed. However, light absorption leads to an increase in the oxidation potential of the sensitizer and electron transfer processes become allowed (Fig. 17b).

Analogous considerations are valid for the case of an oxidized metal complex and a reduced sensitizer.

Both types of sensitized electron-transfer reactions have advantages and disadvantages. Reactions proceeding according to (a) are distinguished by the strong suppression of back electron transfer, but unfortunately slow dark reactions also compete with the photoreactions. Type (b) reactions show no dark reactions, but back electron transfer processes may suppress the sensi-

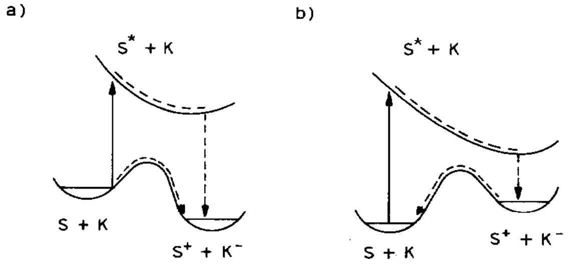


Fig. 17. Simplified potential energy diagram of photoinduced redox reactions between a sensitizer S and a coordination compound K. (a) Exergonic thermal reaction; (b) endergonic thermal reaction.

tized reaction completely, if no additional barriers prevent that process. Such barriers may be achieved by micellar and membrane effects, as mentioned previously [121], by fast ligand-exchange reactions [197,198], by the addition of appropriate scavengers [199–203], and by fast changes in the spin systems of the complexes [1b,204].

Energy transfer based on exchange interactions as well as on electron transfer requires the formation of encounter complexes, since the reactions proceed bimolecularly. However, besides the bimolecular dynamic sensitization, some possible advantages are given here for static sensitization processes (see Section D(iii)).

(i) Dynamic sensitization processes

The following kinetic scheme (eqn. (40)) illustrates the dynamic sensitization pathway

$$\mathrm{S} \xrightarrow{h\nu} \underset{\substack{\downarrow k_\mathrm{S}\\ \cdots}}{\mathrm{S}^*} \xrightarrow[k_\mathrm{d}]{\mathrm{K}} \underset{\substack{\text{encounter}\\ \text{complex}\\ \downarrow k_\mathrm{SK}\\ \cdots}}{\mathrm{S}^*\ldots\mathrm{K}} \underset{k_\mathrm{r}}{\overset{k_\mathrm{sens}}{\rightleftharpoons}} \text{products} \tag{40}$$

The efficiency of sensitized formation of products, η_prod, is diminished by a number of competitive reactions, as illustrated by the sum of the rate constants k_S and k_SK

$$\eta_\mathrm{prod} = \frac{k_\mathrm{d}[\mathrm{K}]}{k_\mathrm{d}[\mathrm{K}] + \Sigma k_\mathrm{S}} \, \frac{k_\mathrm{sens}}{k_\mathrm{sens} + k_\mathrm{r} + \Sigma k_\mathrm{SK}} \tag{41}$$

The most critical barrier to formation of sensitized photoproducts is the diffusion-controlled formation of the encounter complex, since the generation of S*...K can be quenched completely by an inadequate lifetime for S*, by a high viscosity of the medium or by an unfavourable ionic strength. Further deactivation processes must also be considered, as illustrated previously (eqn. (39)).

Despite these disadvantages for dynamic sensitization, literature examples exist in which energy transfer reactions lead to both substitution and rearrangement reactions of metal complexes [186]. Some results have been described in terms of sensitized electron-transfer processes, e.g. between organic dyes [205–211] and intensively coloured metal complexes [212–214] with appropriate coordination compounds. Of special interest are the well-known Oster reactions [215–217]. The Oster systems should be considered as indirect dynamic sensitization processes because mediators like triethanolamine, EDTA, and other secondary and tertiary aliphatic amines are essential to the reactions. The Oster systems consist of the following: excited organic dyes which are reduced by appropriate amines; reduced dyes which are able to reduce metal ions or metal complexes with concomitant restoration of the dye; and mediators (organic amines) which have to be selected in such a manner that no redox reactions can proceed in the dark. The Oster reaction was initially described on the basis of the methylene blue/EDTA/iron(III) system. Figure 18 illustrates the general pathway, which is also valid for other systems. Depending on the concentration of EDTA, it is possible to reduce a considerable excess of photochemically sensitized iron(III). Oster systems have already been used as sensitizers in special image-recording materials [98,218–221].

(ii) The concept of static sensitization

To overcome some of the disadvantages of dynamic sensitization processes, the concept of static sensitization [184] is proposed. The idea behind this concept lies in the linking of a sensitizer and a coordination compound in one closed unit (S–K) by an ionic, covalent or coordinate bond interaction between both components. Under such circumstances molecular diffusion is no longer a restriction, and the kinetic scheme of sensitization is reduced considerably, especially when compared with dynamic processes as shown below

$$(\mathrm{S{-}K}) \xrightarrow{h\nu} \underset{\overset{\downarrow k_{\mathrm{SK}}}{\cdots}}{(\mathrm{S{-}K})^*} \overset{k_{\mathrm{sens}}}{\rightleftharpoons} \text{products} \tag{42}$$

As essential competitive processes against the sensitized formation of the products, we have only to consider the different deactivation processes (k_{SK}) and the back electron transfer (k_r). In such a case the efficiency $\eta_{\mathrm{prod}}^{\mathrm{stat}}$ is primarily a function of the behaviour of the S–K unit and is independent of solvent properties to the extent that it has no influence on the stability of the sensitizer/complex unit

$$\eta_{\mathrm{prod}}^{\mathrm{stat}} = \frac{k_{\mathrm{sens}}}{k_{\mathrm{sens}} + k_r + \Sigma k_{\mathrm{SK}}} \tag{43}$$

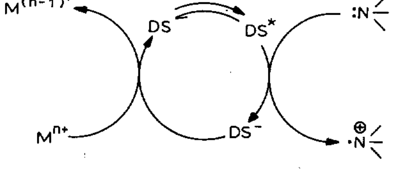


Fig. 18. Indirect dynamic sensitization based on the Oster system [215–217].

The following pathways have been proposed for realizing the concept of static sensitization:

(a) Static sensitization by ion-pair or ion-multiplet formation

$$[\mathrm{ML}_n]^{m\pm} + \mathrm{S}^{\mp} \rightleftharpoons \{[\mathrm{ML}_n]^{m\pm} \cdot \mathrm{S}^{\mp}\} \tag{44}$$

$$[\mathrm{ML}_n]^{m\pm} + s\mathrm{S}^{\mp} \rightleftharpoons \{[\mathrm{ML}_n]^{m\pm} \cdot s\mathrm{S}^{\mp}\} \tag{45}$$

(b) Static sensitization based on mixed-valence compounds with IT (intervalence transfer) behaviour

$$[\mathrm{L}_n\mathrm{M}_1\mathrm{X}] + \mathrm{M}_2\mathrm{L}_n\mathrm{Y} \rightleftharpoons [\mathrm{L}_n\mathrm{M}_1\text{–}\mathrm{X}\text{–}\mathrm{M}_2\mathrm{L}_n] + \mathrm{Y} \tag{46}$$

(c) Mixed-ligand complexes with chromophoric ligands (Ch) and/or low-lying CT transitions

$$[\mathrm{ML}_n] + \mathrm{Ch} \rightleftharpoons [\mathrm{ML}_{n-x}\mathrm{Ch}] + x\mathrm{L} \tag{47}$$

Examples of the experimental application of the concept of static sensitization are discussed in the next three sections.

(iii) Static sensitization by ion-pair formation

Spectroscopic sensitization mediated by ion-pair formation may be achieved either by ion pairs consisting of metal complexes with appropriately coloured ions or by systems which are distinguished by low energy ion-pair charge transfer (IPCT) states. Generally, the formation of ion pairs is favoured if the formation constant K_{IP} is high, which is primarily the case in non-polar solvents and media of low polarity. Furthermore, the value of K_{IP} may be influenced conveniently by varying the concentration of the coordination compound to be spectrally sensitized, whereas high concentrations of coloured counter ions are to be avoided in order to preclude inner filter effects.

As discussed above (Section D(i)), the chances of spectroscopic sensitization are strongly dependent on the efficient formation of the encounter complex and consecutive chemical reactions on the one hand, compared with the deactivation of the sensitizer itself on the other. The diffusion-controlled formation of the encounter complex strongly depends on the charge numbers of the reactants [184]. High and oppositely charged sensitizer and metal complex lead to favoured formation of the encounter complex with concomitant increases in the rate constant of sensitized formation of products [222]. Interestingly, this process may proceed by either static or dynamic interactions. Therefore, in the case of static interactions, ion-pair formation must be considered before the irradiation is performed. However, most sensitization reactions of this type described so far are to be considered as dynamic reactions [186].

Ion-pair formation predominates in solvents with low dielectric properties and for species with high ionic charges [223,224]. In the case of exclusively electrostatic interactions between oppositely charged ions, the ion-pair constants K_{IP} can be calculated by using the Eigen–Fuoss equation [225–227]. Among the relatively rare examples of static sensitization based on ion-pair formation, the diversity of spectrally sensitized photoreactions is evident from the following ion pairs: $\{[Mo(CN)_8]^{4-}, [Ru(bpy)_3]^{2+}\}$ [228]; $\{[Mo(CN)_8]^{4-}, UO_2^{2+}\}$ [229]; ion-pairs formed from thionine and safranine-T with iron(II) and tin(II) [207,230], as well as cobalt(III) complexes with both carboxylate [231–233], and azide [234] anions. The mechanism of these sensitized photoreactions consists of an electron transfer process between the excited coloured ion and the metal complex within the ion pair. The scanty results which exist in the literature appear to support the advantage of spectroscopic sensitization achieved through ion-pair formation of this type.

However, especially interesting are ion pairs which are distinguished by electronic interactions in addition to the normal electrostatic forces between counter ions. Such additional electronic interactions often lead to changed spectroscopic and photochemical properties. The new spectroscopic properties are characterized by the appearance of novel transitions that are described as ion-pair charge transfer (IPCT) transitions. Although phenomena of this type were described in the 1940s by Linhard and Weigel [235,236] and later by Navon and co-workers [237] and Endicott et al. [238], the number of investigations that have been carried out on the general and especially the photochemical behaviour of such ion pairs is very small.

Adamson and Sporer [239,240] showed that ion pairs consisting of $\{[Co(NH_3)_6]^{3+}\ I^{-1}\}$ are photosensitive to an irradiation wavelength of 550 nm. This photosensitivity can be attributed unambiguously to excitation of IPCT states. Interestingly, the photoredox reactivity of the $[Co(NH_3)_6]^{3+}$ complex unit is considerably shifted thereby into the low-energy spectroscopic region. Analogous results have been observed for $\{[Co(NH_3)_6]^{3+}\ htc^{-1}\}$ ion pairs, as mentioned earlier (see Section B(i)) [38]. Further examples of spectroscopically sensitized photoredox reactions initiated by excitation of IPCT states were studied by the present authors. In the case of octacyanomolybdate(IV) as well as other easily oxidizable cyanometallates [43,45], ion pairs consisting of these anions and diareneiodonium cations could be detected and distinguished by strong IPCT bands in the visible region. Interestingly, spectroscopic sensitization could be observed up to 550 nm for the photo-oxidation of $[Mo(CN)_8]^{4-}$ and other cyanometallates. Furthermore, in the case of cobalt(III) ammine complexes, ion pairs formed from tetraphenylborate are also distinguished by IPCT bands [42,241]. Irradiation in the region of the IPCT bands up to about 550 nm leads to very efficient and spectroscopically sensitized photoreduction of cobalt(III), with the concomitant oxidative decomposition of the tetraphenylborate anion (eqn. (48)). Some unusual photoreactions involving cobalt(III) complexes described in the literature are due to excitation of IPCT states [242]

$$[Co(NH_3)_6]^{3+}Ph_4B^- \xrightarrow{h\nu^{IPCT}} Co^{2+} + 6\ NH_3 + Ph_4B^{\cdot} \qquad (48)$$

Although experimental results of photochemical reactions initiated by the excitation of IPCT states are very scarce, this type of spectroscopic sensitization may be especially interesting because it can be achieved very easily. However, apart from an initial attempt at a theoretical interpretation of the IPCT phenomenon [243], based primarily on this kind of electronic interaction between a metal complex and an appropriate counter ion, no further explanation of this very interesting mechanism has appeared. Therefore, at present only tentative concepts exist for predicting systems characterized by IPCT behaviour.

(iv) Static sensitization based on mixed-valence compounds with IT behaviour

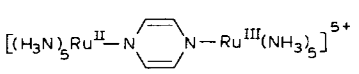
In certain respects, mixed-valence compounds with IT intervalence transfer properties, especially outer-sphere IT systems, are comparable with ion pairs [244,245]. There may be a direct connection between static spectroscopic sensitization based on ion-pair formation and that based on mixed-valence compounds. Mixed-valence compounds distinguished by IT behaviour may be described theoretically within the framework of the conceptual considerations of Robin and Day [246] based on the semiempirical treatment performed by Hush and Allen [247,248]. The general behaviour and the interesting properties of mixed-valence compounds have been excellently reviewed very recently [249]. Mixed-valence complexes, which are distinguished by trapped valencies of both metal centres (class II, using the scheme of classification proposed by Robin and Day [246]) are especially important for spectroscopic sensitization. The minute electron delocalization between the two centres leads to the appearance of IT bands which can be observed from the ultraviolet to the near infrared. Intervalence transitions are due to electron transfer from one metal centre to the other, either within a binuclear bridging complex compound (inner-sphere mechanism) or within an ion pair (outer-sphere mechanism). The position of the IT band depends strongly on the redox asymmetry of both metal centres, the kind of bridging ligand and the dielectric properties of the solvent [249–251]. Therefore, it is possible to prepare a number of mixed-valence complexes which are characterized by spectroscopic transitions from the ultraviolet to the near infrared and which provide interesting long-wavelength spectroscopic sensitization. However, experimental data on photochemical reactions initiated by irradiation in the IT region, which are really due to class II mixed-valence complexes, are very scarce. As far as is known, the first examples of photochemical investigation of class II mixed-valence complexes are the Vogler/Kunkely systems consisting of ruthenium(II) and cobalt(III), as well as iron(II) and cobalt(III) cyano-bridged dimeric compounds [252,253]. The photochemical behaviour of the Vogler/Kunkely system, Ru(II)/Co(III), as well as that of Fe(II)/Co(III), supports strongly the suggestion of the present authors about the advantage of spectroscopic sensitization using IT compounds. For $[(H_3N)_5Co{-}NC{-}Ru(CN)_5]^-$, irradiation in the region of the IT band leads to a very efficient photoredox reaction ($\phi = 0.46$), with the formation of cobalt(II), ammonia and hexacyanoruthenate(III), thus

$$[(H_3N)_5Co{-}NC{-}Ru(CN)_5]^- \xrightarrow[\phi^{IT}=0.46]{h\nu^{IT}} Co^{2+}_{aq} + 5\,NH_3 + [Ru(CN)_6]^{3-} \tag{49}$$

Since neither $[Co(NH_3)_6]^{3+}$ nor $[Ru(CN)_6]^{4-}$ is redox photosensitive in this wavelength region, this reaction may be regarded as being initiated by an IT excited state. Within the framework of the present considerations it is especially important that fast back electron transfer processes are prevented both by extremely fast substitution reactions of the kinetically labile cobalt(II) generated photochemically [253] and by other scavenging reactions [252]. The Vogler/Kunkely system establishes the fact that catalytically interesting cobalt(II) can be generated by photochemical reactions spectroscopically sensitized up to about 550 nm.

The concept of static sensitization based on mixed-valence compounds with IT behaviour can also be applied to other cyanometallates combined with a second metal centre [250,251,254–258]. In the case of octacyanomolybdate(IV), it has been shown that mixed-valence compounds characterized by IT transitions ranging from the ultraviolet to the near infrared can be prepared with a strong dependence on the second metal centre and its coordination sphere [251]. Photochemical investigations have unambiguously indicated photoredox reactions initiated by excitation of IT states [250,251,254–258]. However, very fast back reactions are considered to be the reason for the low efficiency of the spectroscopically sensitized formation of free cyanide, which could be used in a subsequent dark reaction [29] (see Section B(iii)). Very fast scavenging processes must be used to suppress the back electron transfer reactions. In the presence of scavengers it is possible to confirm the role of IT states in initiating the observed photoredox reactions, especially for the copper(II)/$[Mo(CN)_8]^{4-}$ system [250,255,258]. As the use of chemical scavengers proved unsuccessful for various reasons, the use of photons as physical scavengers for short-lived but photosensitive intermediates was tried. A new type of sequential two-photon process, based on mixed-valence compounds with IT behaviour, was thus formulated, using irradiation with conventional light sources (not laser irradiation) and the absorption of photons of diverse energy [250,255,258]. Figure 19 shows the possible mechanism of the sequential two-photon process initiated by IT excitation of $Cu^{2+}/[Mo(CN)_8]^{4-}$ [250,255,258] (NDMA = *p*-nitrosodimethylaniline).

Mixed-valence complexes of class III must also be considered. These complexes, according to the scheme proposed by Robin and Day, are distinguished by stronger electron delocalization between the metal centres [246,249]. The Creutz/Taube [259] ion (50) seems to be better characterized as a compound of class III than as a complex with class II behaviour



(50)

This compound and its interesting behaviour were the starting points for a number of investigations of both homonuclear and heteronuclear mixed-valence compounds distinguished by greater electron delocalization between the two metal centres [246,249,260]. In contrast to the mixed-valence compounds of class II, class III species are distinguished by additional spectroscopic transitions which are not obtained as the sum of the components, but may be attributed unambiguously to normal MLCT transitions. However, irradiation in the region of these bands may also lead to very efficient photoredox reactions in the long wavelength region. Norton and Hurst have described a number of copper(I)/cobalt(III) and ruthenium(III)/copper(I) dimeric compounds bridged by organic ligands which are distinguished by very interesting photochemical behaviour when irradiated in the CT region [261]. However, fast back reactions are considered to lead to spectroscopically sensitized photoreactions which are diminished and suppressed compared with those desired. For example, for pyrazine-bridged copper(II)/ruthenium(II) dimeric complexes, the photoproducts can only be

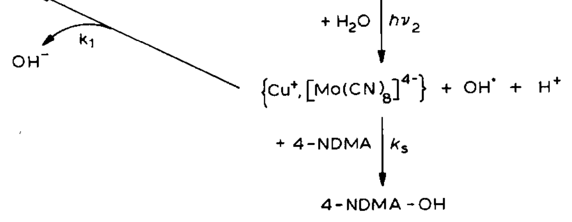
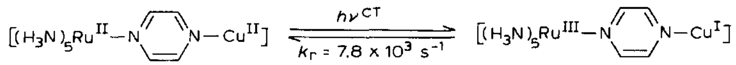


Fig. 19. The potential mechanism of sequential two-photon processes initiated by IT excitation of $Cu^{2+}/[Mo(CN)_8]^{4-}$ [250,255,258] (NDMA = *p*-nitrosodimethylaniline).

observed as short-lived transients [262]



(51)

It should be noted that back electron transfer can be suppressed by scavenging reactions as well as by other fast, and therefore efficient, competitive reactions, such as ligand exchange, decomposition processes or intersystem crossing [252,253,261,263,264].

(v) Static sensitization by mixed-ligand complexes with chromophoric ligands as well as low-lying CT states

Although the first example of static sensitization with chromophoric ligands was reported by Adamson et al. 15 years ago [265], results are very scarce for systems using both additional chromophoric ligands and low-energy CT states for the spectroscopic sensitization of light-sensitive complex units in the long wavelength region. Mixed-ligand complexes containing monodentate or polydentate chromophoric ligands (e.g. azo dyes and other dye chelate ligands) as well as photoredox-sensitive ligands (e.g. oxalate and other acido ligands) have seldom been investigated. However, such systems are interesting since dissociation effects can be neglected for appropriately high formation constants. Furthermore, chromophoric ligands can be selected in such a manner that the whole visible region can be included.

The insertion of mesomerically stabilized substituents or of chromophoric residues (dyes) into a given ligand system can provide complexes with low-energy CT and inner-ligand transitions. The insertion of chromophoric residues can lead to shifts of the absorption band along the whole visible region, whereas bathochromic shifts of more than 200 nm due to the insertion of mesomerically stabilized residues are rarely observed [266]. Furthermore, it is possible to shift the low-energy CT band of a given class of light-sensitive mixed-ligand complexes by coordination of ligands which are characterized by favourable positions of the LUMO and HOMO with respect to the appropriate central metal [267,268,276]. The present authors have shown by experimental and quantum chemical investigations [107,109–111] that the photosensitivity of the cobalt–oxalate unit can be shifted into the visible region by coordination of diverse α-diimine ligands. However, it must be noted that the excitation of such IL and low-energy CT states does not necessarily lead to an electronic perturbation of the complex molecule, which would produce photoredox reactions. Instead of sensitized photoreactions, very fast deactivation of the excited states must be considered as well as other long wavelength photoreactions which are useless as

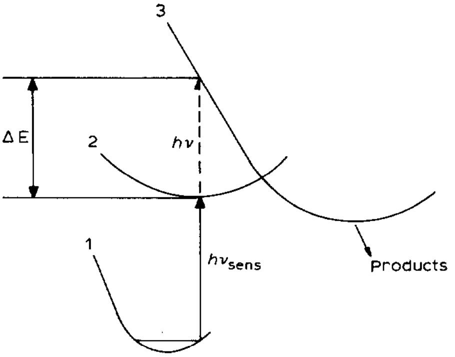


Fig. 20. Long wavelength spectroscopic sensitization achieved by the insertion of chromophoric ligands. The chromophoric ligand leads to light absorption at lower energies, as characterized by ΔE. Spectroscopic sensitization is achieved because the minimum of state 3 is lower than that of state 2, which leads to efficient transitions between states 2 and 3.

catalytic processes. It is obvious that a large number of coordination compounds can be synthesized which absorb in the long wavelength spectroscopic region and which can contain additional redox-sensitive ligands. However, a very interesting point not yet systematically investigated is whether or not these CT or IL states, when added to an a priori photosensitive system, deactivate it by means of inappropriate photochemically reactive states (Fig. 20). Some preliminary results concerning the efficiency of sensitization mediated by azo dye ligands in zinc complexes [269,270] and of eosine and several azo dye ligands in oxalato–cobalt(III) mixed-ligand complexes [271] indicate that this method may yield interesting results.

E. CONCLUSIONS

Photocatalytic reactions mediated by light-sensitive coordination compounds are of considerable and increasing interest. The main aspects concern the use of both photoinduced catalytic and photoassisted reactions in the following fields: the storage and conversion of solar energy; unconventional photographic processes; homogeneous complex catalysis; synthesis—unusual pathways over a wide range of chemistry; light-sensitive metalloproteins and related model systems; coordination-mediated polymerizations and depolymerizations; analysis. Other areas are still being developed. The advantages of photocatalytic reactions include the following: (a) the ready generation of highly reactive species (e.g. coordinative unsaturation, free ligands, changed formal oxidation states, changed acid–base properties, changed redox properties). Contrary to normal thermal reaction pathways, highly reactive species generated photochemically are usually well defined in terms of both their structure and their composition. (b) The physical reagent, light, can be easily adjusted in terms of both the energy and the intensity of the incident photons. (c) Certain reaction pathways can be selected and controlled by excitation of diverse electronically excited states (IL, LF or CT) of appropriate coordination compounds. (d) Chemical reactions can be further controlled by either the switching on (photoinduced catalytic reactions) or switching on and off (photoassisted reactions) of a light source. (e) Both photoassisted and photoinduced catalytic reactions may be carried out under conditions of very low temperature. This is especially important for the preparation of heat-sensitive compounds.

The disadvantages of photoinduced catalytic, as well as photoassisted reactions, are caused mainly by: (a) Fast back-electron-transfer processes and other recombination reactions which strongly influence the real lifetime of highly reactive species (although a number of possibilities for overcoming the disadvantages of fast back reactions do exist). (b) Low turnover numbers for most of the photoinduced catalytic reactions described so far.

Industrial applications of certain photoinduced catalytic, as well as photoassisted reactions, require spectroscopic sensitization over the entire visible spectral region. This is especially important for unconventional photographic processes and for the storage and conversion of solar energy. The subject of spectroscopic sensitization warrants the following comments: (a) Electron transfer processes seem to be of more general importance, when it is possible to suppress the fast back-electron-transfer reactions, than energy transfer processes. (b) Dynamic sensitization based on bimolecular interactions between sensitizers and coordination compounds are characterized by a number of competitive deactivation processes and are to be avoided for practical results. However, Oster systems, for example, clearly demonstrate the efficiency of dynamic sensitization in special cases. (c) The concept of static sensitization can be used to overcome the disadvantages of dynamic sensitization. Static sensitization may be achieved by the direct connection of the sensitizer and the coordination compound in a closed unit. This can be attained by: (i) The formation of ion pairs consisting of a coloured donor ion and an appropriate complex counter ion and by ion pairs which are distinguished by IPCT states of low energy. (ii) The preparation of mixed-valence complexes characterized by IT behaviour. (iii) The syntheses of mixed ligand complexes consisting of photoredox reactive ligands and additional chromophoric centres which lead to low-energy CT bands. (iv) The fast back-electron-transfer processes can generally be prevented by appropriate chemical and physical processes. (v) On the basis of static sensitization, the light sensitivity of certain coordination compounds can be shifted over the whole applicable spectroscopic region.

Sensitization, properly applied to photoassisted and photoinduced catalytic reactions, should provide the key to unlocking a bonanza of industrial applications. The present authors predict a bright future for applied photocoordination chemistry.

Overall, because of the advantages, and despite the disadvantages, of photoassisted and photoinduced catalytic reactions, systematic investigation of such light-induced and light-controlled processes will lead to further surprising results and applications in the near future.

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