ELSEVIER

Coordination Chemistry Reviews
159 (1997) 95–108

COORDINATION
CHEMISTRY
REVIEWS

Photochemistry of copper complexes and their environmental aspects

Ján Sýkora

Slovak Technical University, Faculty of Chemical Technology,
Department of Inorganic Chemistry, Radlinského 9, SK-81237 Bratislava, Slovak Republic

Received 22 December 1995

Contents

Abstract

Based on a brief overview of the main features of copper photochemistry, the importance of copper and its complexes in aquatic biota processes, as well as the role of the coordination compounds of copper and their photochemical properties in environmentally interesting systems, is reviewed and analyzed. Attention is paid mainly to those systems where the environmentally important photochemical processes are substantially influenced by the presence of copper. Results related to the photo-oxidation and photodegradation of organic substrates (pollutants) in homogeneous and heterogeneous systems are reviewed and discussed within the suggested generalized scheme of the Cu(II)–Cu(I) photocatalytic redox cycle thought to be operative in an aqueous environment. Examination of the published results led to the conclusion that the homogeneous reaction pathways involving copper complex formation are also of importance in heterogeneous systems. In addition to photochemistry, secondary thermal reactions were also considered, and the possible relationships between the composition of the (copper) catalyst and reactivity leading to possible catalyst tailoring were stressed. Future prospects in the field based on the Cu(II)/Cu(I) photoredox cycling (e.g. photo-Fenton reactivity) are also formulated. © 1997 Elsevier Science S.A.

---

* Email: sykora@cvtstu.cvt.stuba.sk; tel: +421 732 6021 or 732 5484, ext. 303; fax: +421 749 3198.

PII S0010-8545(96)01299-4

Keywords: Copper photochemistry; Pollutant; Catalyst tailoring; Photoredox cycling

1. Introduction

The photochemistry of coordination compounds has been studied extensively in the past few years [1–5], and progress has also been made in the field of copper photochemistry. The photochemistry of copper complexes has been reviewed [6], and their reactivity has been classified [7] in terms of their catalytic role [8] in phototransformations [9,10] or photo-oxidations [11,12] of organic substrates.

Coordination compounds of copper can participate in many types of predominantly redox reactions arising from the population of metal-to-ligand charge-transfer (MLCT), ligand-to-metal charge-transfer (LMCT), charge-transfer-to-solvent (CTTS), intraligand (IL), interconfigurational metal-centered (IMCT), and ligand-to-ligand charge-transfer (LLCT) excited states [13]. This redox dimension of photoreactivity of copper complexes seems to be important in redox Cu(I)–Cu(II) cycling and copper-induced reactions (e.g. photo-oxidations leading to photodegradation of pollutants) in the environment.

This article addresses the environmental aspects of copper photochemistry and deals with the following issues.

(1) What are the main important features of the presence of copper in the environment?

(2) What is the present status in the study of irradiated systems in the presence of copper and its complexes related to the environment in homogeneous and heterogeneous media?

(3) What are the future prospects for development of research in the field?

2. Copper complexes and the environment

Copper is an essential trace element which is widely distributed in freshwater and the sea. A major fraction of Cu(II) present in the aquatic environment is complexed by organic substances of biological origin [14]. The speciation of Cu(II) controls its bioavailability and toxicity [15]. The surface maxima in vertical profiles of Cu(I) in the upper layers of the Atlantic Ocean are consistent with a photoreduction of Cu(II) to Cu(I) [14,16]. Reduction of Cu(II) along with oxidation of Cu(I) contribute to a dynamic redox cycling of that element in the upper marine water column. It was shown [17] that Cu(I) oxidation and Fe(II) oxidation by H_2O_2 are at least as important as nitrite photolysis as a source of OH radicals in the ocean. The speciation of Cu(I) complexes was also found to be very important in the Cu(I) oxidation step in seawater; the chemistry of the Cu(I)–Cu(II) interconversions has been extensively studied in chemical and biological systems and there is considerable evidence that similar reactions occur in natural waters.

For example, the presence of copper was found to be important in the oxidation of S(IV) in atmospheric water by photo-oxidants and iron [18]. In the absence of transition metals, S(IV) oxidation can be accounted for entirely by reactions with H_2O_2 and $OH^{\cdot}$ in such systems, and the oxidation of S(IV) by HO_2^-–$O_2^{\cdot-}$ is unimportant. In solutions containing dissolved iron, oxidation of S(IV) also occurs through Fe(III)-catalyzed reactions with O_2. However, at the low concentrations of copper (5–100 nM) typically measured in cloud droplets, Fe-catalyzed oxidation of S(IV) is inhibited through the reduction of $FeOH^{2+}$ by Cu(I), which is produced by the reduction of Cu^{2+} by HO_2^-–$O_2^{\cdot-}$. On the contrary, the presence of Cu(II) as a catalyst has been found very effective for the total destruction of phenol by its oxidation by sulfite-oxygen as an oxidant [19].

Moreover, trace metal transport in groundwater is generally controlled by metal interactions with the solid mineral phase and the speciation of the metal in the aqueous phase. For the interaction between natural organic matter (NOM) and Cu(II) in groundwater, several mechanisms [20], including Cu(II) complexation and its subsequent photoreactivity, may influence NOM and Cu(II) transport.

Therefore, there are several reasons for studying the environmental aspects of the photochemistry of copper complexes.

First, the photoreactions of copper coordination compounds may contribute to its toxicity to aquatic biota. High concentrations of copper released by human activities into aquatic environments are toxic to the aquatic environment and it has been designated as one of the US Environmental Protection Agency's "priority pollutants" [21].

Second, copper and its coordination compounds may play the role of a catalyst for photodegradation (in several cases also photomineralization) of various pollutants in irradiated systems. This catalytic effect can be based in principle on the photodegradation of the pollutant as a ligand in the coordination sphere of the copper central atom and/or on the secondary thermal reactions of the active species produced photochemically from the copper complex. Moreover, the presence of copper in addition to another reactant (catalyst) can lead to enhancement of the pollutant photodegradation.

Finally, study of the role of copper and its complexes in environmentally interesting systems may lead to new and exciting mechanistic information of chemical, medical and biological importance.

3. Environmentally interesting photoreactions in the presence of copper complexes

3.1. Homogeneous systems (Table 1)

One of the most interesting studies related to the environment was the study of photochemical reactivity of Cu(II)–amino-acid and related complexes. The LMCT-type irradiation of such complexes leads to photoreduction of Cu(II) to Cu(I) and photo-oxidation of the ligand to carbon dioxide, or to ammonia and formaldehyde in the case of glycine complexes [22]. In air-saturated solutions, rates and quantum yields for Cu(I) formation were sharply reduced and hydrogen peroxide was formed

Table 1
Copper complexes in homogeneous photo-oxidations of organic substrates in condensed media

Organic substrate	Conditions	Active species[a]	Product(s)[b]	Ref.
Amino acids (L′)	aerobic	$Cu(II)L'_x$	$Cu(I)+CO_2$ (H_2O_2)	[23]
Glycine	anaerobic	$Cu(II)L'_x$	$Cu(I)+NH_3+HCHO$	[22,23]
NTA	aerobic	Cu(II)NTA	Cu(I), HCHO, CO_2, IDA	[30,31,34]
IDA	acidic media	Cu(II)IDA	Cu(I), HCHO, CO_2, glycine	[32]
IDA	neutral media	Cu(II)IDA	Cu(I), HCHO, CO_2	[33]
Alcohols, benzene, toluene	ACN	$CuCl_x$	Cu(I), aldehydes, ketones, chloroderivatives	[38]
Phenol	ACN–O_2	$CuCl_x$	Cu(I), pbq, dhb	[43]
Phenol	ACN–O_2	CuL_x	Cu(I), pbq	[48]
Methylsubstituted phenols	ACN–O_2	$CuCl_x$	Cu(I), monomeric benzoquinones	[44,45]
Phenol	ACN–water–O_2	CuL_x	Cu(I), CO_2, pbq	[35]
Phenol	ACN–water–O_2	CuL_x	Cu(I), CO_2, pbq	[50]
Phenol	water–O_2	CuL_x, $CuCl_x$	pbq, CO_2	[54]
Phenol	water–O_2	CuL_x	pbq, CO_2	[55,56]
TNT	ACN–water–O_2	$CuCl_x$, CuL_x	CO_2	[57]

[a] L = bpy, phen; [b] dhb = dihydroxybenzene.

[23], which may further react with Cu(I) to produce hydroxyl radicals. These photoreactions are known to damage biological systems [24]. Glutamic acid, aspartic acid and glycine along with alanine are major amino acid components of humic and fulvic acids, which are widespread organic substrates in the aquatic environment [25]. The coordination of copper was also observed when copper sorbed to microbial surfaces [25,26] in the aquatic environment. The results of direct photolysis [27] of copper complexes with amino acids [22] and amines as ligands help to account for the sunlight-induced reduction of Cu(II) in natural waters [23].

Another interesting aspect of these studies is the enhanced toxicity of copper in the environment as a result of the photochemical properties of Cu(II)–amino-acid complexes. Their observed toxicity [28] may be connected with increased concentration of the highly toxic ‘free’ copper formed as a photoproduct and/or with cleavage of proteins taking place within the photoreactions of Cu(II) on cell surfaces, thus impairing biological functions. Also, the subsequent reactions of radicals formed in the Fenton–Haber–Weiss reaction between the Cu(I) produced by photoreduction of Cu(II) on cell surfaces and hydrogen peroxide could result in destruction processes [24]. The enhancement of light-induced peroxidation on photosynthetic membranes [29] is also known to be related to the photoinduced radical reactions initiated by reduction of Cu(II) by superoxide radicals.

The photodegradation of the aminopolycarboxylic acids nitrilotriacetate acid (NTA) and iminodiacetic acid (IDA) induced by complexation with copper(II) has been studied [30–33]. When uncomplexed, NTA and IDA in water do not absorb solar light and their phototransformation is unimportant. The degradation reactions of NTA [30] are of interest owing to its use as a substitute for phosphate in detergents and its eventual accumulation in wastewater. The complexation of NTA with Cu(II) present in natural waters leads to a relatively efficient process of NTA photodegradation [30,31]. The products of phototransformation of the CuNTA complex are Cu(I), HCHO, CO_2 and IDA. Similarly, the CuIDA complex is phototransformed to Cu(I), HCHO, CO_2 and glycine [32] in acidic medium. However, under neutral experimental conditions copper(II) is complexed by glycine and subsequent photooxidation takes place; the formation of HCHO along with Cu(II) to Cu(I) photoreduction was observed. The easy reoxidation of Cu(I) to Cu(II) by dioxygen makes this system catalytic (similar to the Cu(I)–Cu(II) photocatalytic redox system previously developed in non-aqueous media [34]) and therefore interesting with regard to the fate of both NTA and IDA aminopolycarboxylic acids in the environment upon excitation by solar light [33].

Photocatalytic aerobic oxidation of organic contaminants appears to be one of the most promising new technologies for addressing environmental problems. It was shown [12] that copper complexes act as catalysts for homogeneous photo-oxidation of hydroxylic organic substrates (very often pollutants) [35]. For example, the irradiation of $CuCl_x$ complexes in acetonitrile (ACN) in the region of the lowest spin-allowed charge-transfer excited state (vis) results in the photoreduction of the Cu(II) metal center to Cu(I) [36] and $Cl^{\cdot}$ radical ($Cl_2^{\cdot -}$) known as strong oxidizing agents [37] towards other organic substrates (primary and secondary aliphatic alcohols, benzene, toluene) present in the system [38]. The yield of oxidation products was strongly dependent on the composition of the copper complexes, which offers the possibility of useful control and tailoring of copper catalyst properties. It was shown that photoproduced Cu(I) is reoxidized by oxygen, and, in fact, the actual rate of Cu(II) photoreduction is lowered [38]. This observation, often regarded as a drawback in photochemical studies, is of importance in raising the yield of oxidation products and led to the suggestion of a photocatalytic Cu(II)–Cu(I) redox cycle [39] working under visible light [40].

To extend the application of copper complexes [41,42] as catalysts in oxidations of organic substrates [11,12] with special emphasis to the environment, a study of a novel route of phenol homogeneous oxidation by dioxygen in the presence of copper chlorocomplexes has been undertaken [43]. *p*-Benzoquinone (pbq) and dihydroxybenzene (known as intermediates in the total photodegradation of phenol to CO_2 and water) were found as major products in this liquid-phase catalyzed photo-oxidation of phenol. The continuous irradiation of the ACN solution of cuprous [44,45] chloro complexes in the presence of *o*-cresol, *m*-cresol, *p*-cresol, 2,4-dimethylphenol, and 2,5-dimethylphenol led to the very effective (98% yield, 98% selectivity, and 100% conversion) phototransformation of phenol to monomeric quinones.

Thus, the aerobic photo-oxidation of phenol in the presence of CuX and CuL_2 complexes (where $X = Cl^-$; $L = 2,2'$-bipyridine (bpy), 1,10-phenanthroline (phen)) in ACN resulted in pbq formation [43–49] and/or in total decomposition of phenol to CO_2 in aqueous solution [50]. The enhancement of phenol to pbq transformation in irradiated systems is explained by the increased formation of phenoxy radicals (coming from photoredox rupture of the Cu(II)–phenolate bond) and, in the case of CuX complexes, also from secondary reaction of $Cl^{\cdot}$ radicals [51] (evidenced also as $Cl_2^{\cdot -}$ anion radicals [40,52]) with phenol [53]). This is one reason why the difference between product formation in irradiated and dark systems was found to be much higher for CuX than that for CuL_2 systems. The addition of water to the ACN system led to increased phenol to CO_2 photodegradation [50]. This observation opened new perspectives for using these copper complexes as catalysts for phenol remediation in pure aqueous media [54].

In fact, it was found [55] that the photo-oxidation of phenol in an aqueous solution led to the degradation of phenol to CO_2 in the presence of copper complexes. Our recent results [56], performed in nanopure water, have also shown that phenol is readily photodegraded in the system $[Cu(bpy)_2]^{2+}$–phenol–O_2–water ($\lambda_{irr} > 290$ nm). The observed strong pH dependence of the phenol disappearance rate constants k_p (k_p increases with decreasing pH) is explained in terms of the excited state properties of the free protonated bpy ligand. Chemical scavenging and kinetic isotopic studies supported by thermodynamics evidenced the involvement of $^{\cdot}OH$ radicals in the rapid photodisappearance of phenol in highly acidic aqueous media. More interestingly, the CuL_x (where $L = Cl^-$, bpy, phen) complexes were also found to accelerate the photodegradation rate (with subsequent CO_2 evolution) of such degradative stable pollutants as trinitrotoluene (TNT) in aqueous media (ACN–water mixtures) [57].

The above results allow us to suggest the generalized scheme (Fig. 1) of environmentally interesting photo-oxidations based on the Cu(I)–Cu(II) photocatalytic redox cycle important from the point of view of photodegradation of organic substrates (pollutants). It may also contribute to a better understanding of copper-based processes in the aquatic environment.

The main features of this cycling process cover the photoreduction of the Cu(II) metal center to Cu(I) with the concomitant oxidation of the ligand L to L_{ox}. This oxidized ligand L_{ox} (or other strong oxidants R formed in the course of L_{ox} secondary thermal reactions) may oxidize the organic substrate Q to environmentally acceptable species (H_2O, CO_2 or non-toxic simple inorganic acids and ions), and the photoproduced Cu(I) is then reoxidized by dioxygen to Cu(II). The reoxidation pathway of

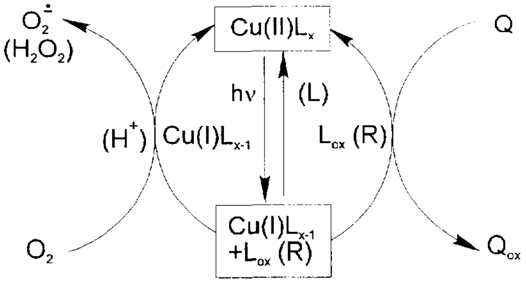

Fig. 1. Environmentally interesting photo-oxidations based on Cu(II)–Cu(I) photocatalytic redox cycle in the Cu(II)/Cu(I)–L(Q)–O_2 homogeneous system (L and/or Q = pollutant, $R = L_{ox}$ or $R \neq L_{ox}$ = oxidant).

Cu(I) is important not only for closing the catalytic cycle but also for the formation of the $O_2^{\cdot -}$ anion radical. This leads to the hydrogen peroxide H_2O_2 needed for OH radical formation as a necessary species responsible for the photodegradation and damaging processes produced within the Cu(I)–H_2O_2 interaction (Fenton reaction [58]) or direct H_2O_2 photolysis [59]. This type of reaction (photochemical production of Fenton reagent) is referred to as a 'photo-Fenton reaction' [60]. This has been used for the photo-oxidation of several agrochemicals in freshwaters [61], as well as an effective photochemical wastewater treatment process (novel photochemical degradation method for organic contaminants) [62]. It is obvious that this cycle only works in the presence of sufficient ligand L ($L=Q$ or $L \neq Q$) concentration in the system as an electron donor for reduction of Cu(I). When oxidation of the organic substrate Q takes place outside of the coordination sphere of the copper metal center, the concentration of the copper metal catalysts can be several magnitudes lower than the real amount of organic substrate Q photodegraded, which makes this approach very advantageous.

In the most optimal case, the photochemically produced L_{ox} may be reduced again to L during a secondary thermal reaction with Q leading to oxidation of organic substrate Q and the photodegradation of the latter to an environmentally acceptable species.

The decisive electron acceptor for the recovery of Cu(II) from photochemically formed Cu(I) is thus the dioxygen molecule always being present in sufficient concentration in the systems under aerobic conditions. The weak coordination ability towards copper (compared with the original L or Q) of the final photodegradation products (which is very often fullfilled, e.g. in the case of CO_2 or several inorganic ions) may also increase the efficiency of the system.

3.2. Heterogeneous systems (Table 2)

The photocatalytic decomposition of pollutants on semiconductor surfaces (heterogeneous systems) has been widely studied [63–69]. Numerous studies have demonstrated the efficiency for the photocatalytic oxidation of organic compounds when using aqueous TiO_2 suspensions [70–77]. This process has gained attention for its potential application in the removal of organic contaminants from wastewaters and drinking water supplies because it yields rapid, non-selective oxidation of a broad range of pollutants to CO_2, H_2O and simple mineral acids or inorganic ions. These heterogeneous photocatalytic oxidation reactions [78] are now the members of what are referred to as 'advanced oxidation processes' (AOPs) and lead to complete destruction of numerous organics, against direct photolysis and natural biodegradation under ambient conditions.

The first step in this type of photocatalytic oxidation is the photogeneration of pairs of electrons and holes (h^+) as a consequence of UV illumination ($\lambda < 400$ nm) absorbed by TiO_2:

$$TiO_2 \xrightarrow{h\nu} h^+ + e^- \tag{1}$$

Table 2
The role of copper presence in heterogeneous photo-oxidations of organic substrates in aqueous media

Organic substrate	Conditions	Active species	Effect of copper on degradation rate of organic substrate	Product(s)	Ref.
Toluene	TiO_2 (pH 3)	10^{-5} M Cu(II)	increase	CO_2	[79]
Chlorobenzene	TiO_2 (pH 3)	ternary complex Cu(II)-O_2-H_2O_2-OS	increase	N.D.	[79]
Formic acid	TiO_2	Cu(II) or $[Cu(HCOO)]^+$	increase	CO_2	[93]
Acetic acid	TiO_2	monoacetato Cu(II) (diacetato Cu(II) is poison)	increase	CO_2	[94]
Propionic acid	TiO_2		increase	CO_2	[95]
Toluenes	TiO_2 (pH 1)	10^{-2} M Cu(II)	increase	benzaldehyde, CO_2	[83]
Phenol	TiO_2-H_2O_2	Cu(II)	increase	CO_2	[82,98]
Phenol	TiO_2	Cu(II)	increase/decrease	CO_2	[77]
Toluene	TiO_2	Cu(II) in high conc.	detrimental	CO_2	[79,81]
Phenol	TiO_2	Cu(II) > 1 mM	detrimental	Cu^0, Cu_2O	[86]
Phenol	TiO_2	Cu(II)	detrimental	CO_2	[82]

N.D.: not determined.

The conduction band electron can be subsequently trapped by surface-adsorbed O_2 to form a superoxide ion $O_2^{\cdot -}$ and the generated electron holes h^+ react with adsorbed species in oxidative reactions. The most important of these reactions is oxidation of adsorbed water molecules or hydroxide ions to produce hydroxyl radicals [71,72]. These radicals are widely believed to be the most important oxidizing species in TiO_2 photocatalytic systems:

$$h^+ + H_2O_{(ads)} \rightarrow {}^{\cdot}OH + H^+ \quad (2)$$

$$h^+ + 2OH^-_{(ads)} \rightarrow {}^{\cdot}OH + OH^- \quad (3)$$

Addition of dissolved transition metals has been reported to influence profoundly the rate of TiO_2 photocatalytic oxidation [79]. Both an increase [71,73,77,80–85] in the photo-oxidation rate by a factor of between 1 and 5 (compared with metal-ion free systems) and a detrimental effect [77,81,82] have been observed.

The observed rate increase has been attributed to electron trapping at the semiconductor surface [73,77] which prevents electron–hole recombination and results in an increased rate of OH radicals formation through the reactions in Eqs. (2) and (3):

$$M^{n+} + e^- \rightarrow M^{(n-1)+} \quad (4)$$

(where $M^{n+} = Cu^{2+}$, Fe^{3+}, Mn^{3+}).

The above considerations are strictly valid only in the absence of added H_2O_2 where the OH radicals can only be generated by the photocatalytic system itself. For example, the H_2O_2 may be formed from the dissolved dioxygen in the presence of illuminated semiconductors and it will be decomposed to the OH radical. The addition of transition metal ions may induce the Fenton-type reaction, generally called a photo-Fenton-type reaction [83,84]. Therefore, the second reason for the increase of the oxidation rate may be the participation of metal ions in Fenton-type reactions as an additional source of OH radical formation:

$$M^{(n-1)+} + H_2O_2 \rightarrow M^{n+} + {}^{\cdot}OH + OH^- \qquad (5)$$

The detrimental effect of high metal concentrations has been explained as being due to oxidation of reduced metal ions by OH radicals or by photogenerated holes proceeding in competition with the reactions in Eqs. (2) and (3) [83,84]:

$$M^{(n-1)+} + h^+ \rightarrow M^{n+} \qquad (6)$$

The observed detrimental effect of high concentrations of Fe(III) (as well as Cu(II) and Ni(II)) on the rate of toluene oxidation is also explained well by absorbance of UV radiation by metal species [81]. In addition, precipitation of dissolved metals as hydroxides (observed at 10^{-4} M for Cu(II) (pH = 7) and at 10^{-3} M for Fe(III) (pH = 3)) probably decreased the rate of photocatalytic oxidation by reflecting UV illumination through increased solution opacity [79].

The above arguments can also be applied to explain the inhibition effect of dissolved Cu^{2+} ions (in concentrations higher than 1 mM) on TiO_2-photocatalyzed phenol (initial phenol concentration of 1 mM) degradation found in a very recent study [86]. The observed photodeposition of metallic copper and Cu_2O onto the TiO_2 surface may modify the processes of charge carriers and radical intermediate generation and recombination [75,87] which, along with Eq. (4), result in inhibition of phenol photodegradation.

On the contrary, in the presence of low Cu^{2+} concentrations (10^{-5} M) a significant increase in the reaction rate for photocatalytic TiO_2 oxidation of toluene was observed at pH = 3 [79]. When using chlorobenzene as the target organic, an increase in the rate of its removal upon Cu(II) addition under identical experimental conditions was found. These results led to the conclusion [79] that the increase in degradation rate observed on addition of metal ions (copper included) to the TiO_2 photocatalytic systems is not a function of the organic substrate used. More interestingly, the results of Butler and Davis [79] indicated that dissolved metals increase the reaction rate via a homogeneous pathway rather than a TiO_2 surface reaction because negligible adsorption of metals onto TiO_2 was measured. Actually, no more than 0.1 μmol m^{-2} of the Cu(II) or Mn(II) metals were adsorbed onto the TiO_2 surface under the experimental conditions producing the highest reaction rate (i.e. pH = 3 and a metal concentration of 10^{-5} M) [79,88,89]. These data show little evidence that adsorption of metal cations and subsequent electron trapping (Eq. (4)) is the mechanism by which dissolved metals enhance the rate of TiO_2 photocatalysis. Therefore, a mechanism involving formation of a ternary reactive complex between the metal, the organic or its oxidation intermediate, and an oxygen-containing species such as H_2O_2, O_2 or $O_2^{\cdot -}$ is proposed to explain the experimental data [79] (similar to that suggested for homogeneous systems [90,91]). Thermodynamic considerations indicate that formation of such a complex is favored at low pH.

The decisive role of copper complex formation has also been stressed in TiO_2-catalyzed photo-oxidation of some carboxylic acids [92]. Bideau and coworkers [93–95] observed that the catalytic TiO_2–Cu^{2+} system was very effective in the photo-oxidation of formic [93], acetic [94] and propionic acid [95]. The copper carboxylato complexes and their composition were found to play a determining kinetic role both in the dissolved as well as adsorbed state [95]. For example, it was concluded [94] that the monoacetato complex of copper was the intermediate active species and the diacetato complex (i.e. neutral salt) was a poison. The results obtained for propionic acid [66] were quantitatively explained in the same way. The kinetic data agreed with a 'rake scheme' [80,95] which involved acetic acid as an intermediate between propionic acid and the final product CO_2.

A transition metal ion (copper included [59]) has been widely used to catalyze the decomposition of H_2O_2 in order to generate hydroxy radicals. However, in the presence of organic substrates, such as acetone, acetic acid and *tert*-butyl alcohol, the catalytic effect varied [96]. Fujihira et al. [83] found that Cu^{2+} was a more powerful oxidant in the TiO_2 photocatalytic oxidation of toluene than Fe^{3+} owing to its lower reversible redox potential at semiconductor particle surfaces. The substitution of Cu^- for Fe^{2+} ion as the Fenton reagent [97] had several advantages in the direct transformation of benzene to hydroquinone. The cupric ion was found to be a positive or negative catalyst at different concentrations in the photocatalytic decomposition of phenol over TiO_2 powder [77].

As found by Wei at al. [82], H_2O_2 added to the TiO_2 system plays the role of an accelerator and significantly increases the photocatalytic oxidation of the substrate. They have shown [82,98] that the presence of both the ferric and cupric ions enhance the phenol oxidation rate drastically. A $1\ g\,l^{-1}$ phenol solution was completely photomineralized within 1 h and the total organic carbon (TOC) removal reached 80%. It was concluded that the photocatalytic oxidation of phenol is controlled by the rate of H_2O_2 decomposition and the metal ions were needed as catalysts to decompose the H_2O_2. At the same time, the generation of OH radicals from the TiO_2 surface becomes less important [98].

In the absence of H_2O_2 the added ferric ion induces the occurrence of the photo-Fenton-type reaction so that the phenol removal is enhanced from 23% to 33% within 8 h [82]. It should be noted that the nature and composition of the photochemicallly active Fe(III) species leading to Fenton-active Fe(II) was not determined. However, the addition of cupric ions to the same H_2O_2 system shows a negative effect. Since phenol oxidation without any metal ions is pH dependent [99] (it decomposes faster at higher pH), it is also important to consider the different initial pH values of the cupric ions system (owing to different hydroxide precipitation considerations the pH was 4) compared with that of iron (initial $pH=2$). Actually, the pH effect is in favour of the system with cupric ions added and therefore the negative effect in these systems does not come from the initial pH change. This effect was attributed by Okamoto et al. [77] to be the result of severe short circuiting of the cupric ion, as the Cu(I)–Cu(II) couple creates a cyclic process without generating active hydroxyl radicals.

4. Conclusions and future prospects

Based on the data described in this contribution, the study of environmental aspects of the photochemistry of copper and its complexes deserves attention. The examples presented here highlight some of the salient features of such research. There are several ways that can be suggested that could lead in future to a better understanding of the environmental aspects of the photochemistry of coordination compounds of copper.

Achieving better knowledge of the composition, the structure of copper complexes, and their photochemical and thermal redox properties is essential for understanding the mechanism operating in environmentally interesting systems. Such data about the identity of the photoactive copper complex are important not only in pure homogeneous systems but also in heterogeneous media, where the importance of the homogeneous pathway is increasingly being accepted in the literature.

Thus, research purposefully oriented towards mechanistic studies is very desirable in the future. However, to establish the precise complex (mostly kinetically labile in the case of copper) of known structure and composition in solution, to separate the surface and solution reactions, as well as to identify the photochemical and thermal reaction pathways in a particular system is rather complicated.

From the point of view of thermal reactivity (which cannot be excluded when considering any photochemical process) mainly the possibility of a copper-based photo-Fenton-like reaction seems to be very reasonable. Despite years of discussion about the real nature of the mechanism of the Fenton-reactions (for copper [100,101] as well as for classic iron systems [102]), the substantial influence of copper and iron was clearly experimentally proven and also practically exploited (see for example the new iron-based wastewater treatment process [62] without, however, specification of the photochemically active species).

The extended use of several experimental techniques enabling the identification of short-lived intermediates (mainly oxygen-derived radicals), like the chemical scavenging method [103], EPR spin trapping or flash photolysis and pulse radiolysis, along with the exploitation of kinetic data may contribute to overcome these difficulties.

Acknowledgements

The author acknowledges the support within the Project 1.4 of the US Environmental Protection Agency/University of Georgia Cooperative Agreement, Athens, Georgia, USA and Grant No. 1/1414/94 from the Slovak Grant Agency, Slovak Republic.

References

[1] J. Sýkora and J. Šima, Photochemistry of Coordination Compounds, Veda, Bratislava, Czechoslovakia, 1986.
[2] H. Hennig and D. Rehorek, Photochemische und Photokatalytische Reaktionen von Koordinationsverbindungen, Teubner, Stuttgart, Germany, 1988.
[3] M.A. Fox and M. Chanon (eds.), Photoinduced Electron Transfer, Elsevier, Amsterdam, 1988.
[4] J. Sýkora and J. Šima, Photochemistry of Coordination Compounds, Elsevier–Veda, Amsterdam, 1990.
[5] O. Horváth and K.L. Stevenson, Charge Transfer Photochemistry of Coordination Compounds, VCH, New York, 1993.
[6] G. Ferraudi and S. Muralidharan, Coord. Chem. Rev., 336 (1981) 45.
[7] J. Sýkora, Chem. Listy, 376 (1982) 1047.
[8] J. Sýkora, in H. Yersin and A. Vogler (eds.), Photochemistry and Photophysics of Coordination Compounds, Springer, Heidelberg, 1987, p. 193.
[9] C. Kutal, Coord. Chem. Rev., 364 (1985) 191.
[10] R.G. Salomon, Tetrahedron, 339 (1983) 485.
[11] J. Sýkora, E. Brandšteterová and A. Jabconová, in C. Kutal and N. Serpone (eds.), Photosensitive Metal Organic Systems: Mechanistic Principles and Applications, American Chemical Society, Washington, DC, 1993, p. 377.
[12] J. Sýkora, J. Inf. Rec. Mater., 317 (1989) 415.
[13] C. Kutal, Coord. Chem. Rev., 399 (1990) 213.
[14] J.W. Moffett and R.G. Zika, in R.G. Zika and W.J. Cooper (eds.), Photochemistry of Environmental Aquatic Systems, Advances in Chemistry Series 327, American Chemical Society, Washington, DC, 1987, p. 116.
[15] W.G. Sunda and R.R.L. Guillard, J. Mar. Res., 34 (1976) 511.
[16] J.W. Moffett and R.G. Zika, Geochim. Cosmochim. Acta, 52 (1988) 1849.
[17] J.W.Moffett and R.G.Zika, Environ. Sci. Technol., 21 (1987) 804.
[18] D.L.Sedlak and J. Hoigné, Environ. Sci. Technol., 28 (1994) 1898.
[19] U.S. Kulkarni and S.G. Dixit, Ind. Eng. Chem. Res., 30 (1991) 1916.
[20] W.I. Oden, G.L. Amy and M. Conklin, Environ. Sci. Technol., 27 (1993) 1045.
[21] L.H. Keith and W.A. Telliard, Environ. Sci. Technol., 13 (1979) 416.
[22] S. Das, G.R.A. Johnson, N.B. Nazhat and R.S. Nazhat, J. Chem. Soc. Faraday Trans., 80 (1984) 2759.
[23] K. Hayase and R.G. Zepp, Environ. Sci. Technol., 25 (1991) 1273.
[24] S. Goldstein and G. Czapski, J. Am. Chem. Soc., 108 (1986) 2244.
[25] E.M. Thurman, Organic Geochemistry of Natural Waters, M. Nijhoff and Dr. W. Junk, Dordrecht, 1985.
[26] W. Mohl, H. Motschi and A. Schweiger, Langmuir, 4 (1988) 580.
[27] G. Ferraudi and S. Muralidharan, Coord. Chem. Rev., 36 (1981) 45.
[28] V. Borgmann and K.M. Ralph, Water Res., 17 (1983) 1697.
[29] G. Sandman and P. Böger, Plant Physiol., 66 (1980) 797.
[30] S.L. Andrianirinaharivelo and M. Bolte, J. Photochem. Photobiol. A: Chem., 73 (1993) 213.
[31] C.H. Langford, M. Wingham and V.S. Sastri, Environ. Sci. Technol., 7 (1973) 820.
[32] G. Mailhot, S.L. Andrianirinaharivelo and M. Bolte, J. Photochem. Photobiol. A: Chem., 87 (1995) 31.
[33] S.L. Andrianirinaharivelo, G. Mailhot and M. Bolte, Sol. Energy Mater. Sol. Cells, 38 (1995) 459.
[34] E. Cervone, F. Diomedi-Camassei, I. Giannini and J. Sýkora, J. Photochem., 311 (1979) 321.
[35] J. Sýkora, J. Kováčová, E. Brandšteterová and A. Jabconová, in G. Ondrejovič and A. Sirota (eds.), Contributions to Development of Coordination Chemistry, Slovak Technical University Press, Bratislava, 1993, p. 385.
[36] J. Sýkora, E. Horváth and J. Gažo, Z. Anorg. Allg. Chem., 442 (1978) 245.
[37] G.S. Laurence and A.T. Thornton, J. Chem. Soc. Dalton Trans., (1973) 1637.

[38] J. Sýkora, M. Jakubčová and Z. Cvengrošová, Collect. Czech. Chem. Commun., 47 (1982) 2061.

[39] J. Sýkora, E. Horváth and J. Gažo, Proc. 4th Symp. on Metal Complexes in Catalytic Oxidation Reactions, Karpacz–Bierutowice, Poland, June 4–12, 1979, Polish Chemical Society, Wroclaw, 1979, p. 86.

[40] E. Cervone, F. Diomedi-Camassei, I. Gianini and J. Sýkora, J. Photochem., 311 (1979) 321.

[41] J. Sýkora and J. Šima, Coord. Chem. Rev., 107 (1990) 1.

[42] C.L. Bailey and R.S. Drago, Coord. Chem. Rev., 79 (1987) 321.

[43] P. Engelbrecht, Ph. Thomas, H. Hennig and J. Sýkora, Z. Chem., 26 (1986) 137.

[44] J. Sýkora, P. Engelbrecht, H. Hennig, Ph. Thomas and H. Gliesing, German Patent DD 256 323 A1, 1988.

[45] J. Sýkora, P. Engelbrecht, H. Hennig, Ph. Thomas and H. Gliesing, Czech. Patent 255 399, 1987.

[46] J. Sýkora, A. Lopatová and M. Molčan, Proc. 6th Symp. on Photochemical and Thermal Reactions of Coordination Compounds (SOPTROCC 6), Bratislava–Smolenice, Czechoslovakia, April 19–22, 1988, Slovak Technical University Press, Bratislava, 1988, p. 157.

[47] J. Sýkora, E. Brandšteterová and A. Jabconová, Proc. 9th Int. Symp. on Photochemistry and Photophysics of Coordination Compounds, Fribourg, Switzerland, July 14–19, 1991, University of Fribourg, Fribourg, 1991, p. 47.

[48] J. Sýkora, E. Brandšteterová and J. Jabconová, Bull. Soc. Chim. Belg., 101 (1992) 821.

[49] J. Sýkora, A. Lopatová and M. Molčan, Proc. 12th Conf. on Coordination Chemistry, Smolenice–Bratislava, Czechoslovakia, June 6–9, 1989, Slovak Chemical Society, Bratislava, 1989, p. 377.

[50] J. Kováčová, J. Sýkora, E. Brandšteterová and I. Kentošová, in G. Ondrejovič and A. Sirota (eds.), Contributions to Development of Coordination Chemistry, Slovak Technical University Press, Bratislava, 1993, p. 391.

[51] P. Bergamini, A. Maldotti, S. Sostero, O. Traverso and J. Sýkora, Inorg. Chim. Acta, 385 (1984) L15.

[52] J. Sýkora, I. Giannini and F. Diomedi-Camassei, J. Chem. Soc. Chem. Commun., (1978) 207.

[53] G. Grabner, G. Li, R.M. Quint, R. Quint and N. Getoff, J. Chem. Soc. Faraday Trans., 87 (1991) 1097.

[54] J. Sýkora, Proc. 11th Int. Symp. on the Photochemistry and Photophysics of Coordination Compounds, Krakow, Poland, July 9–13, 1995, Polish Chemical Society, Krakow, 1995, p. 31.

[55] J. Sýkora and C. Kutal, Proc. 15th IUPAC Symp. on Photochemistry, Prague, Czech Republic, July 17–22, 1994, Prague Institute of Chemical Technology, Prague, 1994, p. 164.

[56] J. Sýkora, C. Kutal and R.G. Zepp, in G. Ondrejovič and A. Sirota (eds.), Current Trends in Coordination Chemistry, Slovak Technical University Press, Bratislava, 1995, p. 263.

[57] J. Sýkora, in R.G. Zepp and C. Kutal (eds.), Rep. to Project 1.4 of the US Environmental Protection Agency/University of Georgia Cooperative Agreement, Environmental Research Laboratory, 1993 (US Environmental Protection Agency, Athens, GA, USA).

[58] H.J.H. Fenton, J. Chem. Soc., 65 (1894) 899.

[59] S. Luňák and P. Sedlák, J. Photochem. Photobiol. A: Chem., 68 (1992) 1.

[60] R.G. Zepp, B.C. Faust and J. Hoigné, Environ. Sci. Technol., 26 (1992) 313.

[61] Y.I. Skurlatov, R.G. Zepp and G.L. Baughman, J. Agric. Food Chem., 31 (1983) 1065.

[62] G. Ruppert, R. Bauer and G. Heisler, J. Photochem. Photobiol. A: Chem., 73 (1993) 75.

[63] O. Legrini, E. Oliveros and A.M. Braun, Chem. Rev., 93 (1993) 671.

[64] J. Peral, J. Casado and J. Domenech, J. Photochem. Photobiol. A: Chem., 56 (1990) 113.

[65] D.F. Ollis and H. Al-Ekabi (eds.), Photocatalytic Purification and Treatment of Water and Air, Elsevier, Amsterdam, 1993.

[66] D.F. Ollis, E. Pelizzetti and N. Serpone, in N. Serpone and E. Pelizzetti (eds.), Photocatalysis Fundamentals and Applications, Wiley, New York, 1989.

[67] M. Schiavello (ed.), Photocatalysis and Environment, Kluwer Academic, Dordrecht, 1988.

[68] R.A. Larson, K.A. Marley and M.B. Schlauch, in D.W. Tedder and F.G. Pohla (eds.), Emerging Technologies in Hazardous Waste Management II, American Chemical Society, Washington, DC, 1991, p. 66.

[69] D. Bahnemann, J. Cunningham, M.A. Fox, E. Pelizetti, P. Pichat and N. Serpone, in D. Crosby,

G. Helz and R. Zepp (eds.), Aquatic and Surface Photochemistry, Lewis, Boca Raton, FL, 1994, p. 261.

[70] C. Kormann, D.W. Bahnemann and M.R. Hoffmann, Environ. Sci. Technol., 25 (1991) 494.

[71] R.W. Matthews, J. Catal., 111 (1988) 264.

[72] R.W. Matthews, Water Res., 20 (1986) 569.

[73] E. Pelizzetti, M. Borgarello, E. Borgarello and N. Serpone, Chemosphere, 17 (1988) 499.

[74] C. Minero, V. Maurino, L. Campanella, C. Morgia and E. Pelizzetti, Environ. Technol. Lett., 10 (1989) 301.

[75] M.A. Fox and M.T. Dulay, Chem. Rev., 93 (1993) 341 and references cited therein.

[76] C.S. Turchi and D.F. Ollis, J. Catal., 119 (1988) 483.

[77] K. Okamoto, Y. Yamamoto, H. Tanaka, M. Tanaka and A. Itaya, Bull. Chem. Soc. Jpn., 58 (1985) 2015.

[78] N. Serpone, Sol. Energy Mater. Sol. Cells, 38 (1995) 369.

[79] E.C. Butler and A.P. Davis, J. Photochem. Photobiol. A: Chem., 70 (1993) 273.

[80] M. Bideau, B. Claudel, L. Faure and H. Kazouan, J. Photochem. Photobiol. A: Chem., 84 (1994) 57.

[81] A. Sclafani, L. Palmisano and E. Davi, J. Photochem. Photobiol. A: Chem., 56 (1991) 113.

[82] T.Y. Wei, Y.Y. Wang and C.C. Wan, J. Photochem. Photobiol. A: Chem., 55 (1990) 115.

[83] M. Fujihira, Y. Satoh and T. Osa, Bull. Chem. Soc. Jpn., 55 (1982) 666.

[84] M. Fujihira, Y. Satoh and T. Osa, Chem. Lett. (Chem. Soc. Jpn.), 1981 (1981) 1053.

[85] M. Fujihira, Y. Satoh and T. Osa, Nature, 293 (1981) 206.

[86] V. Brezová, A. Blažková, E. Borošová, M. Čeppan and R. Fiala, J. Mol. Catal., 98 (1995) 109.

[87] D.L. Sedlak and J. Hoigné, Atm. Environ. A, 27 (1993) 2173.

[88] W.F. Bleam and M.B. McBride, J. Colloid Interface Sci., 110 (1986) 335.

[89] M.F. Ottaviani, E.M. Ceresa and M. Visca, J. Colloid Interface Sci., 108 (1985) 114.

[90] K. Eckschlager, I. Horsak and J. Vepřek-Šiška, Collect. Czech. Chem. Commun., 39 (1974) 2353.

[91] D.L. Sedlak and A.W. Andren, Environ. Sci. Technol., 25 (1991) 777.

[92] M. Bideau, B. Claudel, L. Faure and M. Rachimoellah, J. Photochem., 39 (1987) 107.

[93] M. Bideau, B. Claudel, L. Faure and M. Rachimoellah, Chem. Eng. Commun., 93 (1990) 167.

[94] M. Bideau, B. Claudel, L. Faure and H. Kazouan, J. Photochem., 61 (1991) 269.

[95] M. Bideau, B. Claudel, L. Faure and H. Kazouan, J. Photochem. Photobiol. A: Chem., 67 (1992) 337.

[96] C. Walling and A. Goosen, J. Am. Chem. Soc., 95 (1973) 2987.

[97] S. Ito, A. Kunai, H. Okada and K. Sasaki, J. Org. Chem., 53 (1988) 296.

[98] T.Y. Wei, Y.Y. Wang and C.C. Wan, J. Photochem. Photobiol. A: Chem., 69 (1992) 241.

[99] V. Augugliaro, L. Palmisano, A. Sclafani, C. Minero and E. Pelizzetti, Toxicol. Environ. Chem., 16 (1988) 89.

[100] A. Sobkowiak, A. Qui, X. Liu, A. Llobet and D.T. Sawyer, J. Am. Chem. Soc., 115 (1993) 609.

[101] G.R.A. Johnson, N.B. Nazhat and R.A. Saadalla-Nazhat, J. Chem. Soc. Chem. Commun., (1985) 407.

[102] D.T. Sawyer, C. Kang, A. Llobet and C. Redman, J. Am. Chem. Soc., 115 (1993) 5817.

[103] R.V. Bensasson, E.J. Land and T.G. Truscott (eds.), Excited States and Free Radicals in Biology and Medicine, Oxford University Press, New York, 1993, p. 101.