

PHOTOOXIDATION EFFECT OF CUPRIC COMPLEXES ON ALIPHATIC ALCOHOLS IN NONAQUEOUS SOLUTIONS

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Dedicated to Professor Dr J. Klikorka on the occasion of his 60th birthday.

In the photolysis of copper(II)-chloride-alcohol-acetonitrile systems ($c_{\text{Cu}} = 1 \text{ mmol l}^{-1}$, copper(II)-to-chloride molar ratio 1 : 2 to 1 : 8, 10% (v/v) alcohol), Cu(II) is reduced to Cu(I), and methanol, ethanol, 1-propanol, or 1-butanol is oxidized to the corresponding aldehyde, 2-propanol to acetone. In the case of 1-propanol and 1-butanol, chlorinated aldehydes are formed in addition too. The measured quantum yields of the photoreduction of Cu(II) to Cu(I) lay in the range of $\Phi_{\text{Cu(II)}} = 4.5$ to $40 \text{ mmol einstein}^{-1}$, the absolute quantum yields of the alcohol oxidation products were 2.3 to $47 \text{ mmol einstein}^{-1}$. The photoactive components are chlorocupric complexes $[\text{CuCl}_x]^{(2-x)+}$ ($x = 1-4$). The presence of complexes with a higher number of chloro-ligands in the coordination sphere ($x = 3, 4$) brings about a decrease in the Cu(II) photoreduction rate. The decrease in the photoreduction rate observed in the presence of dioxygen is explained in terms of re-oxidation of copper(I) by the latter, resulting in an increase in the concentration of the photochemically active cupric complexes. The catalytic aspects of the systems in question are discussed with respect to this effect.

Irradiation of methanolic solutions of CuCl_2 by polychromatic radiation brings about oxidation of methanol to methanal¹; 2-propanol, if used as the solvent, is transformed into acetone on the photolysis. Acetonitrile and acetic acid remain intact in the same conditions. In the suggested mechanism of the photooxidation of methanol and 2-propanol, the primary photochemical process is assumed to involve formation of chlorine radical. On the other hand, in the detailed study² of the primary photochemical effects taking place on irradiation of CuCl_2 solutions in methanol, ethanol, 2-propanol, and other alcohols, no chloro radicals were detected (in contrast to the work¹), but alcohol radicals were found. If, however, acetonitrile is used as solvent, the photolysis of the chloro cupric complexes present in the copper (II) chloride-acetonitrile system leads in the primary photochemical process to the oxidation of the chloro ligand to the chlorine radical identified³ in the Cl_2^- form, with a simultaneous reduction of the central Cu(II) atom to Cu(I) (refs⁴⁻⁷).

The data indicating that in the given experimental conditions, acetonitrile is inert with respect to chlorination¹⁻³, in conjunction with the fact that the Cl or Cl_2^- radical

exhibits strong oxidizing properties ($E^0 = 2.3 \text{ V}$ for Cl_2^- in acetonitrile⁸), brought us to the idea that the photosensitivity of chlorocupric complexes in acetonitrile as an inert solvent might be utilized for photooxidations of more reactive organic substrates. The aim of the present work was to verify the assumption of a possible photooxidation effect of chlorocupric complexes on some alcohols in copper(II)-chloride-organic-substrate-acetonitrile systems, using methanol, ethanol, 1-propanol, 2-propanol, and 1-butanol as the substrate. Since in the study¹ the photochemically active region of the radiation was not specified and no attention was paid to the composition of the photoactive component, these aspects have been dealt with in the present work; the results are summed up so as to form a basis for a more detailed study of the mechanism of the reactions involved.

EXPERIMENTAL

The techniques used and the conditions applied in the photochemical study have been published previously⁶. Acetonitrile (Apolda) was allowed to stand for 24 h with KMnO_4 , and afterwards heated for 1 h under reflux condenser and distilled under normal pressure; K_2CO_3 was then added and the acetonitrile was rectified on a column with 60 theoretical plates. The fraction boiling at 81.6°C was used. Concentration of copper(II) in the solution was 1 mmol l^{-1} and the system contained 10% (v/v) alcohol. Solutions for continuous photolysis were prepared from $1 \cdot 10^{-2} \text{ M-CuCl}_2$ and $1 \cdot 10^{-2} \text{ M-LiCl}$ solutions in acetonitrile. All chemicals used were of reagent grade purity. The solutions were placed in closed quartz cells accommodated in a thermostated

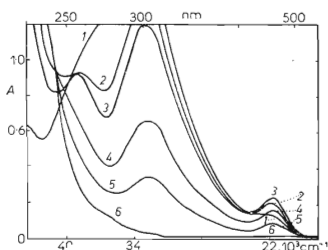


FIG. 1

Electronic absorption spectra of CuCl_2 -1-butanol-acetonitrile system ($[\text{Cu(II)}] : [\text{Cl}^-] = 1 : 2$) taken during the irradiation; $\lambda_{\text{irrad}} = 313 \text{ nm}$, irradiation period (min): 1 0, 2 20, 3 30, 4 40, 5 47, 6 70

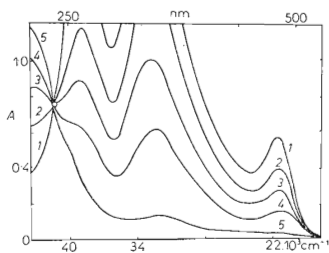


FIG. 2

Electronic absorption spectra of CuCl_2 -LiCl-1-butanol-acetonitrile system ($[\text{Cu(II)}] : [\text{Cl}^-] = 1 : 8$) taken during the irradiation; $\lambda_{\text{irrad}} = 313 \text{ nm}$, irradiation period (min): 1 0, 2 25, 3 33, 4 39, 5 51

holder at $20.0 \pm 0.2^\circ\text{C}$ and irradiated by monochromatic radiation of $\lambda = 313\text{ nm}$ under argon. The decrease in the concentration of Cu(II) due to its photoreduction to Cu(I) was monitored spectrophotometrically, and the quantum yields $\Phi_{\text{Cu(I)}}$ were calculated according to⁹. Prior to the photolysis, the systems were deoxygenated by purging for 20 min with argon saturated with acetonitrile. The intensity of the monochromatic radiation, determined by ferrioxalate actinometry¹⁰, was $I_0 = 7.25 \cdot 10^{-7}\text{ einstein min}^{-1}$. The alcohol oxidation products were identified gas chromatographically on a Hewlett-Packard 5830 A instrument fitted with a double FID, and their quantum yields were calculated in the conventional manner¹¹ based on the amounts of the oxo compounds determined by the direct calibration method. The corresponding chloro derivatives were determined from the calibration curve of the oxo compounds. The separating systems employed were: a) 5% Carbowax 20M on Chromaton N-AW DMCS, grain size 0.125–0.16 mm, packed in a 100 cm glass column of the inner diameter 3 mm. The samples were analyzed isothermally at 60°C ; injection chamber temperature 150°C , detector temperature 150°C , carrier gas (nitrogen) flow rate 13 ml min^{-1} . b) 10% OV 17 on Chromaton N-AW DMCS, grain size 0.125–0.16 mm, packed in a 140 cm glass column of the inner diameter 3 mm. The working temperature varied within the region of $60\text{--}250^\circ\text{C}$: after a 10 min period of isothermal regime at 60°C , a temperature gradient of $20^\circ\text{C min}^{-1}$ was applied. The injection chamber temperature was 200°C , detector temperature 270°C , nitrogen flow rate 20 ml min^{-1} . c) 5% Carbowax 20M — terephthalic acid, grain size 0.125–0.16 mm, in a glass column 140 cm long, inner diameter 3 mm. The samples were analyzed isothermally at 50°C ; injection chamber temperature 200°C (TCD), nitrogen flow rate 16 ml min^{-1} (a Packard 430 instrument).

RESULTS

Spectrochemical investigations evidenced that the copper(II)-chloride-alcohol-acetonitrile systems are sufficiently thermally stable, so that the spectral ranges appearing on the irradiation can be ascribed to radiation-induced reactions solely.

The shape of the electronic absorption spectra and changes occurring in them during the irradiation were alike for all the systems examined, being only dependent on the copper(II)-to-chloride molar ratio at the beginning of the process; so it is sufficient to present the spectra for two copper(II)-to-chloride ratios, *viz.* 1 : 2 and 1 : 8 (Figs 1 and 2, respectively). The dependences of the relative absorbance in the maximum of the peak at $21\,740\text{ cm}^{-1}$ (put 100% in the time $t_{\text{irrad}} = 0$) on the irradiation period for the two copper-to-chloride ratios are shown in Figs 3 and 4, respectively.

In the copper(II)-chloride-alcohol-acetonitrile systems, Cu(II) is reduced to Cu(I) on irradiation, and oxidation products of the alcohols appear. The irradiation periods requisite for a complete photoreduction of Cu(II) are longer for systems with the copper-to-chloride ratio 1 : 8 than for those with the ratio 1 : 2 (Table I), and also depend on the alcohol involved: methanol exerted the highest effect on the reduction rate, 2-propanol and 1-butanol affected it to the least extent. The photolyzed solutions were analyzed gas chromatographically to find that the corresponding aldehydes had formed from methanol, ethanol, 1-propanol, and 1-butanol, while 2-propanol had given rise to acetone. In the systems containing 1-propanol or 1-butanol, propanal or butanal chloro derivatives were also formed in addition to the alde-

hydres themselves; their presence was inferred from the retention times of the chromatographic peaks of the products after the irradiation.

The quantum yields $\Phi_{\text{Cu(I)}}$ of the reduction of Cu(II) to Cu(I) approximated to $t_{\text{irrad}} = 0$ as well as the absolute quantum yields of the alcohol photooxidation products for the copper(II)-to-chloride molar ratio 1 : 8 are given in Table I.

DISCUSSION

The electronic absorption spectra of the copper(II)-chloride-alcohol-acetonitrile systems and the changes in them occurring during the irradiation resemble those for the copper(II)-chloride-acetonitrile system; the alcohol oxidation products formed on the photolysis in addition to Cu(I) and HCl (ref.⁶) appeared in so low concentrations and gave rise to so small absorbance changes (with respect to the Cu(II) and Cu(I) complexes) that they did not show up even in the UV spectral region and could only be detected by GLC. As has been demonstrated, the character of the spectral changes^{6,12} as well as the quantum yields of the reduction¹³ of Cu(II) in the photolysis of chlorocupric complexes in acetonitrile solutions depend principally on the copper(II)-to-chloride molar ratio, because this value governs the concentration distribution¹⁴ of the various $[\text{CuCl}_x]^{(2-x)+}$ complexes ($x = 0-4$) in solution.

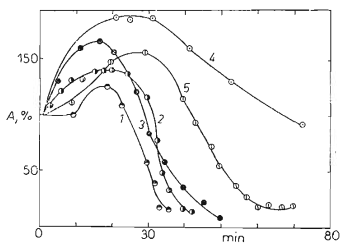


FIG. 3

Dependence of absorbance (A , %) of the absorption band at $21\,740\text{ cm}^{-1}$ on the irradiation period for the CuCl_2 -alcohol-acetonitrile systems ($[\text{Cu(II)}] : [\text{Cl}^-] = 1 : 2$); $\lambda_{\text{irrad}} = 313\text{ nm}$, alcohol used: 1 methanol, 2 ethanol, 3 1-propanol, 4 2-propanol, 5 1-butanol

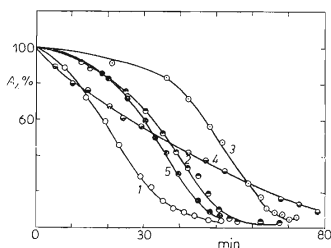


FIG. 4

Dependence of absorbance (A , %) of the absorption band at $21\,740\text{ m}^{-1}$ on the irradiation period for CuCl_2 -LiCl-alcohol-acetonitrile systems ($[\text{Cu(II)}] : [\text{Cl}^-] = 1 : 8$); $\lambda_{\text{irrad}} = 313\text{ nm}$, alcohol used: 1 methanol, 2 ethanol, 3 1-propanol, 4 2-propanol, 5 1-butanol

Since, owing to the photoreduction of Cu(II) to Cu(I), the copper(II)-to-chloride ratio varies during the process, the spectral changes of the alcohol-containing systems with the copper(II)-to-chloride ratios 1 : 2 and 1 : 8 taking place during the irradiation will be different; their character will be determined by the changes in the distribution of not only cupric, but also cuprous complexes, which also depends on the copper(I)-to-chloride ratio¹⁵.

The interpretation of the spectral changes for systems with the copper(II)-to-chloride ratio 1 : 8 is considerably more straightforward than for systems with the ratio 1 : 2, as in systems containing chloride in excess a single complex predominates¹⁴ and is transformed into the corresponding chlorocuprous complex on the irradiation. The equilibrium between the two complexes, shifted in favour of the latter as the irradiation periods lengthens, gives rise to an isosbestic point at $41\,670\text{ cm}^{-1}$, increasing absorbance at $\nu > 4\,670\text{ cm}^{-1}$, and monotonically decreasing absorbance over the entire spectral region of $\nu < 41\,670\text{ cm}^{-1}$ (Figs 2 and 4).

In irradiated systems with the copper(II)-to-chloride molar ratio 1 : 2 are present various cuprous and cupric complexes with different numbers of chloride ions in the coordination spheres of Cu(II) (ref.¹⁴) and Cu(I) (ref.¹⁵); the isosbestic point at $41\,670\text{ cm}^{-1}$ is absent, hence a more complex and variable equilibrium establishes between the cupric and cuprous complexes. Photoactive will be particularly the $[\text{CuCl}_x]^{(2-x)+}$ complexes with $x = 2$, but the distribution of the complexes in the systems in question will vary during the irradiation, owing to the variable copper(II)-to-chloride ratio, in favour of complexes with $x > 2$, which absorb radiation to a higher extent than those with $x \leq 2$. Then the isosbestic point at $23\,530\text{ cm}^{-1}$ (Fig. 1) can be attributed to the equilibrium between the $[\text{CuCl}_2]$ and $[\text{CuCl}_3]^-$ complexes, the increase in the absorbance at $21\,740\text{ cm}^{-1}$ observed in the first stage of irradiation being due to the shift of the equilibrium in favour of the latter complex. As of the $[\text{CuCl}_x]^{(2-x)+}$ complexes the $[\text{CuCl}_3]^-$ complex exhibits the highest molar absorptivity¹⁶, a further irradiation is bound to result in a drop of the absorbance in the region $41\,670\text{--}44\,440\text{ cm}^{-1}$ (Figs 1 and 2), typical of Cu(I) in acetonitrile¹⁷.

In view of the fact that the quantum yields of reduction of Cu(II) to Cu(I) decrease with increasing number of chloride ions in the coordination sphere of the former¹⁸, the Cu(II) photoreduction period was anticipated to be longer for systems with the copper(II)-to-chloride ratio 1 : 8 as compared with systems with the ratio 1 : 2; this assumption was experimentally found true (Table I).

The results obtained indicate that the photochemically active components in the systems under study are chlorocupric complexes, and photoactive radiation is that inducing electron transfer from the ligand to the central atom, $\sigma, \pi(\text{Cl}) \rightarrow 3d\text{ Cu(II)}$. The Φ values of the photoreduction of Cu(II) to Cu(I) depend on the irradiation period due to the effect of several simultaneous secondary reactions on the overall mechanism of the photooxidation. The fact that there is a number of such reactions,

with different kinetics, may be responsible for the $\Phi_{\text{Cu(I)}}$ values not being always consistent with the observed periods of reduction of Cu(II) to Cu(I) for the various alcohols. The secondary thermal reactions also affect to a considerable extent the formation of the alcohol oxidation products. Although so far there are not sufficient data available for a detailed mechanism of the photooxidation to be set forth, some new, interesting aspects can be pointed out. For instance, since the quantum yield of propanal exceeds that of Cu(I), the mechanism of formation of the former probably involves not only the primarily created chloro radicals (whose quantum yield necessarily equals that of Cu(I)), but also other radicals, created either in the primary photochemical process or in secondary thermal reactions. As these mutually competitive reactions are radical ones by nature, the interpretation of the experimental data calls for a detailed study of the ways of formation and deactivation of the radicals as well as of the kinetics of the processes involved.

Based on the results of this work, the following overall pathway of the photooxidation effect of cupric complexes on the aliphatic alcohols in acetonitrile solutions can be suggested: By photooxidation of methanol or ethanol, methanal or

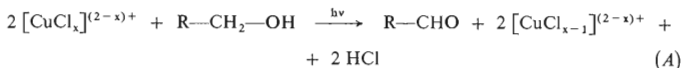
TABLE I

Data from the photolysis of Cu(II)-chloride-alcohol-acetonitrile systems in anaerobic conditions; $\lambda_{\text{irrad}} = 313 \text{ nm}$, $t = 20^\circ\text{C}$, $c_{\text{Cu(II)}} = 1 \text{ mmol l}^{-1}$, 10% (v/v) alcohol

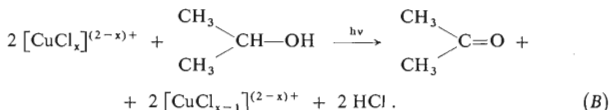
Alcohol	Cu(II)→Cu(I) reduction period, (min), for the [Cu(II)] : [Cl ⁻] ratio		$\Phi_{\text{Cu(I)}}$ mmol einstein ⁻¹	Alcohol oxidation product	Φ_{product} mmol einstein ⁻¹
	1 : 2	1 : 8			
Methanol	38	50	40	methanal	^a
Ethanol	45	65	12	ethanal	2.5
1-Propanol	60	75	4.5	propanal propanal chloro derivative	47 2.3
2-Propanol	>100	>100	28	propanone	9.5
1-Butanol	70	75	8.0	butanal butanal chloro derivative	5.3 5.3

^a Only qualitative detection.

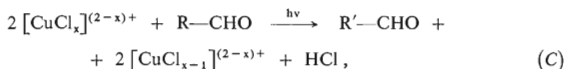
ethanal is formed:



(R = H or CH₃), whereas 2-propanol is converted into acetone



In system involving 1-propanol or 1-butanol, the formation of the aldehydes (reaction (A), R = C₂H₅ or C₃H₇) is succeeded by additional formation of their chloro derivatives:



where R' is C₂H₄Cl or C₃H₆Cl.

It should be noted that in addition to the factors discussed, the rate of Cu(II) photo-reduction is affected also by the content of oxygen in the system. Spectrophotometric investigations carried out in aerobic conditions evidenced that Cu(I) formed by the photoreduction of Cu(II) is oxidized by oxygen; as a consequence, in systems that have not been freed from oxygen by purging with argon, the observed rate of reduction of Cu(II) is lower. This fact, often regarded as a drawback in photochemical syntheses, is of significance in the case in question as it offers a possibility of raising the yield of oxidation products¹⁹ by photo-assisted catalytic reaction of the Cu(II)–Cu(I) redox cycle²⁰. As the recent experimental data²¹ indicate, it is possible to achieve higher yields in the photooxidation of organic substances, in addition to the catalytic cycles, also by altering the composition of the systems of chlorocupric complexes in acetonitrile. Obviously then, in spite of the comparatively low quantum yields of the oxidation products in the systems so far examined, a further study of such systems is of interest from both the theoretical and practical points of view.

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