Photocatalysis induced by light-sensitive coordination compounds

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Abstract – Electronic excitation of both WERNER-type complexes and light-sensitive organometallics may lead to coordinatively unsaturated complex fragments, metal complexes with unusual formal oxidation numbers of the central atoms, free ligands and ligand oxidation products, respectively, which may exhibit catalytic activity. For the description of processes involving photogeneration of catalytically active species and subsequent catalyzed reactions, the terms photoinduced catalytic reactions and photoassisted reactions, respectively, have been applied. General features of photoinduced catalytic and photoassisted reactions and their applications are discussed. Particular emphasis is placed on the use of photosensitive coordination compounds as catalysts for organic syntheses. Photooxygenation of phenols and terpenes in the presence of copper(I)/(II) complexes and metalloporphyrins, respectively, as well as photoinduced cyclisation reactions of unsaturated hydrocarbons in the presence of azido complexes of nickel(II), palladium(II) and platinum(II) are discussed in more detail.

INTRODUCTION

The photochemistry of both classical WERNER-type coordination compounds (refs. 1,2) and organometallic complexes (refs. 3-7) has opened new fields for potential applications such as unconventional imaging processes (refs. 8-10) and solar energy conversion (refs. 11-14). In this context, we have discussed the problem of spectral sensitization of photosensitve coordination compounds (refs. 8,15-18).

Compared with organic compounds, transition metal complexes are distinguished by a larger variety of electronic states which are accessible upon light absorption and which may yield different photoproducts. In principle, by choosing the proper excitation wavelength, the photochemical generation of any desired photoproduct should be possible. Many of these photoproducts exhibit catalytic activity for the transformation of organic substrates under mild thermal conditions. Therefore, photochemistry of coordination compounds has attracted increasing interest among chemists as a convenient novel method for organic syntheses in a preparative scale (refs. 19,20).
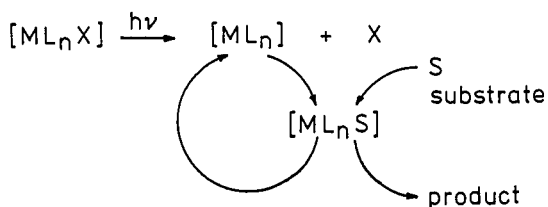
As demonstrative examples, we describe here the photo-oxygenation of phenols and terpene derivatives as well as some photoinduced transformations of unsaturated hydrocarbons in the presence of transition metal complexes. Although this choice is quite arbitrary, we consider these examples useful in order to discuss the general principles of photocatalysis that underly these reactions.

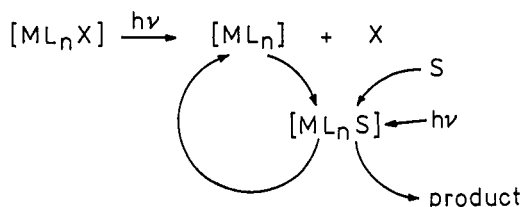## BASIC PRINCIPLES OF PHOTOCATALYSIS

Here, the term photocatalysis is applied for reactions in which a catalytic process is initiated under the action of light. Depending on whether the catalyst formed by photolysis requires further activation by light or not, two types of photocatalytic reactions may be distinguished: photoassisted and photoinduced catalytic reactions (refs. 17,18,21,22,24 Scheme I).

Scheme I

Photoinduced catalytic reaction   Photoassisted reaction

$$[ML_nX] \xrightarrow{h\nu} [ML_n] + X$$

S
substrate

$[ML_nS]$

product

$$[ML_nX] \xrightarrow{h\nu} [ML_n] + X$$

S

$[ML_nS] \longleftarrow h\nu$

product

In a photoinduced catalytic reaction, the catalyst formed does not require further excitation by light in order to catalyze the transformation of substrates. Hence, the quantum yield for product formation may well exceed unity.

A typical example for a photoinduced catalytic reaction is the formation of heterocyclic 1,2-enedioles from heterocyclic aldehydes (ref. 23, Fig. 1). Here, cyanide ions formed by photosubstitution of octacyanomolybdate(IV) act as catalysts. Although the quantum yield for formation of cyanide is only about 1, the total number of enediole molecules formed per number of light quanta absorbed was found to be about 1000 which is strong evidence for a photoinduced catalytic process.

$$[Mo(CN)_8]^{4-} \xrightarrow{h\nu} 4\ CN^- + [Mo(CN)_4O(H_2O)]^{2-}$$
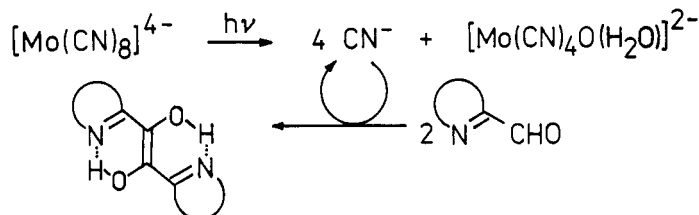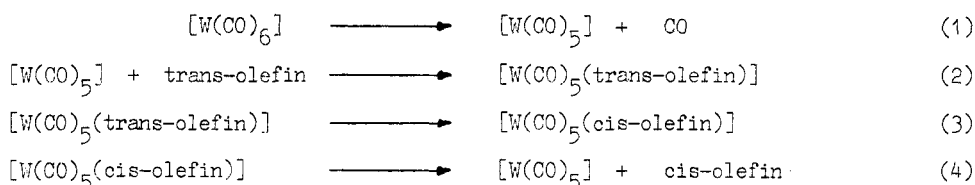
Fig. 1   Photoinduced catalytic formation of enedioles from heterocyclic aldehydes

Although there are further examples (ref. 18) for which the overall-quantum yield of product formation is even higher, photoinduced catalytic reactions with product yields greater than 10 molecules per light quanta absorbed are still exceptional. This is mainly due to deactivation of the catalyst by undesired side-reactions. However, it should be noted that for photoinduced catalytic processes the overall-quantum yield for product formation depends on a number of factors, including the reaction time and substrate concentration (for a detailed discussion see refs. 24,25).

In a photoassisted reaction, a catalytically active species is formed which may act as a catalyst for substrate transformation only if a further light quantum is absorbed by the catalyst-substrate complex (ref. 26). Therefore, quantum yields for product formation in photoassisted reactions are relatively low and, per definition, do not exceed unity. However, since catalyst deactivation may occur in photoinduced catalytic reactions, quantum yields of photoassisted reactions very often are comparable with those of photoinduced catalytic reactions and further mechanistic investigations are required in order to differentiate between these reactions. In fact, the mechanisms of many of the hitherto known photocatalytic reactions are yet to be elucidated.

As can be seen from Scheme I, photoassisted reactions require the absorption of light energy by the catalyst-substrate complex. Therefore, photoassisted reactions terminate immediately after light is turned off whereas photoinduced catalytic reactions may proceed even after the irradiation source is removed. However, due to catalyst poisoning continuous irradiation leads to improvement of product yields also for photoinduced catalytic reactions.

Typical examples for photoassisted reactions are the photochemical trans-cis isomerizations of olefins in the presence of tungsten hexacarbonyl (refs. 26,27).
In the first step (1), pentacarbonyltungsten is formed which reacts with the trans-olefin. The thus formed mixed ligand complex is converted photochemically to the unstable complex of the cis-olefin. By releasing the cis-olefin the catalyst [W(CO)$_5$] is regenerated and the photoassisted catalytic cycle may start again.

$$[W(CO)_6] \longrightarrow [W(CO)_5] + CO \qquad (1)$$

$$[W(CO)_5] + trans\text{-}olefin \longrightarrow [W(CO)_5(trans\text{-}olefin)] \qquad (2)$$

$$[W(CO)_5(trans\text{-}olefin)] \longrightarrow [W(CO)_5(cis\text{-}olefin)] \qquad (3)$$

$$[W(CO)_5(cis\text{-}olefin)] \longrightarrow [W(CO)_5] + cis\text{-}olefin \qquad (4)$$

In the following, we like to discuss some further examples for photocatalytic reactions studied in our laboratory very recently.

PHOTOOXYGENATION OF ALKENES WITH METALLOPORPHYRINS

The selective oxygenation of hydrocarbons with molecular dioxygen remains an attractive goal for synthetic application of metal catalysts. Although the photochemistry of metalloporphyrins has been the subject of extensive studies in terms of solar energy storage problems and photoredox properties, only few studies (refs. 28-32) are devoted to the photocatalytic oxygenation of alkanes and alkenes with metalloporphyrins using dioxygen as an oxidant.

Porphyrins provide strong four-dentate ligands which are capable of stabilizing both low and high oxidation states of transition metals. Irradiation of five- or six-coordinated tetraphenylporphyrin (TPP) complexes with visible light may result in photoreduction of the central metal:

$$[M^{n+}(TPP)L] \longrightarrow [M^{+(n-1)}(TPP)] + L^{\cdot} \qquad (5)$$

$$[M^{+(n-1)}(TPP)] + O_2 \longrightarrow [M^{+(n-1)}(TPP)O_2] \qquad (6)$$
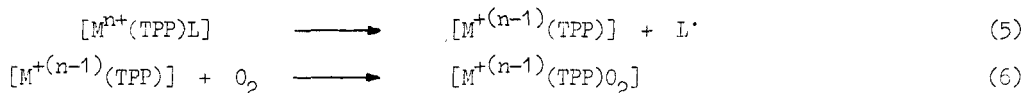
Coordination of molecular dioxygen to low-valent metal species offers the possibility of a general concept of photocatalytic oxygen activation for hydrocarbon oxygenation reactions. α-Pinene 1 was chosen as a suitable substrate to study effectivity and chemoselectivity of different oxygenation pathways and active species.

The reaction of singlet oxygen with α-pinene 1 yields pinocarveyl hydroperoxide 2 only (ref. 33), whereas a broad product mixture is obtained in radical-initiated autoxidation (Table 1).
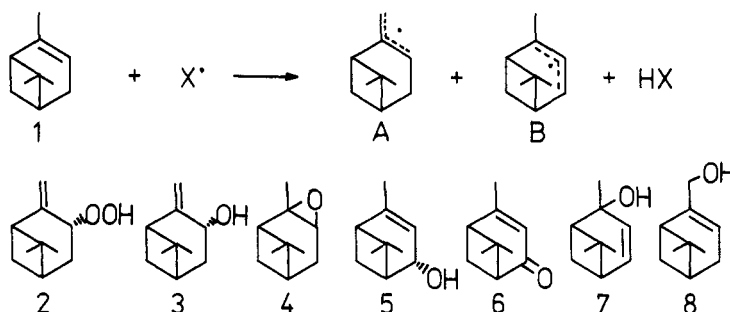
TABLE 1   Product distribution for photocatalytic oxygenation of α-pinene 1

Catalyst	TO[a]	Products (%)[b]					
		4	5	6	7	3	8
t-BuOOH[c]	74	23	18(16)	16	9(16)	6(13)	–
Cr(TPP)OH*2H$_2$O	1424	18	19	6	33	24	–
Mn(TPP)Cl	250	–	14	–	86	–	–
Fe(TPP)Cl	480	29	16	30	25	–	–
Co(TPP)Cl	–						
[Nb(TPP)]$_2$O$_3$	524	30	12	3	48	7	–
MoO(TPP)OCH$_3$	72	47	23	–	30	–	–
[WO(TPP)]$_2$O$_3$	327	–	7(2)	8	–	23(32)	10(17)

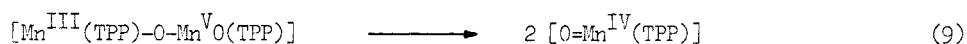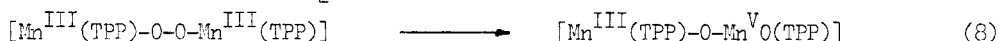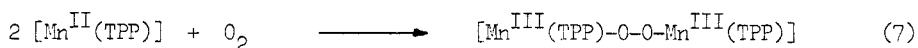a) Turnover numbers: moles product formed per mole catalyst
b) Reaction conditions: 0.1 mol α-pinene and 10^{-5} mol complex dissolved in 15 ml dry benzene, 8 h irradiation by a 500 W mercury lamp
c) 1 mmol t-butyl hydroperoxide used as a radical initiator instead of porphyrin complex

As seen from Table 1, product distributions close to tert-butoxy radical-initiated autoxidation were found for chromium and niobium porphyrin catalyzed photooxygenation of α-pinene. In the presence of phenyl-N-tert-butyl nitrone (PBN) as a spin trap, EPR signals of spin adducts resulting from trapping alkoxy and ˙OOH radicals, respectively, were detected. An epoxide/allylic alcohol ratio close to 1 was obtained in the case of molybdenum porphyrin indicating a controlled formation of the thermodynamically favoured allyl radical B.
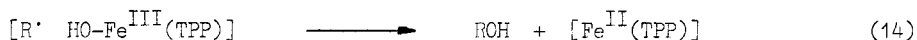
Equimolar amounts of pinene oxide 4 and alcohols 5 and 7 were formed by subsequent molybdenum(IV)-catalyzed oxygen transfer from the resulting verbenyl and pin-3-en-2-yl hydroperoxides to pinene (ref. 34).

Exclusive formation of allylic alcohols trans-verbenol 5 and pin-3-en-2-ol 7 in the presence of chloro(tetraphenylporphinato)manganese(III) points towards an oxygenation mechanism different from radical chain autoxidation. Reaction of dioxygen with manganese(II) porphyrins has been described to yield mixed-valence μ-oxo dimers (ref. 35). Photoinduced cleavage of the μ-oxo bond produces the catalytically active oxo-manganese(IV) species.

$$2\ [Mn^{II}(TPP)]\ +\ O_2 \longrightarrow [Mn^{III}(TPP)\text{-}O\text{-}O\text{-}Mn^{III}(TPP)] \qquad (7)$$

$$[Mn^{III}(TPP)\text{-}O\text{-}O\text{-}Mn^{III}(TPP)] \longrightarrow [Mn^{III}(TPP)\text{-}O\text{-}Mn^{V}O(TPP)] \qquad (8)$$

$$[Mn^{III}(TPP)\text{-}O\text{-}Mn^{V}O(TPP)] \longrightarrow 2\ [O\text{=}Mn^{IV}(TPP)] \qquad (9)$$

$$RH\ +\ [O\text{=}Mn^{IV}(TPP)] \longrightarrow [R^{\cdot}\ HO\text{-}Mn^{III}(TPP)] \qquad (10)$$

$$[R^{\cdot}\ HO\text{-}Mn^{III}(TPP)] \longrightarrow ROH\ +\ [Mn^{II}(TPP)] \qquad (11)$$

Selective hydrogen abstraction from pinene would produce a hydroxomanganese(III) complex and a pinenyl radical. Fast recombination of this radical with hydroxyl radicals in a radical cage finally yields the allylic alcohol and manganese(II) which may enter the cycle again. Slower rate of recombination and diffusional escape of the radical from the metalloporphyrin would lead to reaction products with dissolved dioxygen and, hence, to a product distribution similar to the autoxidation process. With respect to the classification of photocatalytic reactions, catalytic photooxygenation of pinene in the presence of manganese porphyrins apparently belongs to the latter group.

A combined mechanism seems to be responsible for the formation of allylic oxidation products and pinene oxide with the iron(III) complex. Photoreduction of the chloro(tetraphenylporphinato)iron(III) and reaction with dioxygen yields immediately μ-oxo iron(III) porphyrin. Similar to the manganese compound, this complex is converted into oxo-iron(IV) species and iron(II) porphyrin during photolysis.

$$[Fe^{III}(TPP)\text{-}O\text{-}Fe^{III}(TPP)] \longrightarrow [O\text{=}Fe^{IV}(TPP)]\ +\ [Fe^{II}(TPP)] \qquad (12)$$

$$RH\ +\ [O\text{=}Fe^{IV}(TPP)] \longrightarrow [R^{\cdot}\ HO\text{-}Fe^{II}(TPP)] \qquad (13)$$

$$[R^{\cdot}\ HO\text{-}Fe^{III}(TPP)] \longrightarrow ROH\ +\ [Fe^{II}(TPP)] \qquad (14)$$

Partial escape of radicals from the cage and reaction of hydroperoxides formed with pinene oxide as well as further oxidation of trans-verbenol 5 to verbenone 6 is consistent with the obtained product composition.

Upon irradiation of μ-oxo-bis[oxo(tetraphenylporphinato)tungsten(V)] in the presence of pinene we observed the formation of the photoreduced oxo-tungsten(IV) complex. Its conversion into the initial μ-oxo complex is fairly slow. Prolonged irradiation of the reaction mixture led to complete demetallation of the complex and formation of H$_2$TPP, a known singlet oxygen sensitizer.

Slower deactivation of the catalyst via demetallation was also observed in the case of chromium and niobium porphyrins which is reflected by the singlet oxygen reaction product pinocarveol 3 in the product mixture.

PHOTOCATALYTIC OXYGENATION OF PHENOLS IN THE PRESENCE OF COPPER(I)/(II) COMPLEXES

Copper complexes are well-known catalysts for thermal oxygenation processes and the copper-containing enzyme tyrosinase, which is capable of oxidizing phenols, has been the subject of numerous studies (refs. 36,37). On the other hand, little is known about the photocatalytic behaviour of copper complexes towards phenols. Since copper compounds are relatively inexpensive materials, their use in a preparative scale appeared to be very attractive.

While copper(II) halides are catalytically inactive in acetonitrile solution, the corresponding copper(I) compound may act as a catalyst for the oxidation of phenols (ref. 38). Polychromatic irradiation of acetonitrile solutions of $CuCl_2^-$ (0.1 M) in the presence of phenol (0.1 M) by a 500 W mercury lamp required only 40 % of the reaction time of the thermal reaction (ref. 39). Both 1,2- and 1,4-oxygenation products were observed. For 4-methyl phenol no products were observed in the absence of light.

The reaction mechanism was found to be rather complex. In the course of the reaction chlorocuprates(II) are formed by photoreaction.

$$[CuCl_2]^- + Cl^- + PhOH + 1/2\ O_2 \longrightarrow [CuCl_3]^- + OH^- + PhO \cdot \qquad (15)$$
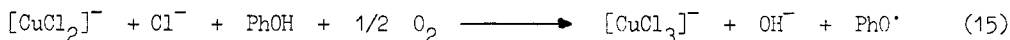
Since chlorocuprates(II) are photosensitive, the copper(I) catalyst can be regenerated by light and, therefore, the reaction reaction is accelerated. In addition, the product distribution differs from the one obtained in the thermal reaction where less 1,4-oxygenation products are formed. This may be explained by the enhancement of photoinduced Cu-phenol bond cleavage leading to an increase of phenoxy radicals which are considered to be the precursors of 1,4-benzoquinone. Since the amount of 1,2-benzoquinone increases when either phenol or copper complex is added, it is assumed that 1,2-oxygenation products are formed by direct interaction of coordinated phenols with dioxygen bound to copper(I). In summary, photocatalytic oxygenation of phenols by copper(I) complexes appears to be a complex reaction which cannot be described neither as purely photoassisted nor as a photoinduced catalytic process.

PHOTOCATALYTIC CYCLOTRIMERIZATION OF ACETYLENE

Platinum and palladium complexes of the type $[M(PR_3]$ (M = Pt, Pd) provide useful catalysts for a large variety of chemical reactions, e.g., hydrosilation, H_2/D_2 exchange and deuteration of acetone (ref. 40). In order to design a photocatalytic cycle by using these species, we have studied the photoreactions of the corresponding azido complexes $[M(PR_3)_2(N_3)_2]$ of M = nickel, palladium and platinum. In contrast to previous reports on the low-temperature photochemistry of $[Pt(PPh_3)_2(N_3)_2]$ (refs. 41,42), we found that both $[Pd(PPh_3)_2(N_3)_2]$ and $[Pt(PPh_3)_2(N_3)_2]$ undergo one-electron reduction with azidyl radicals and metal(I) complex formed (refs. 43,44).

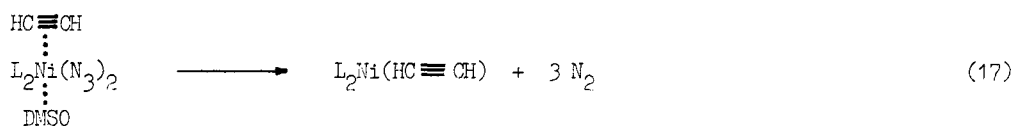$$[M(PPh_3)_2(N_3)_2] \longrightarrow [M(PPh_3)_2N_3] + \cdot N_3 \qquad (16)$$

Although the corresponding azidonickel(II) complexes did not show any photoreactivity in the absence of suitable substrates, they proved to be useful catalysts for the photocatalytic cyclotrimerization of acetylene (see Table 2), whereas the palladium and platinum complexes turned out to be inactive.

TABLE 2   Photocatalyzed cyclotrimerization of acetylene to benzene[a]

Complex	Yield	Number of cycles
$[Ni(N_3)_2(PBu_3)_2]$	165.2 mg	212
$[Ni(N_3)_2(PBu_3)_2]/Ph_2CO$	traces	–
$[Ni(N_3)_2(PBu_3)_2]/NaBH_4$	11.2 mg	14
$[Ni(N_3)(dppe)]$	281.6 mg	361
$[Ni(N_3)_2(dppe)]/Ph_2CO$	9.6 mg	12
$[Ni(N_3)_2(dppe)]/NaBH_4$	65.4 mg	84

a) solvent: dimethylsulfoxide; $1.25\ 10^{-4}$ moles catalyst; irradiation
    time: 30 min

The exact mechanism of the nickel-catalyzed photocyclotrimerization has still to be elucidated. However, a photoassisted process appears to be very likely. At the present stage of investigations, we assume a six-coordinate complex shown in eqn. (17) to be the photoactive species.

$$\begin{array}{c} HC\equiv CH \\ \vdots \\ L_2Ni(N_3)_2 \\ \vdots \\ DMSO \end{array} \longrightarrow L_2Ni(HC\equiv CH) + 3\ N_2 \qquad (17)$$

However, alternative models (ref. 45) should also be taken into consideration.

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