Inorganica Chimica Acta, *85* (1984) L15–L17

Photochemical Redox Reactivity in Chlorocopper(II) Complexes

PAOLA BERGAMINI, ANDREA MALDOTTI, SILVANA SOSTERO, ORAZIO TRAVERSO*

Centro di Studio sulla Fotochimica e Reattività degli Stati Eccitati dei Composti di Coordinazione del C.N.R., Istituto Chimico, Università di Ferrara, Via L. Borsari 46, 44100 Ferrara, Italy

and JÁN SÝKORA

Department of Inorganic Chemistry, Slovak Technical University, 812 37 Bratislava, Czechoslovakia

Received December 16, 1983

The photochemical redox reactivity of a series of Cu(II) complexes $[CuCl_x]^{2-x}$ (x = 1–4) has been examined from the following viewpoints:

i) the transient absorbance at 350–500 nm obtained in flash photolysis;

ii) the generation of intermediates such as $Cl^\bullet$, Cl_2^- and a copper(I) complex;

iii) E.S.R. studies based on radical trapping reactions.

It is concluded that the charge transfer ligand to metal (CTTM) excitation leads to radical processes via splitting of the Cu–Cl bond in chlorocopper complexes.

Labilization of Cu–Cl bonds as a result of CTTM excitation is a source of chlorine atoms [1]. This process makes the $[CuCl_x]^{2-x}$ complexes potential candidates for photoinduced chlorination of organic substrates in solution [1, 2]. The following is reported here:

i) The spectra of transients observed after flash photolysis, which indicate that two reactive intermediates are generated;

ii) E.S.R. studies based on radical-trapping experiments, which provide evidence of $Cl^\bullet$ radical formation;

iii) The effect of radical-trapping agents on the photoreaction quantum yield values.

Experimental

The compounds under consideration were prepared as previously described [2, 3]. Solvents were of spectroscopic grade and were dried by distillation from phosphorous pentoxide. The N-t-butyl-α-phenylnitrone (PBN) and acrylonitrile were commercial samples used as received. The apparatus used for continuous and flash photolysis have been described elsewhere [4]. The E.S.R. experiments were performed with a Bruker ER 200 D spectrometer. Manipulations were conducted under vacuum or under purified nitrogen.

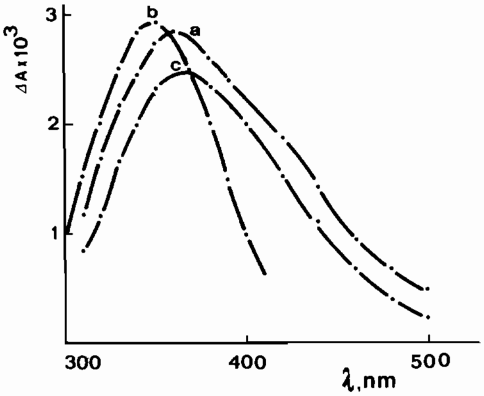


Fig. 1. Spectra of transients observed after flash irradiations of: (a) $CuCl_4^{2-}$ (10^{-3} mol dm^{-3}) in acetonitrile; (b) hexachlorocyclopentadiene (10^{-2} mol dm^{-3}) in acetonitrile; (c) hexachlorocyclopentadiene (10^{-2} mol dm^{-3}) and CuCl (2 × 10^{-3} mol dm^{-3}). The shape of the absorption spectrum obtained at zero time in the flash irradiation of $[CuCl_x]^{2-x}$ (x = 1, 2) complexes is similar to that of the transient a.

Results and Discussion

Transient Spectra

The $[CuCl_x]^{2-x}$ (x = 1, 2, 4) complexes were flash irradiated (λ excit ⩾ 280 nm) in deaerated acetonitrile solutions. These irradiations produced transient absorbances at 350–500 nm (Fig. 1). The disappearance of these absorbances for $CuCl_4^{2-}$ follow a first order rate law with a ratio of the rate constant to the extinction coefficient, $k/\epsilon = 2.5 \times 10^6$ cm sec^{-1} at 380 nm. In addition, the $CuCl_4^{2-}$ complex (10^{-3} mol dm^{-3}) was flash irradiated in solutions where acrylonitrile (10^{-1}–10^{-3} mol dm^{-3}) was used as an intermediate scavenger. The transient absorbance values, measured for λ = 380 nm at zero reaction time, decreased with increasing acrylonitrile concentrations. A limiting value of the transient absorbance was obtained for scavenger concentrations equal to or larger than 0.1 mol dm^{-3}. The limiting absorbance decay was observed as a process with $\tau \simeq 20$ μs.

These results show that two reactive intermediates are generated in the photolysis of $CuCl_4^{2-}$. These metastable species were assigned, by means of their chemical reactivity and optical spectra, as Cl_2^- [2, 5] radicals and a Cu(I) complex, probably

---

*Author to whom correspondence should be addressed.

0020-1693/84/$3.00

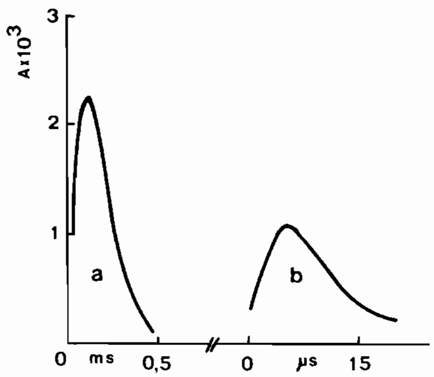


Fig. 2. Absorbance against time curves observed in flash photolysed hexachlorocyclopentadiene (10^{-2} mol dm^{-3}) in acetonitrile (a) and in the presence of CuCl (2×10^{-3} mol dm^{-3}) (b) at 366 nm. Absorbances relative to that of the solutions before the flash. The different timescales for (a) and (b) are to be noted.

$CuCl_3^{2-}$. In this regard the observed photochemistry of the $[CuCl_4]^{2-}$ complex may have its origin in the population of a charge transfer ligand to metal state, CTTM, as is indicated for the primary process in eqn. 1. The fate of the primary species seems to be well described by eqns. 2–6:

$$CuCl_4^{2-} \xrightleftharpoons{h\nu} CTTM \longrightarrow [CuCl_3^-, Cl^\bullet] \tag{1}$$

$$[CuCl_3^-, Cl^\bullet] \longrightarrow \begin{cases} CuCl_4^{2-} \\ CuCl_3^{2-} + Cl^\bullet \end{cases} \tag{2}$$

$$Cl^\bullet + Cl^- \longrightarrow Cl_2^- \tag{3}$$

$$Cl^\bullet + Cl \longrightarrow Cl_2 \tag{4}$$

$$Cl_2^- + Cl_2^- \longrightarrow Cl_2 + 2Cl^- \tag{5}$$

$$CuCl_3^{2-} + Q \xrightarrow{Cl^-} CuCl_4^{2-} \tag{6}$$

$[Q = Cl_2; Cl_2^-; Cl^\bullet; Cu(I)]$

The major pathway from $CuCl_4^{2-}$ to $CuCl_3^{2-}$ and $Cl^\bullet$ intermediates, involving formation of Cl_2^- radicals, is supported by flash photolytic and E.S.R. results based on radical trapping reactions.

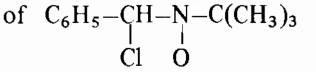
Reaction of the Radical Anion Cl_2^- with Cu(I) ion

When a deaerated solution of hexachlorocyclopentadiene in CH_3CN is exposed to flash photolysis, the transient absorbance of Cl_2^- radicals at 300–400 nm is observed (Fig. 1(b)). Flash photolysis of deaerated solutions containing 10^{-2} mol dm^{-3} of C_5Cl_6 and CuCl (2×10^{-3} mol dm^{-3}) produced a broad transient absorption, peaking between 350–500 nm (Fig. 1c)), similar to that observed for flashed solutions of $CuCl_4^{2-}$. The half-life for signal decay (10–15 μs) depending on [Cu(I)], is comparable to the value 5.5 of μs calculated by pulsed photolysis experiments for the system Cu(II)/Cu(I) in acetonitrile [2].

Absorbance time curves observed when no Cu(I) was present had the shape shown in Fig. 2(a). The initial fall in the Cl_2^- radical anion absorbance was slower than that in the presence of Cu(I) ions because only reaction (5) was removing Cl_2^-. The rapid decrease in absorbance when Cu(I) ions were present is due to Cl_2^- removal which disappears by the very rapid reaction [1]:

$$CuCl + Cl_2^- \longrightarrow CuCl_2 + Cl^- \tag{7}$$

Radical Trapping Experiments

On mixing the complex $CuCl_4^{2-}$ (10^{-3} mol dm^{-3}) and PBN (N-t-butyl-α-phenylnitrone; 2×10^{-3} mol dm^{-3}) in acetonitrile, the E.S.R. signal [6] of t-butyl nitroxide radical $PhCHRNOBu^t$(IA) was obtained. Flash irradiation of an acetonitrile solution of $CuCl_4^{2-}$ (10^{-3} mol dm^{-3}; at this concentration light absorption by spin trap is negligible) led to the E.S.R. spectrum of  $C_6H_5-\underset{Cl}{\underset{|}{C}}H-\underset{O}{\underset{|}{N}}-C(CH_3)_3$ adduct (IB). A computer-simulated spectrum with hyperfine constants $A_N = 12.10$, $A_{Cl}35 = 6.25$, $A_{Cl}37 = 5.15$, $A_H = 7.5$ G) agrees well with the observed spectrum and proves the identity of the IB adduct. Using the technique of flash photolysis–E.S.R., the ratio IA/IB was found to vary extensively as a function of PBN. At high PBN concentrations (10^{-2}–2×10^{-3}) IA/IB is large, that is, the IA triplets of doublets dominate, while at low PBN concentrations IA/IB is small indicating that the radical IB is the major spin adduct observed. Hence, the observation of the IB spin adduct at low concentrations of PBN is consistent with the above mechanisms.

Quantum Yield Measurements

Continuous and flash photolysis studies show that $[CuCl_x]^{2-x}$ (x = 1, 4) generally undergoes a photoreduction reaction but relatively quantum yields [2] result from efficient recoupling of metastable intermediates (eqn. 6). Subsequent experiments were designed to test for this possibility. Photolysis of $CuCl_4^{2-}$ (λ = 404 nm) was carried out in acetonitrile with acrylonitrile added (1%) as a trap for $Cl^\bullet$ intermediates and compared to photolysis identically carried out but without addition of acrylonitrile. The presence of acrylonitrile caused a pronounced increase in the photoreduction quantum yield (from 0.05 to 0.12). This is a strong indication that the reactive $Cl^\bullet$ is efficiently trapped by acrylonitrile. Thus the $Cl^\bullet$ radicals combine less readily with each other and hence the quenching processes (eqn. 6) are increasingly more difficult.

Acknowledgements

The award of the Czechoslovak-Italian agreement on cultural and scientific cooperation (to J. S.) is gratefully acknowledged.

References

1 G. Ferraudi and S. Muralidharan, *Coordination Chemistry Reviews, 36,* 45 (1981).

2 E. Cervone, F. D. Camassei, I. Gianninni and J. Sýkora, *J. Photochem., 11,* 321 (1979).

3 E. Horvart, J. Sýkora and J. Gazo, *Z. Anorg. Allg. Chem., 442,* 255 (1978).

4 S. Sostero, O. Traverso, P. DiBernardo and T. J. Kemp, *J. Chem. Soc. Dalton,* 658 (1979).

5 A. T. Thornton and C. S. Laurence, *J. Chem. Soc. Dalton,* 1637 (1973).

6 E. G. Janzen, B. R. Knauer, R. T. Williams and W. B. Harrison, *J. Phys. Chem., 74,* 3025 (1970).