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Advantages and disadvantages of photocatalysis induced by light-sensitive coordination compounds

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Dedicated to Professor Vittorio Carassiti on the occasion of his 70th birthday

Abstract

Light-sensitive transition metal compounds have attracted considerable interest with respect to light-induced catalytic processes since electronic excitation of these compounds may lead to species distinguished by considerable catalytic reactivity. As such species may be regarded coordinatively unsaturated compounds, complexes with changed oxidation state, free ligands and ligand redox products. Depending on the lifetime of the catalytically active species it is advantageous to distinguish between *photoinduced catalytic* and *photoassisted reactions*. Definitorial approaches to characterize these limiting cases of photocatalysis are discussed and examples illustrating both kinds of photocatalytic reactions are given.

1. INTRODUCTION

The increasing interest in photocatalysis has obviously to do with two fascinating chemical processes, the *photosynthesis of the green plants* as the greatest chemical plant on the earth on the one hand and the *classical photographic process* on the other one. Both, the natural and the artificial process are strongly related to the topics of this article: They are kept going or initiated by the influence of light and they are to be considered as catalytic concerning chemical substrate conversions. Furthermore, both reaction pathways touch two important fields of present human activities: The modeling of solar energy conversion into chemical energy and the designing of unconventional information storage materials.

Thus, it is no wonder that photocatalysis has attracted the interest of generations of chemists. Plotnikow [1] was among

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the first who dealt with the description and definition of photocatalysis. In his textbook of photochemistry he defined all chemical reactions accelerated by light as photocatalytic ones. This definitorial approach may be considered as one of the milestones with respect to all further discussions about the phenomenon of photocatalysis. Here, we will summarize some essential contributions published during the past decade. This summary will be limited, however, to homogeneous photocatalysis based on light-sensitive transition metal compounds, preferably Werner-type complexes.

One of the main reasons when dealing with photocatalysis based on metal complexes as well as organometallic compounds obviously consists in the broader diversity of reaction pathways induced by light as compared with organic compounds. In organic photochemistry the general features of electronic excitation and the resulting photochemical reactions can usually be described by the assumption of only three electronic states involved: Singlet ground state, first excited singlet state and the corresponding triplet excited state formed by inter-system crossing.

Transition metal complexes are distinguished from organic compounds by the number as well as the spin multiplicity of electronically excited states. Therefore, depending on the wavelength of irradiation, various kinds of electronically excited states may be observed. This may result in the population of thexi states of different reactivity. This circumstance may allow for tuning the photochemical reactivity and switching between various reaction pathways such as electron transfer, dissociation/substitution/rearrangement reactions and ligand-centered conversions.

The electronic excitation by light can be used for the generation of coordinatively unsaturated species, transition metal compounds with changed oxidation state, free ligands and ligand redox products, respectively. Most of these species are known as being very reactive and therefore of practical interest regarding catalytic reactions induced by light. Consequently, it is not surprising that photocatalysis based on light-sensitive transition metal complexes and organometallic compounds has attained considerable attraction (see [9-12], e.g.).

Photoimaging processes [13], waste water recycling and other environmental preserving or decontamination processes [14], storage and conversion of solar energy [15], simulation and modeling of light-sensitive metalloenzymes [16] and organic synthesis [10], [11], [17], [35] have found particular consideration in the application of photocatalysis.

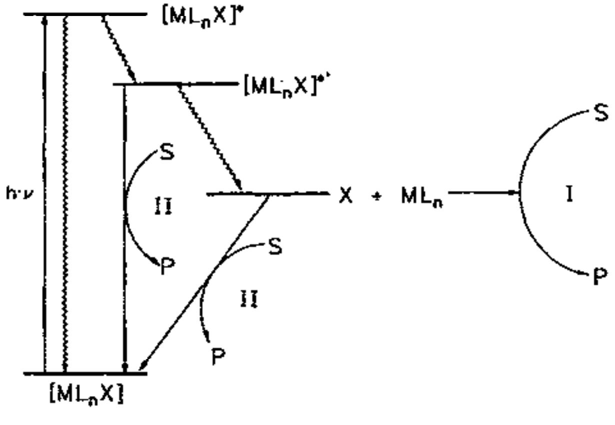
Several authors have contributed to answer the question what is meant by photocatalysis. Independent of our earlier comments to this subject [3-7], [20], [21] Wrighton [8], Moggi [9], Kutal [11], Balzani [2], Kisch [34], and Salomon [10] have proposed detailed mechanistic rules to specify photocatalytic reactions. Carassiti [19] outlined some definitorial issues due to careful thermodynamic considerations. Recently, Pelizzetti and Serpone [12] have edited an excellent book reviewing the recent state of the art in photocatalysis containing a very comprehensive and critical review by Chanon [18].

It seems to be accepted generally that photocatalysis includes that both light and a catalyst are necessary to bring about a corresponding reaction. It has to be stressed that the term catalyst will be used for both catalytically active species and catalyst precursors (nominal catalysts) or initiators to be activated by light.

For practical reasons it seems to be reasonable to distinguish between only two limiting cases of reactions being both light-induced and catalytic with respect to any transformations of a substrate S to a product P achieved by a pathway not accessible thermally under ambient conditions:

- The photogeneration of a stable catalyst in its electronic ground state from a catalyst precursor (nominal catalyst) or of a chain carrier from an initiator may result in a *photoinduced catalytic reaction*. (For objections to include photoinduced chain reactions among *photoinduced catalytic* ones see Chanon's comments [18], e.g.).

- The photogeneration of short-lived catalytically active species like metal complexes in electronically excited states or intermediates which recombine very fast to the catalyst precursor after the conversion of one molecule of substrate may bring about *photoassisted reactions*.



Scheme 1. Schematic representation of *photoinduced catalytic* (I) and *photoassisted reactions* (II).

Scheme 1 shows the pathways belonging to either *photoinduced catalytic* or *photoassisted reactions*. This scheme, summarizing the limiting cases of photocatalysis, appears to be advantageous for the designing of photocatalytic systems. In most cases it might be of interest to search for reactions with quantum yields and/or turnover numbers higher than unity as it is true for *photoinduced catalytic reactions*. However, one should keep in mind that the most important photocatalytic process, i.e. the photosynthesis of the green plants, is efficient enough despite the fact that its quantum yield is well below unity. Therefore, *photoassisted reactions* should be considered when solar energy conversion into chemical energy is concerned, e.g.

2. BASIC PRINCIPLES OF HOMOGENEOUS PHOTOCATALYSIS

The different aspects of photocatalysis when compared with usual catalysis arise from the constituent "photo" indicating that photons have to be absorbed prior to or within the catalytic cycle.

A convenient quantitative criterion of mechanistic photochemistry is based on the quantum yield. In order to determine the efficiency of the consumption or formation of species relevant to any photocatalytic process we have recently defined [20] three different quantum yield values: The quamtum yield of substrate consumption, Φ_S (ratio of the number of substrate molecules transformed into products in the presence of the catalyst, divided by the number of photons absorbed), Φ_U, the quantum yield of the photochemical reaction observed upon the same conditions, but in the absence of the catalyst, and Φ_C, the quantum yield of the transformation of a catalyst precursor (nominal catalyst) or an initiator into the catalytically active species, again under the same experimental conditions.

Using these quantum yield tests we have defined a reaction as photocatalytic if eqn. (1) applies for:

$$\Phi_S > \Phi_U \qquad (1)$$

The ratio Φ_S/Φ_C allows to distinguish between *photoinduced catalytic* ($\Phi_S/\Phi_C > 1$) and and *photoassisted reactions* ($\Phi_S/\Phi_C \leq 1$), respectively.

2.1 Photoinduced catalytic reactions

The interaction of light with a transition metal complex or organometallic compound may lead to the formation of a catalytically active species C which is able to react repeatedly in a subsequent dark reaction converting a substrate S into a product P.

The absorption of a single photon may give rise, theoretically, to the transformation of an infinite number of substrate molecules into products. That means, high quantum yield values and turnover numbers are to be expected in the course of *photoinduced catalytic reactions*. This type of photocatalytic reactions often shows an induction period and will continue after switching off the light-source. The reaction proceeds until the catalyst has been deactivated. Further, the catalyst generated photochemically can be applied to a catalytic reaction completely separated from the photochemical step.

Photocatalytic reactions following the quantum yield criterion of eqn. (2) are defined as *photoinduced catalytic reactions*.

$$\Phi_s > \Phi_c \tag{2}$$

With respect to eqn. (2) it should be pointed out that a general criterion $\Phi_s > 1$, proposed earlier by us and other authors has to be used with precaution, because Φ_s may be well less unity if $\Phi_c \ll 1$ or the deactivation of the catalyst proceeds very fast.

2.2. Photoassisted reactions

If the absorption of at least one photon by the transition metal compound is required to close each cycle of a photocatalytic reaction, the quantum yield Φ_s can not exceed Φ_c. In this case the catalytically active species are usually short-lived intermediates or species in an electronically excited state. Both are formed photochemically from catalyst precursors (transition metal complexes or organometallic compounds).

Photocatalytic reactions following the eqn. (3) are defined as *photoassisted reactions*.

$$\Phi_s \leq \Phi_c \tag{3}$$

Consequently, also photosensitized reactions as well as catalyzed photoreactions (substrate in an electronically excited state, catalyst in the ground state!) may be regarded as belonging to the class of *photoassisted reactions*.

One peculiarity of *photoassisted reactions* is marked by the general possibility to generate products higher in energy than the substrates. The excess of free energy in the products originates from the energy of the absorbed photons required to initiate each photocatalytic cycle.

As a rule, the quantum yield of *photoassisted reactions* can not exceed unity (4):

$$\Phi_s \leq 1 \tag{4}$$

Exceptions of this rule with respect to catalyzed photoreactions have been discussed elsewhere [20].

In the literature a tremendous variety of much more complex mechanistic schemes are discussed which are mostly extensions or combinations of the general limiting cases discribed above.

However, with respect to practical points of view it seems to be advantegeous to limit photocatalytic reactions to only two general definitorial boarderlines.

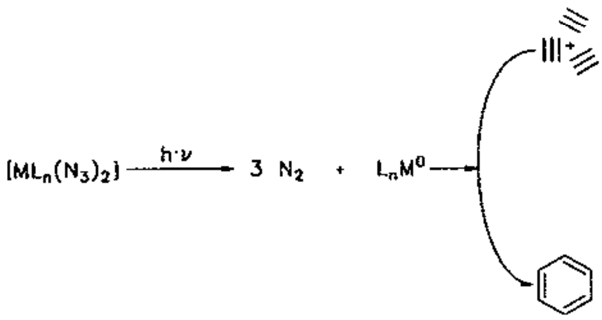
Finally, it has to be pointed out that the proper assignment of photocatalytic reactions to one or the other type or their combinations requires thorough mechanistic studies. Such careful mechanistic investigations are known only for some few reactions. As it has also been pointed out by critical comments of Carassiti [19] and Chanon [18] one should be reserved in using the terms photocatalytic and photocatalysis in the early stages of investigations.

3. EXAMPLES OF PHOTOCATALYTIC REACTIONS

In the following some examples will be given to illustrate both *photoinduced catalytic* and *photoassisted reactions*. The experimental results to be discussed are chosen arbitrarily and are focused to experimental results obtained in our laboratory.

3.1. Examples of photoinduced catalytic reactions

Irradiation of mixed ligand azido complexes of nickel(II), palladium(II) and platinum(II) into the region of their charge transfer bands leads to the very efficient formation of coordinatively unsaturated electron-rich metallofragments [22], [23] which are catalytically active with respect to oligomerization or cyclization reactions of acetylene and alkyne derivatives.

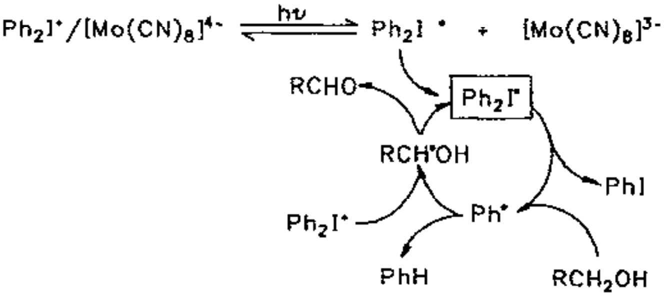


Scheme 2. Photoinduced catalytic cyclotrimerization of acetylene in the presence of mixed ligand azido complexes (M: Ni, Pd, Pt; L: mono- and diphosphane ligands).

Scheme 2 demonstrates the *photoinduced catalytic* cyclotrimerization of acetylene to benzene in the presence of mixed ligand azido complexes as catalyst precursors. Values of $\Phi_S/\Phi_C > 100$ have been observed [24], [17], showing that this reaction belongs unambiguously to the *photoinduced catalytic* ones.

We have been able to show very recently [25] that *photoinduced catalytic* co-cyclotrimerization reactions of acetylene occur in the presence of esters of acetylene dicarboxylic acid or long-chained alkynes, like hex(1)ine and pent(1)ine, e.g. Thus, the formation of phthaloic esters and alkylbenzenes, respectively, in good yields has been observed at low temperature and normal pressure. In the presence of alkyne derivatives alone *photoinduced catalytic* homocyclization reactions leading to the corresponding benzene derivatives have been detected. Cyclotrimerization reactions of acetylene in the presence of organic nitriles yielding pyridine derivatives are very promising.

Nickel(II) mixed ligand azido complexes are of particular interest, because we have been able to detect that the photolysis of these compounds leads primarily to the intermediate formation of nitrene derivatives of nickel(II) [26] and not to azidyl radicals and metal(I) species as it is true in case of the corresponding palladium(II) and platinum(II) compounds [22], [23]. Using bis(diphenylphosphino)ethane or bis(diphenylphosphino)propane as stabilizing ligands in the nickel(II) mixed ligand azido complexes, the photochemical formation of bis[bis(diphenylphospino)ethane/propane]nickel(0) complexes has been shown for the first time. The application of these reactive nickel(0) species as well as of the nitrene derivatives to photocatalytic organic syntheses is presently under investigation.

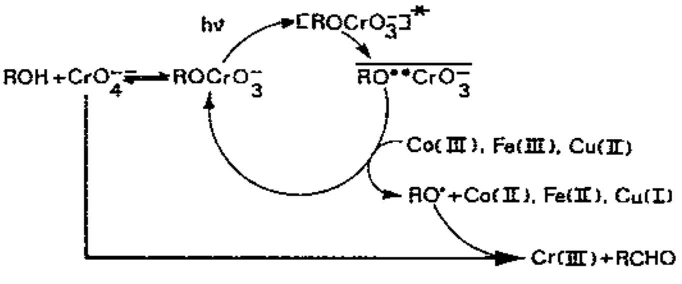


Scheme 3. *Photoinduced catalytic* oxidation of alcohols by diphenyliodonium ions (Ph_2I^+) in the presence of ion pairs of molybdenum(IV)octacyanide and Ph_2I^+.

An example of a light-induced chain reaction, which we count also to the class of *photoinduced catalytic reactions*, is shown in Scheme 3. The ion pair compound $\{Ph_2I^+;[Mo(CN)_8]^{4-}\}$ yields photochemically diphenyliodyl radicals and molybdenum(V). The diphenyliodyl radicals act as chain carriers in the oxidation of alcohols by both phenyl radicals and diphenyliodonium ions present in excess [26], [27]. A remarkable feature of this reaction consists in the initiation of the cycle by excitation of a low energy second-sphere charge transfer transition within the ion pair compound.

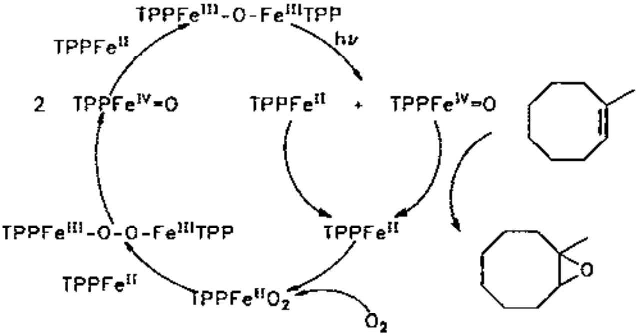
3.2. Examples of photoassisted reactions

An example of a *photoassisted* substrate conversion due to a short-lived intermediate in the ground state is shown in Scheme 4. Chromic acid esters form chromium(V)/alkoxy radical pairs within the photochemical primary reaction. In the presence of such iron(III), cobalt(III), or copper(II) complexes which are able to interact coordinatively or by second-sphere interactions with chromium(V), reoxidation to chromate(VI) occurs within the radical pair cage under simultaneous reduction of the metal complexes to the corresponding iron(II), cobalt(II), and copper(I) species, respectively. Unfortunately, the efficiency of this *photoassisted reaction* is limited by thermal side reactions of alkoxy radicals. They react with additional chromate(VI) to chromium(III) and the corresponding aldehydes and ketones, respectively, the final products of the usual photolysis of chromic acid esters [11], [28-30].



Scheme 4. *Photoassisted reaction* of chromic acid esters with alcohols in the presence of cobalt(III), iron(III) and copper(II) complexes.

The photochemical oxidation of olefins and cycloolefins [17], [31] in the presence of µ-oxobis[(tetraphenylporphyrinato)iron(III)] [16], Scheme 5, belongs to the same kind of *photoassisted reactions*.



Scheme 5. *Photoassisted* oxidation of cyclic olefins in the presence of µ-oxobis[(tetraphenylporphyrinato)iron(III)] (TPPFe^{III}-O-Fe^{III}TPPP).

The catalytically active iron(IV) species reacts again in the ground state and the catalyst precursor (the µ-oxo species) is regenerated by dissolved oxygen immediately after the epoxidation of the olefin has occured. The precursor has to be activated by light again in order to start the next cycle.

4. PERSPECTIVES OF HOMOGENEOUS PHOTOCATALYSIS - ADVANTAGES AND DISADVANTAGES

Both transition metal complexes and organometallic compounds play an important role in the catalytic conversion of inorganic as well as organic substrates. The activation of these transition metal compounds by visible and ultraviolet light provides definite advantages when compared with the usual thermal activation.

The very convenient photochemical generation of catalytically active species should be stressed in particular. Compared with thermal reaction pathways, catalysts are formed photochemically within one reaction step. Hence, the catalysts are formed in high selectivity and their constitution may frequently be identified very easily. This advantage may also be used to contribute to a better understanding of mechanistic details of homogeneous catalytic reactions in general. Further, the population of different electronically excited states, depending on the wavelength of irradiation, provides a tuning between different reaction pathways. Thus, the aimed synthetic designing of transition metal complexes or organometallic compounds as well as the choice of the wavelength of irradiation (ligand field, charge transfer, and inner ligand excitation, respectively) allows for modeling of *photoinduced catalytic* or *photoassisted reactions*.

Photocatalytic reactions can be carried out upon very mild experimental conditions (temperature, pressure). This circumstance can be very advantageous when the substrates or products are heat sensitive or explosive. Photocatalysis accomplished at low temperatures often allows the isolation and identification of reactive intermediates, thus providing further insight into the mechanisms of various reaction pathways particularly in the homogeneous complex catalysis.

However, photochemical side reactions, fast back electron transfer processes and recombination reactions, respectively, may considerably limit the efficiency of photocatalytic reactions and the photochemical decomposition of the catalyst may further lead to the fast termination of photocatalytic cycles.

These disadvantages should also be taken into consideration when dealing with photocatalysis.

Finally, spectral sensitization is essential for the utilization of a broad range of photonic energy (solar energy, e.g.). It has to be considered when practical aspects are concerned [4], [5], [7], [32], [33].

Comparing the advantages and disadvantages of photocatalysis it is rather surprising that photocatalytic reactions have found only little industrial application so far. However, perspectively it can be assumed that attempts to apply photocatalysis in information recording, solar energy conversion, environmental decontamination and/or protection and synthesis of high-price organic compounds will improve considerably, because photons are the most interesting energy sources of the future which will also be used on a larger scale in the chemical industry.

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