Pulsed Laser Photolysis of Chlorocopper(II) Complexes in Acetonitrile: Evidence for Chlororadical Formation

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Summary Nd pulsed laser excitation at 473 nm of the system $CuCl_2$–LiCl–acetonitrile, where $CuCl_4^{2-}$ predominates in the equilibrium mixture, leads to formation of a transient which corresponds to the Cl_2^- radical anion and is not scavenged by the solvent.

COPPER(II) CHLORIDE dissolved in acetonitrile gives rise to an equilibrium mixture of tetraco-ordinated Cu^{II} species in which the number of Cl ligands can be varied by addition of Cl^- as LiCl to the solution.[1] Visible and near u.v. irradiation of this system leads to the photoreduction of the central metal atom to Cu^I.[1,2] Such solutions have been flash photolysed at 473 nm by a neodymium pulsed laser[3] and monitored in the range 320—435 nm. When the ratio $[Cu^{II}]$: $[Cl^-]$ was 1 : 8 (95·4% $CuCl_4^{2-}$ and 4·6% $CuCl_3^-$),[4] a transient was detected one trace of which is shown in Figure 1. This has a first order decay and its lifetime

FIGURE 1. Transient decay curve monitored at 366 nm obtained after excitation at 473 nm from $CuCl_2$ (1·5 × 10^{-3} mol dm^{-3}) and LiCl (9·0 × 10^{-3} mol dm^{-3}), dissolved in acetonitrile. Pulse intensity ca. 1 × 10^{15} photons, pulse width 250 ns, sample thickness 2 mm.

($\tau = 4·0 \mu$s when $[Cu^{II}] = 1·5 × 10^{-3}$ mol dm^{-3}) is unaffected by oxygen. The dependence of its absorbance A on λ was determined with laser flashing at constant pulse intensity (see Figure 2). The position of the peak and the shape of the spectrum correspond closely to those of the Cl_2^- radical anion, as has been observed in flash photolysis[5] and pulse radiolysis[6] experiments. The acetonitrile may account for the small red shift (ca. 10 nm) relative to water.
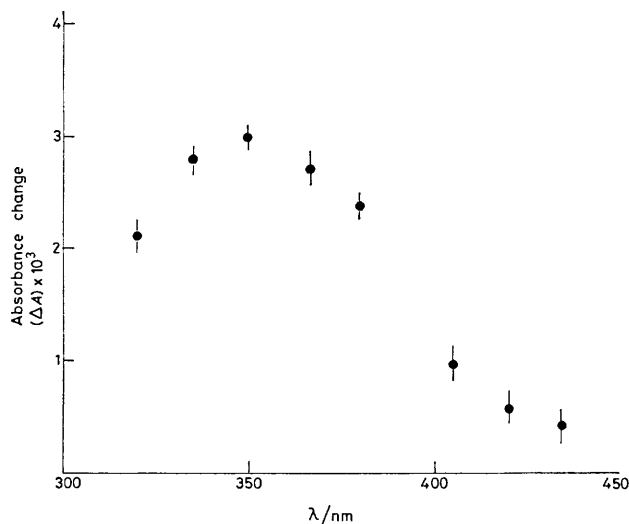

FIGURE 2. Transient absorption spectrum. Changes in absorpance taken by difference of trace signals between transient peaks and complete decay. Conditions are the same as in Figure 1.

Assuming that the Cl_2^- transient originates from the homolytic cleavage of the Cu–Cl bond and subsequent association with Cl^- ion with 100% efficiency,[7] then its quantum yield must be the same as that for Cu^{II} reduction, which can be measured by the decrease of the transient trace, after its complete decay, relative to the baseline. At 366 nm the value obtained for the extinction coefficient was 9600 (±10%) dm^3 mol^{-1} cm^{-1} which is in very good agreement with that found by Anbar and Thomas.[6] This transient exhibits an interesting feature: the $1/\tau$ vs. $[Cu^{II}]$ plot at a constant $[Cu^{II}]$: $[Cl^-]$ ratio of 1 : 8 is linear in the range $(0·2—1·5) × 10^{-3}$ mol dm^{-3}, with the intercept equal to zero. The solvent, therefore, is not a scavenger for Cl_2^-. Moreover, g.l.c. experiments on the solutions (1 : 8) after prolonged continuous irradiation show that the amounts of acetonitrile chloro-derivatives obtained are < 1% of the amount of Cu^{II} that is photoreduced.

These findings help to elucidate the photolytic mechanism of chlorocopper(II) complexes in non-aqueous media. The photoformation of chlorine radicals, previously postulated[1,2,8] or ruled out,[9] has for the first time been proved by direct experiment. The solvent is not involved in the photoreduction of Cu^{II} either in the primary step or in secondary ones, and therefore the lack of detection of solvent chloro-derivatives does not imply that Cl· has not been formed.

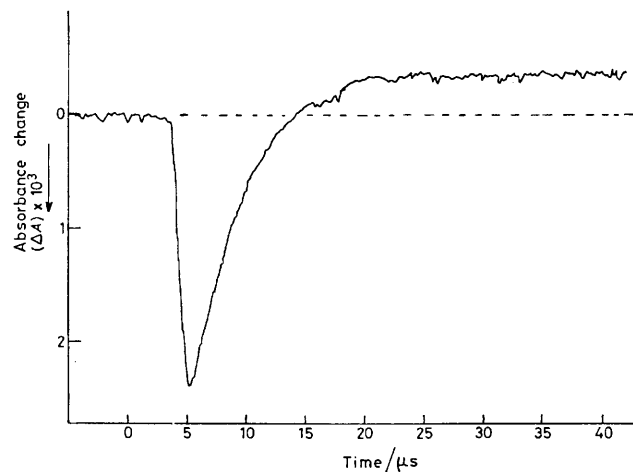Cl_2^- is detected in solutions with ratios of $[Cu^{II}]$ to $[Cl^-]$ of $\leqslant 1:3$ and its signal intensity parallels the decrease in concentration of free Cl^-. For ratios $> 1:3$ (where free Cl^- is no longer present), different transients are observed which are being investigated.

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