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Photocatalysis by transition metal complexes

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ABSTRACT. The principal tendencies in the development of homogeneous photocatalysis by transition metal complexes are examined. Attention is concentrated on the photocatalytic reactions of organic substrates.

The bibliography includes 164 references.

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I. Introduction

Transition metal complexes are well known as excellent highly active catalysts of many homogeneous processes, capable of ensuring not only a high selectivity of the chemical reactions but also the possibility of studying their detailed mechanisms. This makes it possible to act specifically on such reactions by modifying the structure or composition of the catalytic complexes.[1–7] Photochemists have found in their turn that model complexes are objects whose structure and properties can be described quite satisfactorily by modern theories and have used photochemical reactions with participation of transition metal complexes as, on the one hand, an instrument for further improvement of these theories and, on the other, as a means of achieving new chemical reactions which are frequently not merely of academic interest.[8–13] At the junctions of these two fields—homogeneous coordination catalysis and transition metal photochemistry—a new field of physical chemistry, namely photocatalysis by transition metal complexes, has been established and has developed quite vigorously.

Unfortunately the available Russian language monograph and review literature provides an inadequate description of these studies, because it deals mainly with the extremely specific problem of the application of photocatalysis by metal complexes to the direct transformation of solar energy into the energy of chemical fuels (see, for example, Refs. 14–21). The monograph of Kryukov and Kuchmii[13] provides a description of a series of photocatalytic processes on the basis of the photochemical reactions of titanium and iron complexes in aqueous and aqueous organic media. Shul'pin's monograph,[7] devoted to metal complex catalysis as a whole, presents many examples of organometallic photocatalysis, but these are disjointed and are discussed in the context of the problem of the usual thermal catalysis. The only review in Russian devoted directly to the problem of photocatalysis by transition metal complexes is that of Lyashenko.[22]

In the present article, an attempt is made to survey and deal systematically with studies in homogeneous photocatalysis by transition metal complexes in order to acquaint Russian speaking readers with the development and prospects of such research.

In connection with this aspect of the review, the latter is hardly concerned with questions related to the nature of the primary photophysical and photochemical stages of the processes discussed below. Nevertheless, before describing the main material of the review, mention should be made of certain principal characteristics of the nature of the photochemical activity of transition metal complexes.[8]

The following electronic transitions capable of initiating primary photochemical processes take place under the influence of light in transition metal complexes.

Ligand field transitions (LF transitions) or $d-d$ transitions ($f-f$ transitions) occur between orbitals referring to the central ion and are usually observed in the visible region. They are symmetry forbidden for octahedral complexes and the corresponding extinction coefficients are therefore usually small (10^1-10^2 litre mol^{-1} cm^{-1}).

Charge-transfer transitions (CT transitions) are characterised by the transfer of an electron localised predominantly on the central atom to the unoccupied orbitals of the ligand [transition with charge transfer from the metal to the ligand (CTML)] or conversely [transition with charge transfer from the ligand to the metal CTLM)]. Charge-transfer transitions are recorded in the UV region and in the blue part of the visible spectrum. The corresponding extinction coefficients are fairly large—of the order of 10^4 litre mol^{-1} cm^{-1}. A related variety of the transition is phototransfer of an electron from the central metal ion to a solvent molecule or conversely.

Electronic transitions of the above types are responsible for the vast majority of photocatalytic reactions with participation of transition metal complexes. Nevertheless, in many cases other primary photophysical processes, listed below, also play a definite role.

Intraligand transitions (IL transitions), which are frequently called $\pi-\pi$ transitions (because intraligand transitions with participation of σ orbitals lie as a rule in the far UV region and are not manifested in the usual sphere of the complexes), are located in the UV region (with rare exceptions) and are characterised by extinction coefficients up to 10^5 litre mol^{-1} cm^{-1}.

Mention should also be made of charge-transfer transitions which can occur in ion pairs. In dinuclear and polynuclear complexes, there is a possibility of transitions with charge transfer from one metal ion to another (the so called intervalent transitions usually manifested in the presence of a bridging ligand) and also (in the presence of metal–metal bonds) transitions between molecular orbitals) localised on two or more metal ions.

As a result of the absorption of a light quantum, a molecule of the complex receives a large dose of energy: a quantum energy of 2–3 eV corresponds to the visible light and one up to 6 eV corresponds to UV light, while the quantity kT amounts to 0.025 eV at room temperature and the activation energies for the usual thermal ("dark") reactions rarely exceed 1 eV (about 100 kJ mol^{-1}). However, the absorption of a light quantum cannot be regarded as selective 'heating' of an individual molecule. Not the magnitude of the adsorbed energy but a completely definite rearrangement of the electronic structure of the complex is important for the initiation of the photochemical reaction.

For example, as a result of a LF transition, an electron is transferred from a bonding orbital to a non-bonding or antibonding orbital (or from a non-bonding to an antibonding orbital) which entails a weakening of the bond between the central ion and the ligand. Therefore the preferred model of reactions with participation of excited LF states is dissociation or isomerisation of the complexes.

As a result of charge-transfer transitions

$$ML + h\nu \xrightarrow{CTML} M^+L^-$$

$$ML + h\nu \xrightarrow{CTLM} M^-L^+$$

(here and henceforth M and L are understood as the initial states of the metal ion and of one of the ligands of the complex respectively), species differing sharply from non-excited states in their oxidation-reduction properties are formed. Depending on the oxidation-reduction properties of the ligand and the central ion, the nature of the solvent, and the presence in the solution of other compounds, etc., reactions of the excited state of the complex with participation of both $M^+(M^-)$ and $L^-(L^+)$ can take place under these conditions.

Overall, the probability of the occurrence of the primary photochemical reaction in a particular direction can depend on the wavelength of the exciting light, the nature of the excited state, its lifetime, the nature of the solvent, the presence of other substances in solution, etc. Thus the lifetime of the excited state is a parameter which is particularly critical for bimolecular reactions. Indeed, for excitation lifetimes less than 10^{-10} s and reasonable concentrations of the reactants in a homogeneous solution or in the gas phase, the attempts to carry out a bimolecular reaction with participation of such an excited state are virtually hopeless. However, unimolecular reactions (including those with coordinated molecules of substrates) are entirely feasible even for such short times. By altering the wavelength of the exciting light, it is possible to generate more or less selectively various excited states of the same complex or to excite particular compounds among those present in the reaction system and influence thereby the mode of reaction.

Photocatalytic processes are more complex than "simple" photochemical reactions, because they usually include at least two stages. Therefore, before considering specific examples, it is useful to deal with questions of the terminology and classification of the phenomena in the field of photocatalysis.

II. What is understood by the term "photocatalysis"

The term "photocatalysis" and the concepts of "photocatalytic reaction" and "photocatalyst" associated with it are extremely widely encountered in the literature. A whole series of recent books and reviews are fully or partly devoted to photocatalysis.[14–36] At the same time there is as yet no rigorous and generally accepted definition of this concept, which has been noted by almost everyone who has attempted to deal systematically with the terms used in this branch of knowledge.[7,26,28–30,37–39] One of the common approaches consists in the widest possible treatment of the concept of "photocatalysis", which has been firmly expressed by the definition recommended by the IUPAC Commission:[40] "photocatalysis is catalytic reaction involving the absorption of light by the catalyst or the substrate". The reactions included in this definition can be described by the generalising equations

$$S \xrightarrow[K]{h\nu} P \text{ or } S + R \xrightarrow[K]{h\nu} P + Q.$$

Here and henceforth the symbols S and R denote the substrate and reactant molecules, the symbol K represents the initial form of the catalyst or the photocatalyst, and P and Q are reaction products. It is significant that this formulation embraces processes of most varied types. A more rigorous systematic treatment of the process under consideration is therefore proposed below (see also Parmon[39]).

1. Photogenerated (photoinduced photoinitiated) catalysis. The reaction proceeds in accordance with the scheme

$$\begin{aligned} &K \xrightarrow{h\nu} K', \\ &S \xrightarrow{K'} P. \end{aligned} \qquad (I)$$

Here light is used to generate the active form of the catalyst K′, which ensures the occurrence of the usual "dark" catalytic reaction. In principle, if this active form is not deactivated, the rate of the photoinitiated reaction should remain unchanged also after light has been switched off.

2. Catalysis of a photochemical reaction. The scheme

$$\begin{aligned} &S \xrightarrow{h\nu} {}^*S, \\ &{}^*S \xrightarrow{K} P. \end{aligned} \qquad (II)$$

or

$$\begin{aligned} &S \xrightarrow{h\nu} P', \\ &P' \xrightarrow{K} P. \end{aligned} \qquad (IIa)$$

corresponds to this case. After the absorption of light by the substrate S, its excited state *S or the primary photoproduct P′ undergo a catalytic reaction with formation of the final product P.

3. Photosensitised reaction. Reactions involving the transfer of energy from the photosensitiser K to the substrate S are usually referred to this type:

$$\begin{aligned} &K \xrightarrow{h\nu} K^*, \\ &S + {}^*K \rightarrow {}^*S + K, \\ &{}^*S \rightarrow P. \end{aligned} \qquad (III)$$

It is not noteworthy that the term "photosensitisation" is treated, like the term "photocatalysis", very broadly.[38] Thus reactions

involving the phototransfer of an electron, for example in accordance with the scheme

$$\begin{aligned} &K \xrightarrow{h\nu} {}^*K, \\ &{}^*K + S \rightarrow K^+ + S^-, \\ &S^- \rightarrow P, \\ &R + K^+ \rightarrow R^+ + K, \\ &R^+ \rightarrow Q. \end{aligned} \qquad \text{(IIIa)}$$

are frequently classified as photosensitised.

Such extended treatment is apparently not entirely legitimate because electron transfer is a chemical reaction, albeit of the simplest kind, in contrast to the transfer of excitation energy. A reaction in accordance with mechanism (IIIa) should therefore be referred to photocatalysis (type 4).

4. Photocatalysis proper. In the English language literature, reactions of this type are frequently designated as "photoassisted catalysis", i.e. "catalysis with the assistance of light". The simplest cases of photocatalysis are described, together with scheme (IIIa), also by the schemes

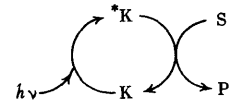
$$\begin{aligned} &K \xrightarrow{h\nu} {}^*K, \\ &S + {}^*K \rightarrow P + K. \end{aligned} \qquad \text{(IV)}$$

[the difference from scheme (III) consists in the absence of the transfer of electronic excitation to the substrate] or

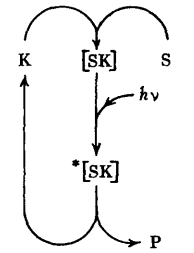
$$\begin{aligned} &S + K \rightarrow [SK], \\ &[SK] \xrightarrow{h\nu} {}^*[SK], \\ &{}^*[SK] \rightarrow P + K. \end{aligned} \qquad \text{(IVa)}$$

In this case, the catalyst participates directly both in the light absorption step, {either in the form of an individual compound of K via scheme (IV) or as a complex with the substrate [SK] via scheme (IVa)}, and in the step involving the catalytic conversion of S into P. Thus a photochemically active catalyst, i.e. the *photocatalyst* proper, is present in the system. In our view, this last factor justifies the naming of reactions of this particular type as truly photocatalytic.

Returning to the extended definition of photocatalysis proposed by IUPAC, we note that it does of course have the right to exist. This is because, for example, the real mechanisms of catalytic reactions occurring under the influence of light are frequently unknown, at any rate in the initial stages of the investigation. Therefore, if it has only been established that the reaction is catalytic and that light influences its rate or pathway, it is reasonable to refer to such reactions as photocatalytic *in a broad sense*. On the other hand, if it is found on closer examination that the reaction is in fact of the dark "thermal" type, as in scheme (I), or the catalyst is not involved in the absorption of light [i.e. is not a photocatalyst, as in scheme (II)], or the reaction is not catalytic at all [i.e. there is no chemical interaction between the light-absorbing compound and the substrate, as in scheme (III)], then in such cases one should avoid using the term "photocatalysis" and apply it only to designate processes illustrated by schemes (IIIa), (IV), and (IVa). This approach to the term "photocatalysis", which we have followed consistently during the last ten years,[15] is based on the definition of the concept of "catalysis" given by Boreskov.[41] The corresponding formulation is as follows: "photocatalysis is the change in the rate or excitation of chemical reactions under the influence of light in the presence of substances (photocatalysts) which, as a result of the absorption of light quanta by them, are capable of inducing chemical reactions of the reactants by entering into intermediate chemical interactions with the latter and regenerating their own chemical composition after each cycle of such interactions". Within the framework of this definition, two situations, illustrated by Schemes (IV) and (IVa), are possible, which can be represented, for greater clarity, by the following cyclic schemes respectively:



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These cyclic schemes differ in the sequence in which light is absorbed and the photocatalyst reacts chemically with the substate. However, in both cases the photocatalyst participates in the two stages indicated.

III. Photocatalytic reactions with participation of transition metal complexes as photocatalysts

To facilitate the subsequent analysis, photocatalytic reactions with participation of transition metal complexes can be divided into two groups: (1) "inner sphere" reactions in which bonds are dissociated and/or formed in the inner sphere of the metal complex; (2) "outer sphere" reactions in which the main transformations of the substrate molecules occur outside the inner sphere of the complex. Reactions of the first type are in fact characteristic of transition metals with their unique ability to form a wide variety of coordinate bonds. Reactions of the second group are in our view not so specific to coordination compounds, because their first stage is always electron phototransfer—a process characteristic of a wide range of compounds, especially organic ones. Nevertheless, certain characteristic features of metals complexes enable them to occupy a special place also among photocatalytic reactions of the second type. The most characteristic features of reactions of both types are considered below in succession.

1. Inner sphere photocatalytic reactions

Among reactions of this type one can distinguish, in their turn, two subgroups: (1) reactions with participation of transition metal complexes with organic ligands; (2) reactions with participation of simple inorganic metal complexes. The difference as regards the type of ligands is extremely arbitrary because in reactions of the first subgroup compounds of the type CuCl frequently occur as initial photocatalytically active substances, while the substrates in reactions of the second group are usually organic compounds which are, in principle, capable of forming coordinate bonds with the ions of the photocatalytically active complex in some stage of the process. However, a significant difference between these subgroups nevertheless exists and is manifested by the nature of the initiated reactions.

Table 1. Inner-sphere photocatalytic reactions with participation of organometallic and other related complexes.

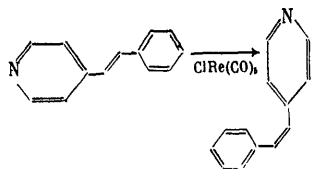
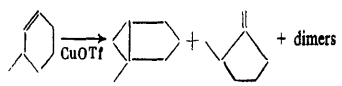
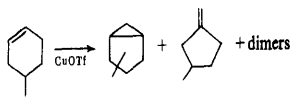
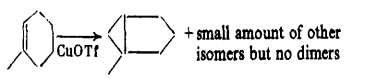
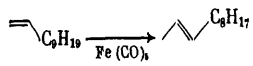
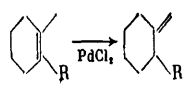
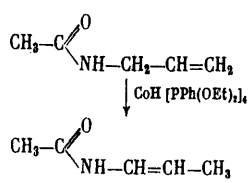
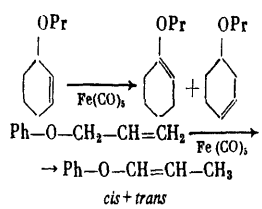
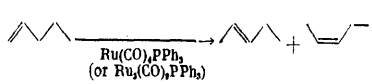
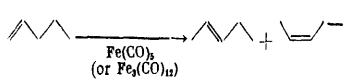
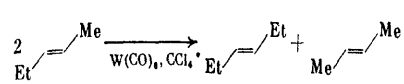
Type of reaction	Examples	Mechanism	Comments	References
Geometrical isomerisation of alkenes		PC	The non-catalytic reaction takes place only under the influence of UV light, while in the presence of $ClRe(CO)_5$ it occurs under the influence of light with $\lambda = 436$ nm	[43]
	Ditto in the presence of $W(CO)_6$	PG+PC		[23, 44]
Skeletal isomerisation of alkenes		PC		[45]
				
				
Allyl shift		PG		[46]
		PC	An anomalous allyl shift involving an increase in free energy takes place under the influence of light	[26]
		PG	Flash photolysis showed that the substrate is coordinated to the catalyst via the double bond and not the nitrogen atom	[47]
		PG	Reactions of this type usually occur on heterogeneous catalysts of the type KNH_2/Al_2O_3, but the first reaction does not occur on them at all while the second affords only the *cis*-product	[48]
		PG	φ reaches 400; the Ru_3 trimer is active in the visible region	[49]
		PG	The photogenerated catalyst exhibits a very high activity compared with the traditional "dark catalyst"	[50]
Metathesis		PG		[51]
	Ditto in the presence of $W(CO)_5L + ZrCl_4$ in *n*-heptane	PG	The reaction proceeds at room temperature with a high selectivity	[52]

Table 1 (cont'd).

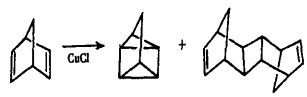
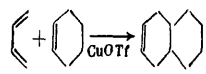
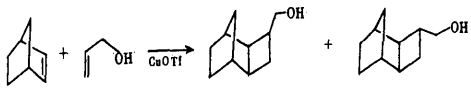
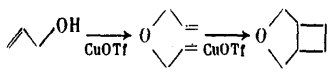
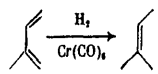
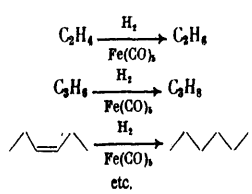
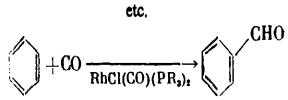
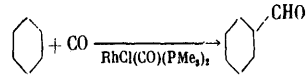
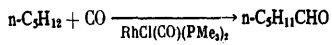
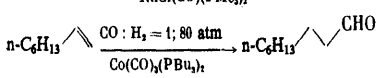
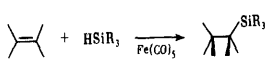
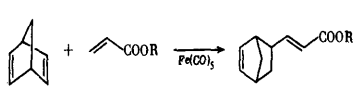
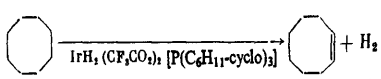
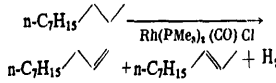
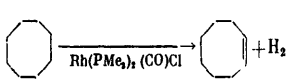
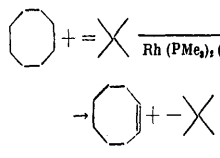
Type of reaction	Examples	Mechanism	Comments	References
Cycloaddition of alkenes		PC	The turnover number of the photocatalyst reaches almost 400; $\varphi = 0.34$ and is independent of the substrate concentration; the formation of a complex between the photocatalyst and the substrate in the ground state is confirmed by UV spectra	[53]
		PC		[54]
		PC	In contrast to the examples presented previously, not only hydrocarbons but also an oxygen-containing compound participates in the reaction	[55]
		PC		[56]
Hydrogenation		PG	The reaction continues for several hours after switching off the light	[57]
		PG	$Fe(CO)_5$ catalyses the reaction also in the absence of illumination but at $T > 150$ °C, while in the presence of light with $\lambda > 366$ nm the reaction takes place at room temperature or even at $T < 0$ °C	[58]
Carbonylation		PG	Flash photolysis showed that CO and not phosphine is split off under the influence of light	[59]
		PG		[60]
		PG		[61]
Hydroformylation		PG	$\lambda = 366$ nm; the photocatalytic reaction takes place at 85 °C but there is no thermal catalysis under these conditions	[62]
Addition to C=C bond		PG		[63, 64]
		PC		[65]
Dehydrogenation		PC		[66, 67]
		PC		[68]
		PC		[69]

Table 1 (cont'd).

Type of reaction	Examples	Mechanism	Comments	References
Dehydrogenation with transfer of hydrogen		PC		[69]
Reduction of CO_2	$CO_2 + N(CH_2CH_2OH)_3 \xrightarrow{Re(bipy)(CO)_3Cl} CO + TEA$ oxidation products	PC	See also Table 3	[70]
Water gas shift reaction	$CO + H_2O \xrightarrow[Co(CO)_4]{} CO_2 + H_2$	PG		[71]
	Ditto in the presence of Ir $[(\eta^5-Me_5C_5)Ir(bipy)X]^+$, where X=$Cl^-$ or H^-	PC		[72]
	Ditto in the presence of $HFe(CO)_4^-$	PC		[73]
Polymerisation	Polymerisation of methyl methacrylate, styrene, and other olefins in the presence of $Ti(CH_2Ph)_4$ or $Zr(CH_2Ph)_4$	PG		[74–76]

Note. PC = "true" photocatalysis; PG = photogenerated catalysis; φ = quantum yield.

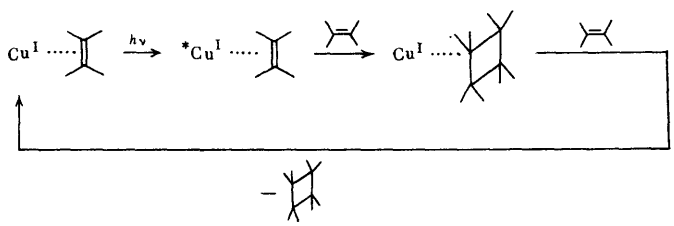
(a) Photocatalysis with participation of complexes containing organic ligands

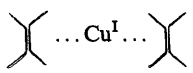
Photocatalysis with participation of complexes containing organic ligands, in particular "organometallic photocatalysis", is a dynamically developing research field (see, for example, the relevant reviews[23,25,26,29,30,38,42]). The wide variety of chemical reactions which have been achieved in systems of this type is noteworthy. Examples are presented in Table 1, which includes only the most typical and interesting reactions. Those wishing to do so, may find an extensive compilation of reactions of this type in another review[26] and also in recent publications.[38,42]

As can be seen from Table 1, this group includes alkene isomerisation reactions (geometrical and skeletal isomerisation, the allyl shift), metathesis, alkene cycloaddition reactions, hydrogenation, carbonylation, and other processes, i.e. reactions which are, in principle, usual for traditional homogeneous catalysis. Furthermore, the majority of the photocatalytically active compounds are at the same time also traditional (thermal) homogeneous catalysts [$M(CO)_n$, $M(CO)_nL_m$, $M(CO)_n(PPh_3)_mL_k$, CuOTf, $Co(OAc)_2$, etc., where M = Rh, Ir, Fe, Ru, etc. and OTf = trifluoromethanesulphonate]. This gives rise to an especially convenient possibility of comparing reactions occurring in photocatalytic and dark (thermal) catalytic regimes and to discover the characteristic features occurring in photocatalytic and dark (thermal) catalytic regimes and to discover the characteristic features of the photocatalytic method of effecting a number of organic reactions. Comparison shows that, firstly, photocatalytic reactions can occur under much milder conditions than the analogous dark reactions. The hydrogenation of olefins in the presence of $Fe(CO)_5$ can serve as an example: when the system is acted upon by light ($\lambda > 366$ nm), the reaction takes place at a temperature lower by ~150 °C than under dark conditions.[58] This feature may be fundamentally important in syntheses with participation of thermolabile reactants or products and the photocatalytic procedure is in such cases the only one possible. Secondly, the catalyst, formed as a result of its photochemical generation, is not usually inferior as regards its activity, and sometimes is actually superior, to the catalysts obtained under similar conditions by the thermal method.[50] This means that the generation of the catalyst under the influence of light can, in principle, compete with the usual thermal activation of the catalyst, ensuring under identical conditions a higher rate of reactions. Thirdly, direct thermal catalysis of reactions accompanied by a significant increase in free energy is as a rule altogether impossible. In such cases, the photocatalytic (or at least photochemical) method of effecting the reaction via the given pathway, capable of "pumping" energy into the system, is the only one possible. Examples of photocatalytic reactions accompanied by an increase in free energy are certain cycloaddition reactions[53] and the anomalous allyl shift[26] (see also Table 1). Fourthly, photocatalysis can promote the occurrence of photochemical non-catalytic reactions, which is manifested, for example, by spectral sensitisation. Thus direct photochemical *trans–cis* isomerisation of 4-styrylpyridine takes place only under the influence of UV light, whereas in the presence of the $ReCl(CO)_5$ photocatalyst it becomes possible under the influence of visible light with $\lambda = 436$ nm.[43] Similarly, the cycloaddition reactions of olefins in the presence of photocatalysts, for example, copper(I) salts, require milder UV light.[53]

The photocatalytic processes under discussion can proceed via one of two dominant mechanisms. The first is true photocatalysis, which can always be described in terms of a sequence of reactions [scheme (IVa)]. This mechanism has been demonstrated quite satisfactorily, for example, for the olefin cycloaddition reaction in the presence of copper(I) salts.[26] Trifluoromethanesulphonate (triflate, OTf^-) is frequently used as the negatively charged ligand, although the reactions take place also when copper(I) is present in the system as

halide salts (chlorides and bromides). In an olefin solution, the central copper(I) ion coordinates the olefin via its double bond. The presence of such coordination is confirmed by UV spectra—a charge-transfer band, more intense than the bands of the initial compounds, arises. This results, firstly, in an increase in the ability of the system to absorb light, which is actually of intrinsic importance because there exists also a purely photochemical reaction pathway. Secondly, the excitation of the copper(I)–olefin complex by light corresponding to the CTML absorption band leads to a redistribution of electron density among the π orbitals of the olefin, so that the cycloaddition reaction in conformity with the Woodward–Hoffmann rule is promoted. Thirdly, and finally, copper(I) can function as a common coordinating site for the two reacting molecules similarly to what happens in the usual coordination catalysis:[26]

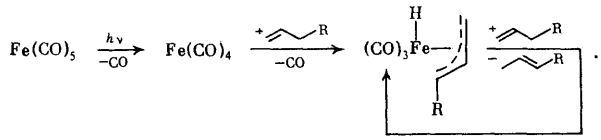


The interaction of the excited complex *Cu...  with another olefin molecule (or the intramolecular transformation of the complex ) results in the formation of a saturated cyclobutane ring, which interacts with copper(I) much more weakly than the C=C bond and is therefore rapidly substituted by a new olefin molecule. The catalytic cycle is thus closed.

The second mechanism operating in the group of reactions considered is photogenerated catalysis [see scheme (I)]. The catalyst is photogenerated as a rule as a consequence of an increase in the lability of complexes in the $d-d$ excited state. As already mentioned, the rate of reaction proceeding via the photogenerated catalytic mechanism should ideally remain unaltered after light has been switched off. In certain cases, the observed reactions do indeed continue for a long time after light has been switched off, as happens, for example, in the hydrogenation of 2-methylbuta-1,3-diene in the presence of $Cr(CO)_6$.[57] However, the deactivation of the active form of the photogenerated catalyst is frequently extremely rapid, i.e. the reaction actually takes place only in the light and is outwardly manifested as a true photocatalytic process. Thus the isomerisation of pent-1-ene to a mixture of *cis-trans*-pent-2-enes in the presence of iron carbonyls ceases after light has been switched off less than 5 s.[50] The activation of the photogenerated catalyst usually takes place as a result of the occurrence of processes which are the reverse of those which take place during its generation. For example, the active form of iron pentacarbonyl is the coordinatively unsaturated compound $Fe(CO)_4$:

$$Fe(CO)_5 \underset{\text{generation}}{\xrightarrow{h\nu}} Fe(CO)_4 + CO \underset{\text{deactivation}}{\longrightarrow} Fe(CO)_5.$$

If the rate of coordination of $Fe(CO)_4$ to the substrate does not exceed appreciably the rate of the reverse addition of CO, then the turnover number of such a species in the catalytic process from the instant of generation to the instant of deactivation will be relatively small, which actually happens in the pent-1-ene isomerisation reaction. The catalytic reaction proper proceeds via the mechanism usual for processes of this type:



The quantum yield of this reaction can reach several tens, which permits its entirely definite assignment to photogenerated catalytic processes.

(b) Photocatalysis with participation of metal complexes containing simple inorganic ligands

Typical photocatalysts of this group are $TiCl_4$, $FeCl_4^-$, CuCl, $CuCl_2$, VCl_3, $SnCl_4$, oxo-compounds of molybdenum and tungsten, and certain others. However, as in the case examined above, a common factor here is not only and not so much the nature and structure of the photocatalysts themselves as the reactions achieved with their aid. Examples of reactions of this group are compiled in Table 2. These are in the main reactions involving addition to the double bond (C=C and C=X) as well as a wide variety of oxidation reactions. Among the latter, those in which the oxidant employed is not oxygen (or any kind of other traditional oxidant, for example, hydrogen peroxide) but protons (hydronium cations), present in water or in mixed aqueous organic media, have attracted special attention. Simultaneously with the oxidation of organic compounds, such processes involve the reduction of water or other proton-containing compounds to molecular hydrogen. A reaction of this kind frequently represents stoichiometrically the dehydrogenation of organic compounds. For example, in the very first study of this topic,[90] the process

$$C_2H_5OH \xrightarrow[VCl_3]{h\nu} CH_3CHO + H_2, \qquad (1)$$

which is equivalent to the dehydrogenation of alcohol to acetaldehyde, was described. Unfortunately the occurrence of processes with photocatalysts of the type indicated requires as a rule UV light, the proportion of which in the solar spectrum is very small. The photocatalytic generation of hydrogen with the aid of such complexes from water and other readily available hydrogen-containing and/or electron-donating compounds, which is attractive from the standpoint of the utilisation of solar energy, is hardly promising for practical application.

The difference between the mechanisms of the reactions under discussion is significant. Thus in the reactions of the first group, described in the previous Section, the primary photochemical processes are as a rule either intramolecular transformations of substrates coordinated to the photocatalyst or photodissociation with formation of a coordinatively unsaturated species responsible for the catalytic activity. On the other hand, the primary chemical step in reactions of the second group is electron phototransfer from the metal ion or to the metal ion. Here the second reactant may be the ligand of the initial complex or directly the substrate present in the first or second coordination sphere. The detailed mechanism of primary photoprocesses of this kind has been investigated in detail[102–112] in relation to iron(III) and copper(II) chloride complexes. In the presence of an organic substrate, whose concentration is sufficient to ensure the presence of substrate

Table 2. Inner-sphere photocatalytic reactions with participation of metal complexes with simple inorganic ligands.

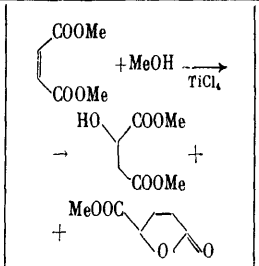
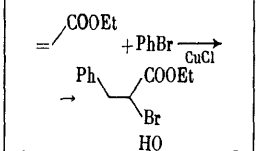
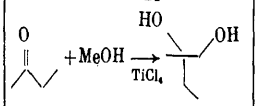
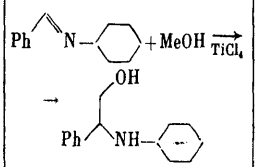
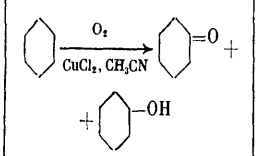
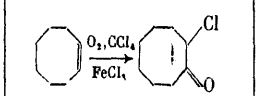
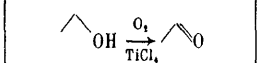
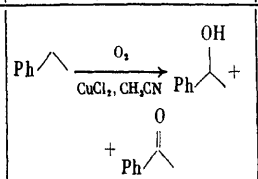
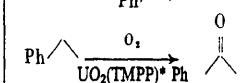
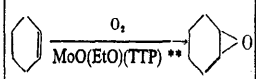
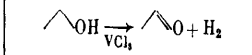
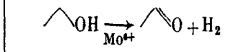
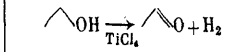
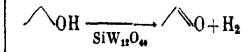
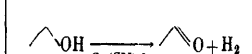
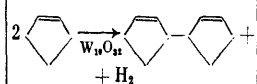
Type of reaction	Examples	Mechanism	Comments	References
Addition to >C=C< bond		PC	Similar reactions occur in the presence of $UOCl_2$	[77]
		PC		[78]
Addition to >C=X bonds		PC		[13, 77, 79–81]
		PC		[77]
Oxidation of alkanes		PC		[82]
	$C_2H_6 \xrightarrow[Hg^{2+}]{O_2} CO_2$ (main product)	PC in the first stage, noncatalytic photochemical reaction (λ_{irr} = 254 nm) in subsequent stages		[83]
	$CH_4 \xrightarrow[\text{polyoxotungstates}]{O_2} HCHO + HCOOH$	PC	CO_2 is hardly formed	[84]
Oxidation of alkenes		PC		[85]
Oxidation of alcohols		PC	$\varphi \simeq 5-7$ as a consequence of chain initiation of the oxidation process	[86]
Oxidation of arenes and alkylarenes	$PhCH_3 \xrightarrow[FeCl_3]{O_2} PhCH_2OOH$	PC		[81]
	Alizarin S $\xrightarrow[Co(NH_3)_5Br]{H_2O_2}$ colourless oxidation products	PG		[87]

Table 2 (cont'd).

Type of reaction	Examples	Mechanism	Comments	References
		PC		[82]
		PC		[88]
Epoxidation		PG(?)		[89]
Evolution of hydrogen		PC	Aqueous ethanol solution	[90, 13]
		PC		[91]
		PC		[92]
		PC		[93, 94]
	$H_2O + CN^- \xrightarrow[Co(CN)_5^{3-}]{} {}^1/_2 H_2 +$ $+ OH^- + CN^-$ oxidation products	PC		[95]
		PC		[96]
		PC		[97]
	$H_2O + SO_3^{2-} \xrightarrow[CuCl_2]{} H_2 + SO_4^{2-}$	PC	The presence of I^- as cocatalyst is necessary	[98, 99]
Decomposition of hydrogen peroxide	$H_2O_2 \xrightarrow[Cu^{2+}_{aq}]{} H_2O + {}^1/_2 O_2$	CPCR***		[100, 101]
	Ditto in the presence of Fe(EDTA)	CPCR***		[101, 102]

* TMPP = 5,10,15,20-tetrakis(4-methoxyphenyl)porphinate.
** TTP = 5,10,15,20-tetrakis(4-tolyl)porphinate.
*** CPCR = catalysis of photochemical reaction; see also the footnotes to Table 1.

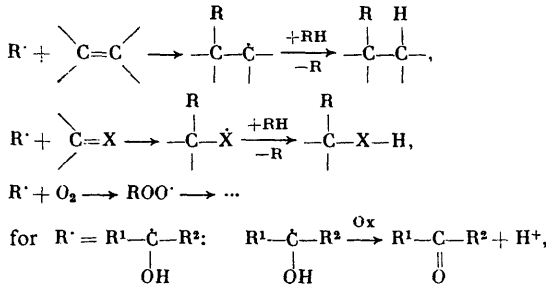
molecules in the second coordination sphere, the following processes take place in the system:

$$MCl_n \xrightarrow[CTLM]{h\nu} {}^*MCl_n$$

$$^*MCl_n + RH \rightarrow M^-Cl_n \ldots R^{\cdot} + H^+,$$

$$M^-Cl_n \ldots R^{\cdot} \rightarrow M^-Cl_n + R^{\cdot}.$$

The organic radical $R^{\cdot}$ can enter into a wide variety of reactions which depend on the structure of the radical itself and on the presence in solution of other organic compounds, for example:[26]



for $R^{\cdot} = R^1-\dot{C}(OH)-R^2$: $R^1-\dot{C}(OH)-R^2 \xrightarrow{Ox} R^1-C(=O)-R^2 + H^+$,

for $R^{\cdot} = R^1COO^{\cdot}$: $R^1COO^{\cdot} \rightarrow (R^1)^{\cdot} + CO_2$.

The completion of the photocatalytic cycle requires the return of the metal ion to the initial oxidation state. In the example presented, this can be achieved either by the "dark" (thermal) oxidation of the reduced metal ion by a sufficiently strong oxidant, for example:

$$M^-Cl_n + O_2 \rightarrow MCl_n + O_2^-,$$

or photochemically. In the latter case, it is possible to use extremely weak or kinetically inert oxidants:

$$M^-Cl_n + RH \xrightarrow{h\nu} MCl_n + R^- + H^{\cdot}.$$

Thus the most important common feature of photocatalytic reactions of the second group is their free-radical mechanism.

In conclusion, we shall attempt to make a prediction of the development of studies in the given field of photocatalysis. Firstly, this will undoubtedly be the search for new types of reactions capable of being effected under photocatalytic conditions. It is extremely likely that such search will lead to the creation of commercially interesting photocatalytic syntheses. Secondly, one may expect a general increase in the quality of the photochemical aspect of the research into photocatalytic processes, for which an urgent need exists. The point is that, among the large total number of publications on the field under discussion, the proportion of studies carried out at a satisfactory photochemical level is relatively small. This is apparently due to the fact that the majority of studies have been performed by specialists in the field of traditional catalysis and not by photochemists. In many of the published investigations, the experiment consisted merely in the irradiation of the catalytic system by light for a fixed time with subsequent analysis of the final products. By no means all the investigations involve the measurement of the quantum yields of the products. So far the only examples remain those where the reaction mechanisms were investigated by the technique of flash photolysis, which makes it possible to identify the intermediates in photochemical reactions (among these studies, mention should be made of Refs. 47, 50, 59, 113, 114). Thus further progress in this field of photocatalysis requires the joint efforts of specialists in catalysis and photochemists.

2. Outer-sphere photocatalytic reactions

The reactions proceeding via Scheme (3a) or via analogous schemes in which the primary step in the outer-sphere biomolecular stage of the electron transfer are described in this Section. At first sight, these reactions have no specific features which would distinguish them from processes initiated by non-metal complex compounds (for example, organic dyes). However, the transition metal complexes widely used in such reactions [the most popular among them is $Ru(bipy)_3^{2+}$, where bipy = 2,2′-bipyridyl] exhibit an important difference from the organic dyes mentioned above despite the similarity of their photophysical, photochemical, and electrochemical characteristics. The point is that the catalytic cycle in Scheme (IIIa) includes the products of the one-electron oxidation (reduction) of the photocatalyst. In the case of organic dyes, such products are organic radical-cations or radical-anions, which are known to enter extremely readily into fact disproportionation, nucleophilic or electrophilic addition or substitution, etc. reactions.[115] This greatly restricts the range of reactions (and their conditions) in which the K^+ and K^- species can participate. On the other hand, in transition metal complexes, usually the metal ion itself undergoes oxidation-reduction. As a result of this, many transition metal complexes can exist in two, three, or even more forms differing in the oxidation state. The transitions between these forms are usually characterised by a high degree of reversibility.

As mentioned above, the initiation of oxidation-reduction reactions by photocatalysts becomes possible by virtue of the significant difference between the oxidation-reduction properties of the complex in the excited state and its properties in the initial state. In principle, these differences arise not only in a charge transfer transition but also in any other types of excitation (intraligand transitions, $d-d$ transitions, etc.). The predominant involvement of precisely the CT-excited states in oxidation-reduction reactions is mainly due to kinetic factors which are favoured by the corresponding redistribution of electron density on excitation of the complex. The formal oxidation-reduction potentials (ORP) of the excited state of the photocatalytic complex can be estimated knowing the formal oxidation-reduction potential of its ground state and the electronic excitation energy. For example, the electrochemical oxidation and reduction potentials of the complex $Ru(bipy)_3^{2+}$ are -1.28 and $+1.26$ V relative to the normal hydrogen electrode (NHE) respectively.[116] The energy of the longest-lived and chemically most reactive excited state of this complex, determined from the position of the luminescence band, is 2.12 eV.[116] Consequently the formal electrochemical oxidation and reduction potentials of $^*Ru(bipy)_3^{2+}$ are $-1.28 + 2.12 = 0.84$ V and $+1.26 - 2.12 = -0.86$ V respectively. Thus the complex, which is extremely inert in the ground state, becomes a powerful oxidant and reductant simultaneously as a result of excitation.

It is also important to emphasise that the photocatalytic oxidation-reduction reactions via the outer-sphere mechanism are frequently induced, in contrast to the processes described above, under the influence of visible and not UV light. This permits the employment of sunlight, which increases the interest in processes of this kind.

(a) Photochemical decomposition of water

Among the outer-sphere oxidation-reduction photocatalytic reactions, the reaction involving the decomposition of water into hydrogen and oxygen has undoubtedly attracted most attention:

$$2H_2O \xrightarrow{h\nu\ K} 2H_2 + O_2.$$

Numerous review articles (see, for example, Refs. 14–21 and the literature quoted therein) have been devoted to the discussion of this process. The photocatalytic decomposition of water can be described by Scheme (IIIa), where the role of the substrates S and R is assumed by the same substance (H_2O). The decomposition of water under the influence of light is a functional analogue of the natural photosynthesis in green plants with the sole difference that the place of the extremely complex process involving the reduction of CO_2 to carbohydrates is taken in this instance by the simpler reaction in which water is reduced to hydrogen. The effective occurrence of this reaction under the influence of visible light (sunlight) would be of enormous practical importance, because it would make it possible to obtain an inexhaustible source of hydrogen—an ecologically clean fuel with a high heat generating capacity. This is why the vast majority of studies on outer-sphere photocatalysis have been devoted to the decomposition of water.

The idea of creating an artificial analogue of plant photosynthesis apparently arose at the very beginning of the study of its mechanism. However, practical applications appeared only in the first half of the 1970s.[117,118] In particular, during this period the trisbipyridylruthenium(II) complex $Ru(bipy)_3^{2+}$ became the first candidate for the role of the photocatalyst of the decomposition of water.[119–121] The most important advantage of this complex is its photochemical activity when the system is acted upon by visible (green and blue) light, the reduction potential of the complex $*Ru(bipy)_3^{2+}$ in the excited state (−0.86 V) being sufficient to reduce water to hydrogen over the entire pH range, while the potential of the oxidised form $Ru(bipy)_3^{3+}$ (+1.26 V) is sufficient for the oxidation of water to oxygen, also over the entire pH range. The achievement of the following photocatalytic cycle is therefore extremely attractive:

$$Ru(bipy)_3^{2+} \xrightarrow{h\nu} *Ru(bipy)_3^{2+}, \quad (2)$$

$$*Ru(bipy)_3^{2+} + H_2O \rightarrow Ru(bipy)_3^{3+} + {}^1/_2H_2 + OH^-, \quad (3)$$

$$Ru(bipy)_3^{3+} + {}^1/_2H_2O \rightarrow Ru(bipy)_3^{2+} + {}^1/_4O_2 + H^+. \quad (4)$$

However, the operation of this scheme requires the preliminary solution of a number of serious problems. In the first place, the oxidation-reduction reactions with direct participation of $Ru(bipy)_3^{2+}$ are one-electron processes, whereas the water reduction and oxidation reactions are respectively two- and four-electron processes. Therefore the formation of the molecular water decomposition products requires the use of additional catalysts. Furthermore, the chemically reactive excited state $*Ru(bipy)_3^{2+}$ is short-lived (620 ns in water at 298 K) and is evidently incapable of participating directly in the catalytic reaction (3). As a consequence of this, the use of an intermediate electron acceptor and the inclusion in the photocatalytic cycle of "auxiliary" reactions with an intermediate electron acceptor A, instead of reaction (3), is inevitable:

$$*Ru(bipy)_3^{2+} + A \rightarrow Ru(bipy)_3^{3+} + A^-, \quad (5)$$

$$A^- + H_2O \rightarrow A + {}^1/_2H_2 + OH^-. \quad (6)$$

An alternative version involves the use of an intermediate electron donor D:

$$*Ru(bipy)_3^{2+} + D \rightarrow Ru(bipy)_3^{+} + D^+, \quad (7)$$

and the introduction of the stages

$$D^+ + H_2O \rightarrow D + {}^1/_4O_2 + H^+, \quad (8)$$

instead of reaction (4). The inclusion of the additional stages (5)–(8) leads to energy losses, which in practice means a narrowing of the pH range in which the reduction (or oxidation) of water is possible. Finally, the main problem consists in the high probability of the recombination of powerful reductants [$*Ru(bipy)_3^{2+}$, A^-, etc.] and powerful oxidants [$Ru(bipy)_3^{3+}$, D^+, etc.], formed as a result of the absorption of light and the occurrence of primary photochemical reactions. In order to solve these problems, studies on the individual stages of the above hypothetical scheme (2)–(8) and their optimisation have been prosecuted since the second half of the 1970s (Table 3).

Photocatalytic reduction of water to hydrogen at the expense of the oxidation of an irreversibly consumed electron donor (usually an organic compound) which is "sacrificed". The communication describing reaction (1) under the influence of UV light[90] was followed by the appearance of a publication[122] by the same authors in which organic dyes sensitive to visible light were used as photocatalysts. After this, systems based on $Ru(bipy)_3^{2+}$ were proposed in a whole series of communications.[123–129] The use of other metal complexes as photocatalysts is also known, among which the most interesting are structural analogues of chlorophyll—metalloporphyrins.[145]

Photocatalytic oxidation of water to oxygen at the expense of the reduction of an irreversibly consumed electron acceptor, which is "sacrificed". This reaction was achieved for the first time in systems, which were in fact based on $Ru(bipy)_3^{2+}$,[130–133] although examples of its occurrence with participation of metalloporphyrins are also known.[146,147]

Processes involving the separation in space and stabilisation of strong one-electron reductants and oxidants, generated under the influence of light, in microheterogeneous stucturally organised systems. The occurrence of such processes makes it possible to prevent the recombination of the primary photogenerated species by direct collisions. Among systems used to carry out processes of this group, the most promising are believed to be lipid vesicles.[148–151] The first advances were achieved using natural and synthetic porphyrins.[152–155] Subsequently much more effective systems based on $Ru(bipy)_3^{2+}$ and its derivatives were proposed.[156–160]

The coupling of all three fragments of the water photochemical decomposition mechanism, which follows logically from studies carried out the first stage of the research, proved extremely difficult. Although examples of the simultaneous photocatalytic generation of both hydrogen and oxygen in suspensions of lipid vesicles are known,[161] there are as yet no experimental data indicating the complete coupling of all three stages. The results of studies of the possibility of the coupling of the processes involving the reduction of water to hydrogen with photochemical charge separation processes in microheterogeneous systems via the phototransfer of an electron through the bilayer membranes of lipid vesicles are hopeful.[162,163] On the other hand, the attempts to couple the water oxidation reaction to the transmembrane charge separation in such systems have encountered appreciable difficulties.[164] Thus the complete water photodecomposition cycle has so far unfortunately not been achieved owing to the existence of a whole series of serious unsolved problems. The present state and prospects of studies in this field are discussed in a monograph.[21]

(b) Photochemical reduction of CO_2

Another problem solved mainly within the framework of outer-sphere catalysis and also associated with the modelling of photosynthesis is that of the photochemical reduction of carbon dioxide. Hitherto, it has been possible to create chemical analogues of bacterial photosynthesis having achieved the reduction of CO_2 at the expense of the oxidation of irreversibly consumed organic compounds (electron donors). The reaction usually proceeds via the mechanisms

$$*Ru(bipy)_3^{2+} + D \rightarrow Ru(bipy)_3^{+} + D^{+}.$$

$$2Ru(bipy)_3^{+} + CO_2 + H_2O \xrightarrow[cat.]{} 2Ru(bipy)_3^{2+} + HCOO^{-} + OH^{-}$$

(or other CO_2 reduction products, for example CO, CH_4, etc.)

$$D^{+} \rightarrow \text{oxidation products};$$

or

$$*Ru(bipy)_3^{2+} + A \rightarrow Ru(bipy)_3^{3+} + A^{-},$$

$$2A^{-} + CO_2 + H_2O \xrightarrow[cat.]{} 2A + HCOO^{-} + OH^{-},$$

$$*Ru(bipy)_3^{3+} + D \rightarrow Ru(bipy)_3^{2+} + D^{+}.$$

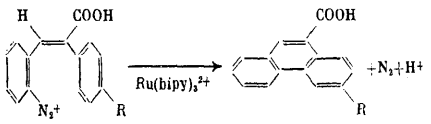
$$D^{+} \rightarrow \text{oxidation products}.$$

Evidently, the photocatalytic CO_2 reduction cycle is virtually identical with the corresponding mechanisms of the evolution of hydrogen from water in "sacrificial" systems. Therefore, in proton-containing media, the usual obstacle to the successful occurrence of the dark stage of the reduction of CO_2 is the occurrence of the competing water reduction reaction. Nevertheless, by selecting the reaction conditions, the CO_2 reduction catalysts, and intermediate electron transferring agents, it has been possible to solve the problem successfully in many instances (Table 3).

(c) Other reactions

In principle, many other chemical reactions requiring the involvement of one-electron oxidants or reductants can proceed via Scheme (IIIa). Thus a system has been proposed in which the hydrogenation and hydroformylation of ethylene and acetylene take place in the presence of $Ru(bipy)_3^{2+}$ and a water-soluble analogue of Wilkinson's complex.[140] A number of photocatalytic reactions described have some kind of bearing on biology. For example, certain enzymic processes (the synthesis of aminoacids and other organic acids by amination or insertion of CO_2), occurring under the influence of NADPH (reduced nicotinamide-adenine dinucleotide phosphate) as the reductant, have been achieved, the reductant being regenerated in the photocatalytic cycle with participation of $Ru(bipy)_3^{2+}$.[141–143] Studies on these lines are apparently promising as regards the development of photocatalytic small-scale syntheses of valuable organic products, biologically active substances, medicinal drugs, etc. Such syntheses may become an alternative to biotechnological industrial processes, particularly if it should become possible to find stable, relatively non-toxic, and relatively cheap compounds to replace enzymes and other substances of biological origin.

Table 3. Outer-sphere photocatalytic reactions with participation of $Ru(bipy)_3^{2+}$ and related compounds.

Reaction	Scheme*	References
Reduction of water	$H_2O + Red \xrightarrow[MV^{2+},\ cat._{H_2}]{Ru(bipy)_3^{2+}} {}^1/_2H_2 + OH^- + Red$ oxidation products	[123–129]
Oxidation of water	${}^1/_2H_2O + Ox \xrightarrow[cat._{O_2}]{Ru(bipy)_3^{2+}} {}^1/_4O_2 + H^+ + Ox$ reduction products	[130–133]
Reduction of CO_2	All the reactions presented below take place in the presence of $Ru(bipy)_3^{2+}$	
	$CO_2 + Red \xrightarrow[MV^{2+}]{} HCOO^- + Red$ oxidation products	[134]
	$CO_2 + Red \rightarrow HCOO^- + Red$ oxidation products	[135, 136]
	$CO_2 + Red \xrightarrow[Ru(bipy)_n(CO)X]{} HCOO^- + Red$ oxidation products	[135–137]
	$CO_2 + Red \xrightarrow[Co(bipy)_3^{2+}]{} CO + Red$ oxidation products	[138]
	$CO_2 + Red \xrightarrow[MPVS,\ Ru_{cat}]{} CH_4 + Red$ oxidation products	[139]
Hydrogenation and hydroformylation	All the reactions presented below take place in aqueous solution in the presence of $Ru(bipy)_3^{2+}$ and of a water-soluble Rh(I) complex Ascorbate $\rightarrow H_2$ + dehydroascorbate C_2H_2 + ascorbate $\rightarrow H_2 + C_2H_4$ + dehydroascorbate C_2H_4 + ascorbate $\rightarrow H_2 + C_2H_6$ + dehydroascorbate $C_2H_2 + CO$ + ascorbate $\rightarrow H_2 + C_2H_5CHO$ + dehydroascorbate	[140]
Amination, carboxylation, reduction of CO_2	The reactions presented below take place in the presence of $Ru(bipy)_3^{2+}$, Red, MV^{2+} on which analogues, $NADP^+$ and the corresponding enzymes: $CH_3-CO-COOH \xrightarrow{CO_2} HOOC-CHOH-CH_2-COOH$ $HOOC-CHOH-CH_2-COOH \xrightarrow[-H_2O]{} HOOC{=}COOH$ $HOOC{=}COOH \xrightarrow{\text{Glutamic acid}} HOOC-CHNH_2-CH_2-COOH$ $HOOC-CO-CH_2-CH_2-COOH \xrightarrow{CO_2} HOOC-CHOH-CH(COOH)-CH_2-COOH$ $CO_2 \rightarrow HCOOH$	[141–143]
Pschorr reaction		[144]

*Notation: Red = irreversibly oxidisable organic compounds (amines, sulphur-containing compounds, etc.); MV^{2+} = dication of Methyl Viologen (*N,N'*-dimethyl-4,4'-bipyridyl); $cat._{H_2}$ = finely dispersed Pt, Pd, Rh, etc.; Ox = irreversibly reducible oxidants [$Co(NH_3)_5Cl^{2+}$, $S_2O_8^{2-}$)]; $cat._{O_2}$ = RuO_2 or Co^{2+}; MPVS = zwitter-ionic Viologen [*N,N'*-di-(3-sulphonato)propyl-3,3'-dimethyl-4,4'-bipyridyl]; Rh(I) $[ClRh^{I}L_3]^{3-}$, where L = 4-sulphonatophenyl-diphenylphosphine; $NADPH^+$ = reduced nicotinamide-adenine dinucleotide phosphate.

IV. Conclusion

The brief survey of the principal types of photocatalytic reactions with participation of transition metal complexes indicates the considerable undiscovered possibilities of this field of science which has arisen at the junction between photochemistry and catalysis. The reactions considered may be of interest for the creation on their basis not only of the fairly widely discussed processes involving the transformation of solar energy but also organic synthetic processes. Speaking of the possibility and usefulness of the practical application of photocatalysis for the purpose of synthesis, one should, however, bear in mind the inevitability of using in this case artificial light sources. Since artificial light is much more expensive as a variety of energy than heat, it is necessary to have, first, an idea about the economic desirability of a particular process being carried out under photocatalytic conditions. Nevertheless, a number of advantages of photocatalytic organic synthesis may serve as a stimulus to the development of studies in the field of photocatalysis with participation of metal complexes. Thus photocatalytic reactions can occur under milder conditions than the analogous dark processes. The activity of photogenerated catalysts is not inferior and is sometimes actually superior to that of catalysts obtained by the thermal method under analogous conditions. If the reaction proceeds with an increase in free energy, then the photocatalytic procedure proves to be the only possible way of achieving it (or of increasing significantly the yield of the product). Photocatalysis can facilitate the occurrence of photochemical non-catalytic reactions. Mention should also be made of the great variety of reactions which may be achieved by the photocatalytic method and also of the advantages of light as one of the reactants (the possibility of varying its properties—intensity and wavelength—widely and smoothly). Finally, the action of light on catalytic systems, which is a convenient means of obtaining intermediate reactive species, may become an important instrument in the study of the usual thermal catalysis.

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