PHOTOREDOX BEHAVIOUR OF CHLOROCOPPER(II) COMPLEXES IN ACETONITRILE: MECHANISM AND QUANTUM YIELDS*

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Summary

Visible anaerobic irradiation of the system $CuCl_2$–$LiCl$ in acetonitrile leads to the formation of Cu(I) with quantum yields Φ in the range 0.04–0.13, which decrease with time and depend on the [Cu(II)]/[Cl$^-$] ratio. The higher this ratio, the higher the Φ values are. The aerobic quantum yields are much smaller and the air quenching effect is more pronounced for the more chlorinated Cu(II) species. Only the Cu(I)—Cl bond appears to be sensitive to molecular oxygen, the Cu(I) being re-oxidized during the time interval required for the photoproduced chlorocopper(I) species to be fully solvated. From pulsed photolysis experiments (using a neodymium laser flashing at 473 nm) it appears that the transient $Cl_2^{\dot-}$ (which originates from Cl$^{\cdot}$ and free Cl$^-$) is quenched only by Cu(II) ($k_{II} = 1.7 \times 10^8$ dm^3 mol^{-1} s^{-1}) and Cu(I) ($k_I = 2.8 \times 10^8$ dm^3 mol^{-1} s^{-1}) and not by Li$^+$, Cl$^-$ or the solvent.

1. Introduction

Although the light sensitivity of $CuCl_2$ dissolved in polar aprotic solvents is well known [1 - 6], it is only recently that the observations have become more quantitative. Quantum yields for photoreduction to Cu(I) have been measured as functions of the complex concentration and also of the solvent used [7]; $CuCl_2$ photocatalysed reactions have also been discovered [8]. Moreover it has been demonstrated that the first chemical event which follows the absorption of a photon is the homolytic splitting of the Cu(II)—Cl

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*This paper is dedicated to Professor H. Hartmann on the occasion of his 65th birthday.

bond with the subsequent association of the chlorine radical with Cl^- present in the solution to give the observed transient Cl_2^- [9].

These findings open the way to interesting possibilities. Firstly, the Cl_2^- radical anion could be an excellent chlorinating agent and therefore the chlorocopper(II) complexes might give rise, with suitable substrates, to photocatalytic systems that are able to work with visible light. Secondly, we have found in preliminary experiments [10] that molecular oxygen is highly efficient in quenching the overall quantum yield for Cu(II) reduction, and therefore free radical oxygen intermediates (postulated by Gray [11] in the thermal oxidation of Cu(I) by O_2) may also take part in some Cu(II) photocatalysed reactions. However, the role of O_2 has previously been ignored [1 - 8]: the reported Cu(I) quantum yields [7] may not be dependable and it is possible that $CuCl_2$ photocatalysed reactions [8] could be initiated by an O_2-derived radical and not by a chlororadical.

We have also found that the Cu(I) species finally photoproduced is not reoxidized by air and therefore different Cu(I) species with various sensitivities to air are produced during the photolysis [10]. This last aspect can both be relevant to catalytic purposes and have biological implications, since the importance of Cu(I) as a catalyst in redox reactions involving molecular oxygen in non-enzymic [12, 13] as well in enzymic systems is well recognized: the reconstitution of biologically active proteins from the corresponding apoproteins requires the participation of Cu(I) [14].

The aim of this investigation is to contribute to a better understanding of these problems. We have measured the Cu(II) → Cu(I) quantum yields of the system $CuCl_2$–LiCl–acetonitrile under aerobic and anaerobic conditions, as well as the quenching constants of Cl_2^-, in order to clarify the redox mechanism of the chloroacetonitrilecopper complexes mentioned earlier.

2. Materials, apparatus and methods

Anhydrous Cu(II)Cl_2 was prepared by dehydration of $CuCl_2 \cdot 2H_2O$ (Lachema) in an atmosphere of hydrogen chloride. Commercial LiCl (Merck) and acetonitrile (C. Erba) were of p.a. quality. Anhydrous $CuCl_2$ was dissolved in CH_3CN in the presence of LiCl to vary the ratio $[Cu(II)]/[Cl^-]$. The final Cu(II) concentrations were in the range $(0.37–1.5) \times 10^{-3}$ mol dm^{-3}. Molecular oxygen was removed, when necessary, by bubbling through the sample cuvette pure commercial nitrogen gas which had been further purified through a column of heated granulated metallic copper. When, however, aerobic irradiations were performed the sample cell was left open to the air. Cu(I) solutions were prepared by adding powdered copper to the acetonitrile solution of $CuCl_2$ (the Cu(II) being quantitatively reduced to Cu(I)) and filtering off the excess metallic copper.

The continuous irradiations were carried out by means of a high pressure 1045 Beckman xenon arc lamp (XBO 450 W). The sample cuvette was kept in circulating water (the temperature was about 20 °C) to avoid heating

effects. The light was filtered through 5-61 and 3-72 Corning glasses: the maximum transmittance was 33% at 471 nm with a halfwidth of 25 nm. In these conditions, the incident light intensity was about 1.2×10^{-7} einstein s^{-1}. The actinometry was determined by using the Reinecke salt according to the prescribed procedure [15]. When the light was not totally absorbed by the solution, a calculation using a graphical procedure [16] was carried out for an accurate evaluation of the amount of transmitted light. The absorption spectra were measured with a Varian 635 D spectrophotometer. The amount of photoreaction (Cu(II) → Cu(I) reduction) was determined by the change in optical density of the peak of the lowest energy intense band, which is located very close to 460 nm for any $[Cu(II)]/[Cl^-]$ ratio: the absorption due to Cu(I) species was considered to be zero. The electron spin resonance (ESR) spectra were recorded at liquid nitrogen temperature with a Varian E-9 spectrometer at X-band frequencies. The gas–liquid chromatographic separations were performed using an Erba G I apparatus with 1.8 m glass columns filled with Carbowax 1500 (5% wt.%) on Chromosorb W 80-100 mesh.

The pulsed laser equipment has been described in detail elsewhere [17]. In this project the neodymium laser (Chromatix model 1020) was operating at $\lambda = 473$ nm as output, with a peak power of about 2.5 kW and at a repetition rate of 30 Hz. The pulse duration was about 250 ns and the number of photons per pulse was about 1.2×10^{15}. The laser beam impinged on a sample cell 2 mm thick at the Brewster angle. The monitoring light (a high pressure mercury arc lamp, HBO 100 W/2) was focused within the laser spot, was filtered by the cut-off 7-54 or 7-59 Corning glasses and was then passed through a high aperture monochromator grating (Spex Minimate). The signals due to the transmitted monitoring light were memorized after each laser pulse in a digital transient recorder (Datalab model 802) and were discharged on an averaging system (Laben model 400). In some measurements the signals were fitted into a computer Laben 70 [18]. The signal-to-noise ratio was enhanced to about 50 by averaging some hundreds of pulses. In the pulsed laser experiments the sample was thermostated at 22 ± 0.5 °C and the increase of temperature due to absorption of the laser photons was negligible (less than 0.1 °C). The oscilloscopic traces were recorded at frequencies in the range 320–435 nm. The lifetimes τ were calculated from a linear fit of a plot of $\log (I_t - I_\infty)$ versus t where I_t and I_∞ represent the trace signal values at time t and after its complete decay.

3. Results and discussion

When $CuCl_2$ is dissolved in CH_3CN it gives rise to an equilibrium mixture of differently chlorinated copper(II) complexes, namely $CuCl^+$, $CuCl_2$, $CuCl_3^-$ and $CuCl_4^{2-}$; their full coordinations are attained by the solvent molecules when needed. The stepwise formation constants have been evaluated [19] and the concentration distribution of the different

chlorocopper(II) complexes has been reported [20]. The absorption spectra obtained at different [Cu(II)]/[Cl⁻] ratios are shown in Fig. 1 together with the transmittance profile of the filter system used for the continuous irradiations.

While the 400 nm band is strongly dependent on the copper(II):chlorine ratio, the band at about 460 nm is always well resolved; this is the lowest energy intense band (ϵ around 10^3 mol^{-1} cm^{-1} dm^3) and is charge transfer ligand-to-metal in character [21, 22]. Because of these features, it has been chosen for both continuous and pulsed irradiations. The most studied system is that having a [Cu(II)]/[Cl⁻] ratio of $\frac{1}{8}$ because in this case the composition is found to be 95.4% $CuCl_4^{2-}$ the remaining 4.6% being $CuCl_3^-$, and the evaluation of the Cu(I) quantum yield for the tetrachlorocopper (II) species does not require any significant correction of the absorbance values (see later).

3.1. Continuous irradiation

For all the compositions studied no metallic copper or precipitate was formed.

The experiments also show that under irradiation the optical density of the 460 nm band decreases when the [Cu(II)]/[Cl⁻] ratios are $\frac{1}{3}, \frac{1}{4}$ and $\frac{1}{8}$. This decrease is interpreted as being due to photoreduction of Cu(II) to Cu(I) [4, 5] whose chloro and/or acetonitrile complexes are generally colourless. To obtain independent proof for the disappearance of Cu(II), the ESR spectra have been recorded for the $\frac{1}{8}$ ratio solution. The non-irradiated solution shows an intense symmetric band with $g = 2.16$ which tends to disappear with irradiation, indicating removal of Cu(II). In contrast,
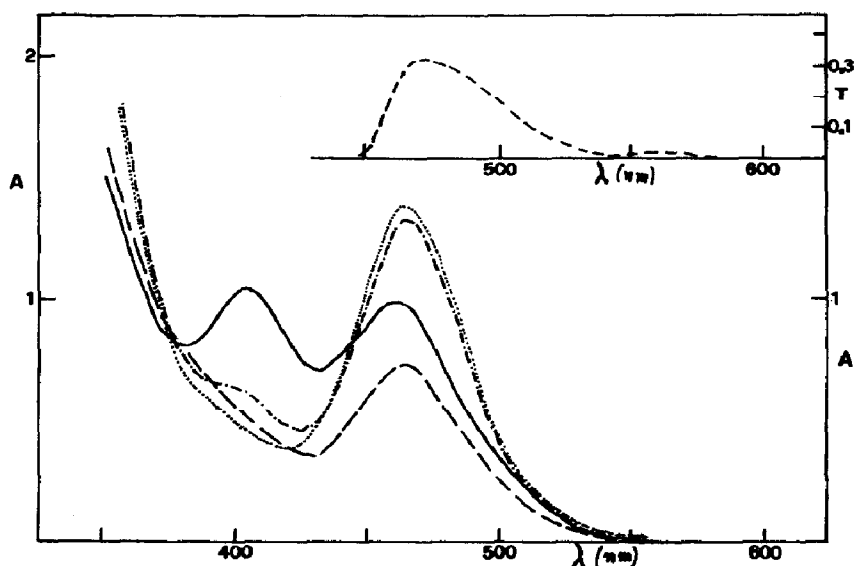

Fig. 1. Absorption spectra of $CuCl_2$ (1.0×10^{-3} mol dm^{-3}), plus LiCl where necessary, dissolved in CH_3CN; for different [Cu(II)]/[Cl⁻] ratios: $-\,-\,-, \frac{1}{2}; \cdots, \frac{1}{3}; -\cdot-, \frac{1}{4}; —, \frac{1}{8}$.

a peculiar behaviour is exhibited by the solution with ratio $\frac{1}{2}$. At first there is an increase of its absorbance and then a regular decrease. The increase indicates that the composition of this system is moving towards smaller [Cu(II)] / [Cl⁻] ratios to which higher absorbances correspond. Cu(II) is in fact photoreduced and the shift of the equilibrium position toward more chlorinated species is initially able to overcome the decrease in optical density due to the disappearance of Cu(II).

The changes in absorbance under irradiation are greatly affected by the presence of molecular oxygen; it is able to quench the amount of photoreaction significantly, particularly when the [Cu(II)] /[Cl⁻] ratio is $\frac{1}{8}$. In this case, the absorbance remains almost unchanged under aerobic irradiation indicating a practically complete reoxidation of Cu(I) to Cu(II) by O_2.

In order to evaluate the Cu(II) → Cu(I) quantum yields, it is necessary to know the new composition of each system after irradiation since the 460 nm peak absorption intensity is not only a function of [Cu(II)] but also of the ratio [Cu(II)] /[Cl⁻].

The apparent Φ values are given in Table 1. These values were obtained by calculating x from the equation

$$D = (1-x)D_B = (1-x)\left(\frac{A-B}{A-C} D_C + \frac{B-C}{A-C} D_A \right) \tag{1}$$

where

$$x = \frac{[\text{Cu(I)}] \text{ photoproduced}}{[\text{Cu(II)}]_0 \text{ before irradiation}}$$

D_A is the peak absorbance of the solution to be irradiated having [Cu(II)]$_0$/ [Cl⁻] = A, D the peak absorbance of an irradiated solution which has shifted its ratio from A to B, D_C the peak absorbance of a solution having [Cu(II)]$_0$/ [Cl⁻] = C and D_B the peak absorbance of a solution having [Cu(II)]$_0$/[Cl⁻] = B; $A > B > C$ ([Cu(II)]$_0$ has the same numerical value for A, B and C) and $B = (1-x)A$.

Equation (1) is valid if the composition of the system of ratio B is independent of [Cu(II)] and also if D_B varies linearly between D_A and D_C. Both requirements are satisfactorily met in that the Beer–Lambert law for D_B holds in the limit of our accuracy, and its linearity is rather well kept in the range A–C for the chosen ratios. In the worst case, the range $\frac{1}{2}$ to $\frac{1}{3}$, the non-linearity is within 10%. The range could be shortened, and hence the linearity improved, by making C closer to B but this improvement was not necessary for our considerations.

For the validity of eqn. (1), it is also necessary that Cl˙ should finally be reconverted to Cl⁻ or else B would be equal to $A(1-x)/(1-Ax)$. We performed some experiments from which it can be deduced that Cl˙ is not lost in any chlorination reaction. A prolonged aerobic irradiation of a solution with ratio $\frac{1}{8}$ caused no change in its spectrum. If the photoproduced chloro radicals did not reconvert to Cl⁻, the equilibrium between the chloroacetonitrilecopper(II) complexes and the free Cl⁻ would shift toward less chlori-

TABLE 1

Photoreduction quantum yields for the reaction Cu(II) → Cu(I) in the system CuCl$_2$–LiCl–acetonitrile at different [Cu(II)]/[Cl$^-$] ratios for irradiation centred at 471 nm

Ratio	Φ			
	Aerobic	Anaerobic Total irradiation time (min)		
		1	4	9
$\frac{1}{8}$	~0	0.053	0.048	0.042
$\frac{1}{4}$	0.006	0.066	0.063	0.061
$\frac{1}{3}$	0.009	0.092	0.063	0.069
$\frac{1}{2}$	0.019	0.13	–	–

nated species and, contrary to observation, the band at 400 nm should disappear. The solution was also analysed by gas chromatography in a search for some acetonitrile chloro derivative, particularly for monochloroacetonitrile or trichloroacetonitrile, but no evidence for these or any other new species was noticed by comparison of the spectra before and after photolysis. As previously stated, irradiation of pure CuCl$_2$ causes an increase of the 460 nm band peak. The maximum value for D was calculated from eqn. (1) by putting $dD/dx = 0$ with $A = 0.5$, $C = 0.333$, $D_A = 0.70$, $D_C = 1.33$ and [CuCl$_2$] = 10^{-3} mol dm^{-3}. D was found to be 0.89 if $B = (1 - x)A$, and 0.73 if $B = A(1 - x)/(1 - Ax)$. The experimental D value of 0.90 fits fairly well with the first hypothesis, *i.e.* Cl$^{\cdot}$ → Cl$^-$.

From Table 1 the following results can be drawn:

(1) Φ increases with the [Cu(II)]/[Cl$^-$] ratio;

(2) O$_2$ is able to quench markedly the apparent values of Φ;

(3) the higher the [Cu(II)]/[Cl$^-$] ratio, the lower is the O$_2$ quenching efficiency;

(4) Φ decreases with the irradiation time.

Further, we observed that, interestingly, when the cuvette of a de-aerated solution of any [Cu(II)]/[Cl$^-$] ratio was open to air, no dark reoxidation occurred for hours; the Cu(I) photoproduct appeared to be stable.

From observations (1) and (3) above we can deduce that the higher the number of coordinated Cl ligands, the higher is the stability of excited Cu(II) toward reduction and consequently the higher is the instability of Cu(I) toward oxidation. From observation (2) it appears that in fact the Cu(I)—Cl bond is very sensitive to O$_2$. Even in the solid state, white CuCl rapidly transforms into yellow–green basic copper(II) chloride if exposed to humid air. Since the final Cu(I) photoproduct is stable in air, it is assumed that it contains no Cu(I)—Cl bonds or, more precisely, that its identity is Cu(CH$_3$-CN)$_4^+$. This species is known and its stability to the atmosphere has been

demonstrated [19]. To obtain corroborative proof of this hypothesis, a weighed amount of CuCl was dissolved under aerobic conditions into aceto-nitrile ([Cu(I)] = 10^{-3} mol dm^{-3}) containing enough LiCl to give a [Cu(II)] / [Cl$^-$] ratio of $\frac{1}{8}$. During this operation about one quarter of the CuCl was oxidized (the absorbance at 460 nm corresponded to a solution of CuCl$_4^{2-}$ species of approximate concentration 0.25×10^{-3} mol dm^{-3}) and the optical density was stable. The solution was allowed to evaporate and, when a slurry was obtained, acetonitrile was added to obtain the same volume as before the evaporation. This time the optical density at 460 nm was exactly the value for the composition corresponding to a complete oxidation of Cu(I) to Cu(II). Therefore the Cu(I) oxidation is possible either when CuCl has not yet lost its Cl ligand or when Cl$^-$ has re-entered the coordination sphere of Cu(I).

From the equilibrium compositions at different [Cu(II)] /[Cl$^-$] ratios [20], it is evident that CH$_3$CN as a solvent is able to compete with Cl$^-$ in coordinating Cu(II). When the central metal has a charge of +1 complete solvation is to be expected. More quantitatively, the formation constant in acetonitrile of CuCl$^+$ is $10^{9 \cdot 7}$ and that of CuCl is only $10^{4 \cdot 9}$ [19]. Thus we have made enough observations to make the reasonable supposition that O$_2$ is only able to oxidize Cu(I) during the time interval that is needed for complete thermal solvation by CH$_3$CN; Cu(I)Cl$_3^{2-}$ photoproduced from CuCl$_4^{2-}$ requires a longer time to be solvated than, for example, Cu(I)Cl photoproduced by CuCl$_2$, since the former has to lose two more Cl ligands than the latter. We have used this reasoning to interpret observation (3).

3.2. Pulsed irradiation

The Cl$_2^-$ transient is photoproduced in solutions having [Cu(II)] /[Cl$^-$] ratios up to nearly $\frac{1}{3}$ [9]. This behaviour is illustrated in Fig. 2(a). Figure 2(b) shows traces at different wavelengths for a solution of ratio $\frac{1}{3}$ (1.9% CuCl$_2$, 96.2% CuCl$_3^-$ and 1.9% CuCl$_4^{2-}$). The transient observed with this last solution has a weaker absorbance than Cl$_2^-$ and, since it exhibits both positive and negative displacements, it should consist of a Cu(II) species.

The signal amplitude with which Cl$_2^-$ is detected in solutions with ratios varying from $\frac{1}{8}$ to $\frac{1}{3}$ is proportional to the concentration of free Cl$^-$ and although it is likely that Cl$^\cdot$ is also photoproduced by the system with ratio $\frac{1}{2}$ (17.1% CuCl$^+$, 52.7% CuCl$_2$, 25.9% CuCl$_3^-$), Cl$_2^-$ is not detected in this case simply because no free Cl$^-$ exists in solution to allow its formation.

Although at the end of its life Cl$_2^-$ reconverts to 2Cl$^-$ (see later), it may have some interesting interactions with other species. It may promote chlorination reactions under the effect of visible light or solar energy. CuCl$_2$ with excess LiCl gives rise to a photocatalytic cycle since the reoxidation of Cu(I) to CuCl$_4^{2-}$ species is virtually complete in air. To investigate this possibility we have tried to determine the chemical properties (especially the redox properties) of this dichloro radical by quenching measurements All the observed transients exhibited first order decay, and no self-quenching occurred among the chloro radicals. The reciprocal lifetimes of the transients were linearly
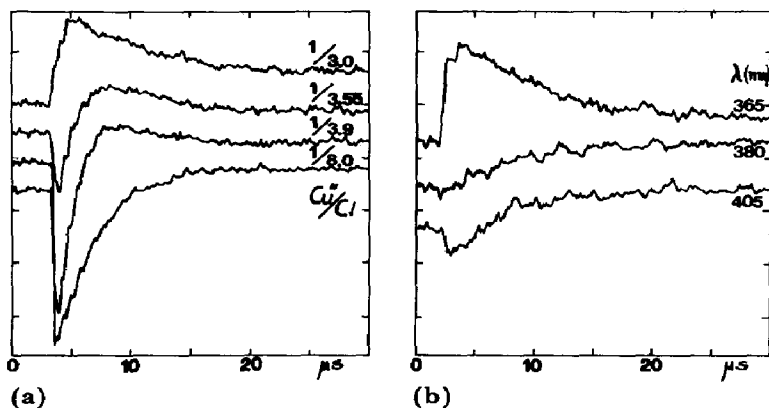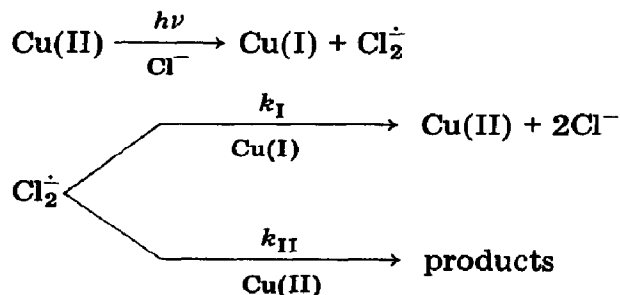
Fig. 2. (a) Transient absorption intensity of acetonitrile solutions with different [Cu(II)]/ [Cl$^-$] ratios vs. time at 365 nm. [Cu(II)] was 2 × 10^{-3} mol dm^{-3}. Each vertical division corresponds to 1 × 10^{-3} of absorbance change. (b) Transient absorption intensity vs, time for a solution with the [Cu(II)]/[Cl$^-$] ratio of $\frac{1}{3}$ monitored at different wavelengths. [Cu(II)] was 1 × 10^{-3} mol dm^{-3}. Each vertical division corresponds to 0.5 × 10^{-3} of absorbance change.

dependent on [Cu(II)] for solutions of constant $\frac{1}{8}$ ratio. The zero intercept (Fig. 3(a)) rules out the solvent (or water dissolved in the solvent) as a direct quencher. It follows that the Cl$_2^{\cdot}$ scavenger must be a species that is contained in the dissolved salts or is produced by them.

Cu(I) added to a $\frac{1}{8}$ solution exhibits transient lifetimes as indicated in Fig. 3(b). Cu(I) is therefore a good scavenger for chloro radicals. The quenching constant k_I for the reaction Cl$_2^{\cdot}$ + Cu(I) → Cu(II) + 2Cl$^-$ is 2.8 × 10^8 dm^3 mol^{-1} s^{-1}. This finding supports the hypothesis that the decrease of Cu(I) quantum yield with irradiation time is due to the increasing probability of the occurrence of this reaction. This effect can be treated quantitatively. For the mechanism

$$Cu(II) \xrightarrow[\text{Cl}^-]{h\nu} Cu(I) + Cl_2^{\cdot}$$

$$Cl_2^{\cdot} \Big\langle \begin{array}{c} \xrightarrow[\text{Cu(I)}]{k_I} Cu(II) + 2Cl^- \\ \\ \xrightarrow[\text{Cu(II)}]{k_{II}} \text{products} \end{array}$$

assuming a stationary state for Cl$_2^{\cdot}$, the following equation holds:

$$\Phi_t = \Phi_0(1 - \tau k_I[Cu(I)]) \tag{2}$$

where Φ_t and Φ_0 are the Cu(I) quantum yields at time t and at zero time. For the $\frac{1}{8}$ system Φ_0 obtained by extrapolation from Table 1 is 0.055.
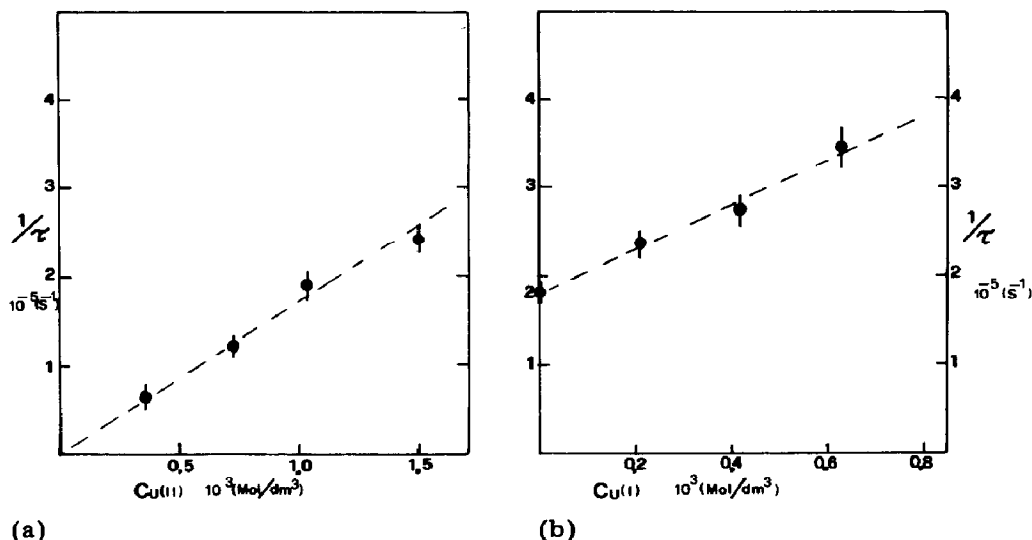
(a)   (b)

Fig. 3.(a) The Cl_2^- reciprocal lifetime τ vs. [Cu(II)] for acetonitrile solutions at a constant [Cu(II)]/[Cl$^-$] ratio of $\frac{1}{8}$. (b) The Cl_2^- reciprocal lifetime τ vs. [Cu(I)] for acetonitrile solutions at a constant [Cu(II)] of 1×10^{-3} mol dm^{-3}. A solution of CuCl was added to the appropriate Cu(II) solutions to keep the [Cu(II)]/[Cl$^-$] ratio constant at $\frac{1}{8}$.

Using in eqn. (2) the values of [Cu(I)] produced after 1, 4 and 9 min irradiation and the corresponding τ values from Fig. 3(b), the calculated Φ_t values give by simple graphical integration overall Φ values which are in good agreement with those of Table 1.

In order to determine the Cl_2^- scavenger when no Cu(I) is added to the solution, lifetimes were measured for two series of solutions. In the first series [Cl$^-$] was varied and [Cu(II)] was constant and in the second series the roles were reversed. The first series ([Cu(II)] = 10^{-3} mol dm^{-3} and [Cl$^-$] = 8×10^{-3}, 14×10^{-3} and 19×10^{-3} mol dm^{-3}) gave constant life times of 5.5 μs, and the second series ([Cu(II)] = 0.5×10^{-3}, 1.0×10^{-3} and 2.0×10^{-3} mol dm^{-3}, and [Cl$^-$] = 19×10^{-3} mol dm^{-3}) gave lifetimes in line with those in Fig. 3(a). Hence Li$^+$ and Cl$^-$ are unequivocally ruled out as scavengers for Cl_2^- and the scavenger must therefore be a Cu(II) species. The quenching constant k_{II} for the process Cu(II) + Cl_2^- → products is 1.7×10^8 dm^3 mol^{-1} s^{-1} for solutions with [Cu(II)]/[Cl$^-$] ratios not exceeding $\frac{1}{8}$. At higher ratios this constant is larger since the measured lifetimes are shorter (see Fig. 2(a)). Therefore the less chlorinated species should be more effective in quenching the chloro radicals.

In the first series, although τ remains unchanged, the amplitude of the Cl_2^- signal decreases with increasing [Cl$^-$]. This might indicate that a rapid equilibrium between Cl$^-$ and Cl_2^- is established just after the flash to give, in all probability, colourless Cl_3^{2-} [23] with zero population of Cl$^-$ [24]. If the factor 2 observed between the amplitudes of the $\frac{1}{8}$ and $\frac{1}{20}$ solutions is all due to the formation of trichloro radical anions, the equilibrium constant for the

reaction $Cl^- + Cl_2^{\cdot} \rightleftarrows Cl_3^{2\cdot}$ can be determined to be about 10^2 dm^3 mol^{-1}. On this basis, the extinction coefficients for $Cl_2^{\cdot}$ previously reported [9, 25] should be increased by a factor of about 1.5.

4. Conclusions

The results obtained allow us to sketch the mechanism of photolysis in this chlorocopper(II) complex system in acetonitrile (Fig. 4).

While it is clear that Cl$^-$ is not consumed during the irradiation (thus these chloro radicals appear as oxidizing species in nature), we have not been able to formulate a hypothesis that can be supported through direct experiments to account for the formation of the final products from O$_2$-derived radicals or from Cu(II) as the chloro radical quencher.

On the basis of certain observations, however, it is possible to make some speculative considerations. Since Cl$^{\cdot}$ (or any of its derivatives) has to be reduced to Cl$^-$ and consequently Cu(II) oxidized to a state which is likely to be trivalent*, we have paid particular attention to the Cu(III) quenching reactions shown in Fig. 5. Comments relative to this scheme are as follows.

With regard to reaction pathway A, no evidence of O$_2$-derived radicals has previously been obtained [11] nor has any been obtained in the course of the experiments described here. Nevertheless air does oxidize Cu(I). The resultant radicals would be unable to react with the solvent because of their negative charge and because of the nucleophilic character of CH$_3$CN. As a matter of fact no solvent-derivative products have ever been found. However, the re-oxidation of the O$_2$-derived radicals by Cu(III) is quite reasonable, is stoichiometric and fits with other scattered results, such as the substantial invariance of pH during irradiation.

With regard to reaction pathway B acetonitrile derivatives have not been found after irradiation performed under either aerobic or anaerobic conditions.
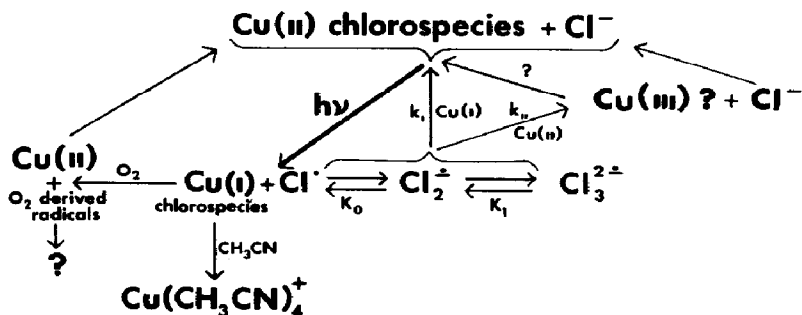

Fig. 4. The photolysis mechanism: $K_0 \approx 10^5$ dm^3 mol^{-1} [24], $K_1 \approx 10^2$ dm^3 mol^{-1}, $k_I = 2.8 \times 10^8$ dm^3 mol^{-1} s^{-1}, $k_{II} = 1.7 \times 10^8$ dm^3 mol^{-1} s^{-1}.

*Cu(III) in acetonitrile is described in ref. 26 and references cited therein.
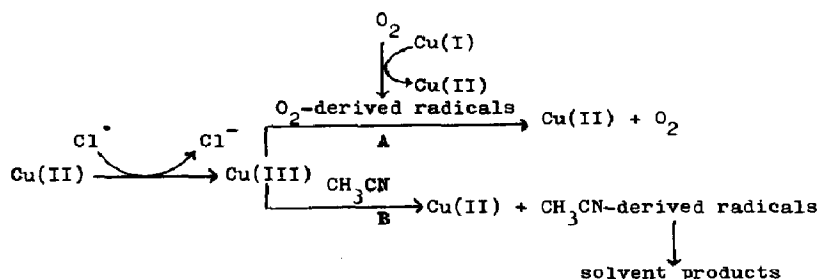
Fig. 5. Possible Cu(III) quenching reactions.

For pathway A, the solvent derivatives produced after up to 24 h irradiation ought to be about 0.17 mol dm^{-3}. Gas chromatograms have been obtained at three different temperatures: 100, 140 and 200 °C. The theoretical amount, if present, should be easily detected by this technique. Our inability to detect any derivative allows us to hypothesize that the solvent is not involved in any reaction to a significant degree, either with Cl·, with the oxygen-derived radicals or with Cu(III).

For pathway B, when no air is dissolved in CH_3CN, Cu(I) is much more readily photoproduced and the O_2-derived radicals are no longer formed. The only possible Cu(III) scavenger is the solvent. The absence of gas chromatographic evidence of solvent derivatives is simply due to the fact that only 1/20 000 parts of solvent have undergone a reaction, i.e. quantitatively as much as the Cu(II) present in the solvent. (Solubility restrictions of LiCl do not allow concentrations greater than 10^{-3} mol dm^{-3} in Cu(II).) This small amount of solvent derivatives lies below the sensitivity level of the gas chromatographic equipment used.

On the basis of the foregoing observations and considerations, we believe that the final electron donors for Cl· → Cl⁻ via Cu(II) are in the presence of air the O_2-derived radicals or in the absence of air the solvent.

Finally we report that prolonged irradiation of a $\frac{1}{8}$ solution gives rise to an ESR signal that is both asymmetric and rather weak with $g = 2.09$. Complete bleaching of the Cu(II) solutions cannot also be achieved even under anaerobic conditions. Some new and unknown Cu(II) species are thus produced (e.g. polynuclear oxygen-bridged or chlorine-bridged complexes) which may be the result of a large variety of reactions, but all of them relatively small in effect.

Acknowledgments

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