

INVESTIGATION OF A LONG-LIVED INTERMEDIATE IN THE PHOTO-OXIDATION OF CHLOROCUPRATE(I) COMPLEXES

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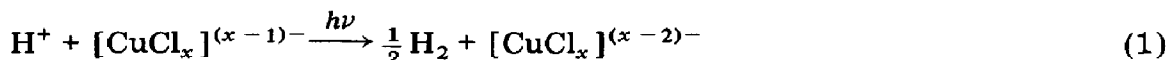
Summary

The decay of a long-lived intermediate formed in the photo-oxidation of acidic solutions of chlorocuprate(I) complexes was examined. The dependences of the decay rate on the components of this system (Cu^{I} , Cu^{II} , Cl^- and H^+) confirmed assumptions that dimeric or polymeric $\text{Cu}^{\text{I}}\text{-Cu}^{\text{II}}$ chloro complexes are formed during the photo-oxidation.

The quantum yield obtained indirectly as well as the estimate for the concentration of the intermediate were in accordance with results from previous experiments.

1. Introduction

The processes occurring in acidic solutions of chlorocuprate(I) complexes under UV irradiation have recently been thoroughly examined. It was established [1] that the hydrated electron formed in the photoinduced redox reaction

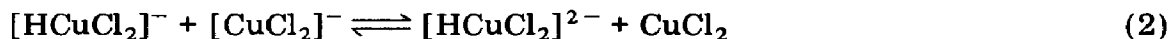


undergoes competitive recombination and scavenging processes according to the Noyes geminate-pair mechanism. Other intermediates are also produced during the reactions.

During experiments carried out using conventional flash photolysis, Ferraudi [2] detected an intermediary species that was assumed to be $[\text{HCuCl}_x]^{(x-1)-}$ which decayed in two successive steps — both with second-order kinetics. The rate of the first step ($k_1 = (5.5 \pm 0.7) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$) depends on the hydrogen ion concentration; the rate of the second (longer) step ($k_2 = 0.17 \pm 0.03 \text{ M}^{-1} \text{ s}^{-1}$) depends on the chloride ion concentration (as well as that of the transient). During the decay of the transient, it was assumed that dimeric or polymeric $\text{Cu}^{\text{I}}\text{-Cu}^{\text{II}}$ chloro complexes form and are then destroyed.

During irradiation ($\lambda_{\text{exc}} = 274 \text{ nm}$) of acidic solutions of chlorocuprate(I) complexes ($[\text{Cl}^-] < 0.4 \text{ M}$; $[\text{H}^+] < 1.0 \text{ M}$), Stevenson *et al.* [3]

noticed a long-lived intermediary yellow species (with a lifetime of several hours under optimum conditions). They found that after the irradiation had been stopped the disappearance of the intermediate was accompanied by the evolution of H_2 while the concentration of copper(II) did not change. The yellow species is assumed to be a hydridochlorocuprate(I) complex formed in the interaction between chlorocuprate(I) and the intermediate observed by Ferraudi:



However, the possibility that dimeric or polymeric complexes (*e.g.* $[HCu_2Cl_3]^{2-}$ or $[HCu_2Cl_4]^{3-}$) were formed was not excluded. The decay of the long-lived species was found to be sensitive to the concentration of Cu^{II} , H^+ and especially Cl^- , but detailed investigations have not been published (because of their unsatisfactory reproducibility).

The main purpose of our work was to study the dependences of the decay of the long-lived intermediate formed during the photochemical oxidation of chlorocuprate(I) complexes on the components of the solutions (Cu^{II} , Cl^- , H^+ and Cu^I), because these species may play a significant role in the mechanism of the photo-oxidation.

It may prove important to extend these investigations because similar hydride intermediates have been observed or assumed in several studies of the photo-oxidation of transition metal complexes in acidic solutions [4, 5]; this suggests that the phenomenon may be common in these reactions.

2. Experimental details

In our experiments the intermediate was produced by continuous irradiation ($\lambda_{exc} = 253.7$ nm) of solutions of copper(I); after addition of $CuCl_2$ solution to the irradiated solution the decay of the long-lived transient was measured using spectrophotometry.

The absolute concentration of the intermediate was also measured (approximately). This species is formed in the reaction between solutions of $CuCl_2$ and KBH_4 . Therefore its molar absorption coefficient can be estimated for use in the spectrophotometric concentration measurements.

The solutions were prepared using HCl , $NaCl$, $HClO_4$, $NaClO_4$, $CuCl_2$ and KBH_4 (all reagent grade). In the copper(I) solutions the traces of copper(II) were reduced by stirring with copper turnings in an inert atmosphere. Therefore the concentrations of copper(I) calculated on the basis of the weight of solid copper(I) chloride used would have been inaccurate. The precise values of C_{CuI} for the solutions were subsequently determined spectrophotometrically using calibration curves.

In each solution the ionic strength was adjusted to 1.0 M and, in the solutions containing mixtures of copper(I) and copper(II), $[Cl^-]$ and C_{H^+} were equal. For this the weights of the chloride used were determined

using complex stability constants [1, 6] calculated at an ionic strength of 1.0 M (in the case of both the copper(I) and the copper(II)).

The copper(I) solutions were irradiated in a quartz cuvette (optical pathlength, 1.000 cm; volume of solution, 2.5 cm³). The solutions were in a nitrogen atmosphere and were also stirred by bubbling nitrogen gas through the solutions. The radiation source was a 16 W low pressure mercury arc lamp (Applied Photophysics) which radiated more than 90% of its energy at 253.7 nm. The light intensity was determined using a potassium tri-oxalatoferate(III) actinometer [7] ($I_0 = 2.9 \times 10^{-6}$ einstein s⁻¹ dm⁻³). The irradiation time was 10 min and the temperature was 20 ± 2 °C.

After irradiation, 0.5 cm³ deoxygenated CuCl₂ solution (with suitable [Cl⁻] and C_{H⁺}) were added to 2.5 cm³ irradiated copper(I) solution using a microburette. The decrease in the concentration of the intermediate in the original cuvette was continuously followed using a spectrophotometer at 334 nm where the absorbances of both the copper(II) and the copper(I) were negligible. This simple method made possible the examination of the intermediate which formed and then disappeared during the photo-oxidation. Usually such observations can be carried out only by using apparatus capable of very fast detection.

3. Results and discussion

3.1. Ranges of concentrations of Cu^I, Cu^{II}, Cl⁻ and H⁺

Since it was found in earlier studies [3] that the decay of the long-lived species formed in the photo-oxidation of chlorocuprate(I) complexes depends on the concentrations of H⁺, Cl⁻ and Cu^{II}, to begin with, each concentration range had to be determined. As the concentrations of copper(I) could only subsequently be determined with accuracy (on account of causes mentioned above) at a given H⁺-Cu^{II}-Cl⁻ composition, four different weights of copper(I) chloride were used. From the results obtained using this method the dependences of the decay of the intermediate on the concentrations of the other components were determined by interpolation. The advantage of this method became evident during preliminary experiments when it turned out that the decay was sensitive to the concentration of copper(I) as well.

The limits for the suitable concentration ranges were obtained from the requirement that the amount of the intermediate should be enough to be measurable and that the decay should not be too fast to be detectable. The lower limit for C_{CuI} was 4.8×10^{-3} M and the upper limit for C_{CuII} was 2.1×10^{-2} M. The upper limit for C_{CuI} was 1.6×10^{-2} M because of the relatively low solubility of CuCl. The lower concentration of the added copper(II) was zero; therefore the results for the C_{CuII} dependence could be corrected by taking into account the amount of copper(II) formed during the photo-oxidation.

The chloride concentration effect was the first to be examined on the accumulation of the yellow species. After irradiation for 10 min of a

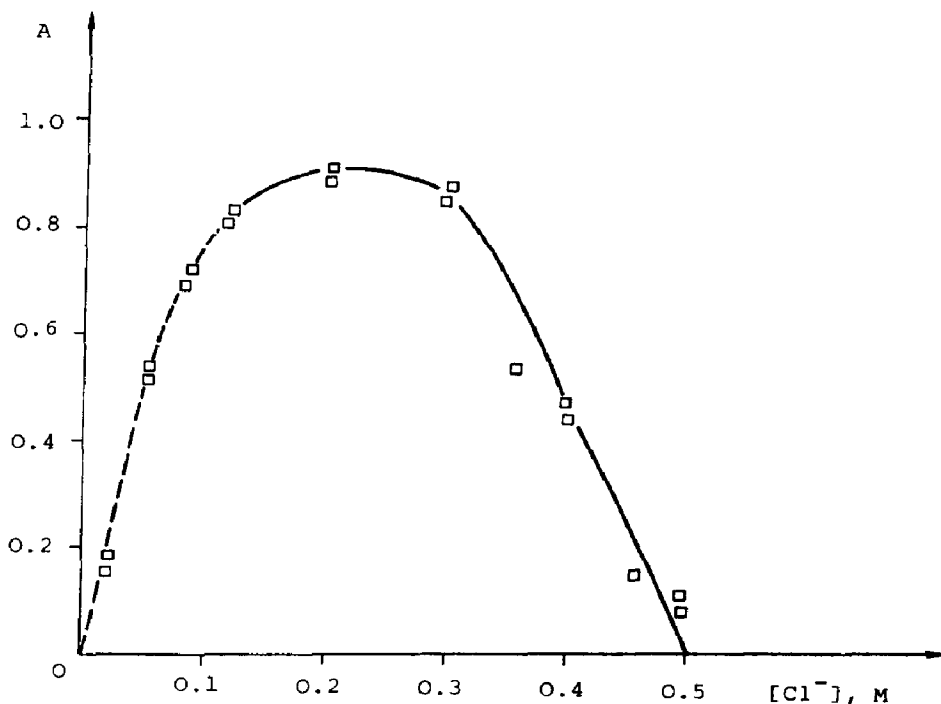


Fig. 1. Dependence of accumulation of the intermediate on chloride ion concentration; irradiation time, 10 min; $l = 1$ cm; $C_{H^+} = 0.5$ M; full line, $C_{CuI} = 8 \times 10^{-3}$ M; broken line, $C_{CuI} < 8 \times 10^{-3}$ M.

solution containing the quantity of CuCl required to give 8×10^{-3} M copper(I), the optical density ($\lambda = 334$ nm) (*i.e.* the relative concentration of the intermediate) showed a maximum in the range 0.1 - 0.3 M (Fig. 1). The decrease at higher chloride concentrations resulted from the accelerated decay due to chloride ions, and at lower concentrations resulted from the decreasing solubility of CuCl — in this latter range $C_{CuI} < 8 \times 10^{-3}$ M (broken line). Thus the range 0.2 - 0.4 M was chosen for the chloride concentration.

Since in the preliminary experiments the addition of hydrogen ion did not show any effect, it was used in the concentration range 0.3 - 1.0 M (on the basis of ref. 3). In the case of fixed C_{CuII} and $[Cl^-]$ these concentrations were 1.5×10^{-2} M and 0.3 M/0.2 M respectively in experiments for the hydrogen ion effect.

3.2. Evaluation of the decay curves

If the changes in the concentration of the other components in a decay are negligible compared with that of the intermediate, the decay may be considered to obey first-order kinetics (*i.e.* its rate depends on the concentration of the species examined). Figure 2 shows a typical decay curve from the series of experiments.

Assuming the relation

$$A(t) = A_0 \exp(-kt) \quad (I)$$

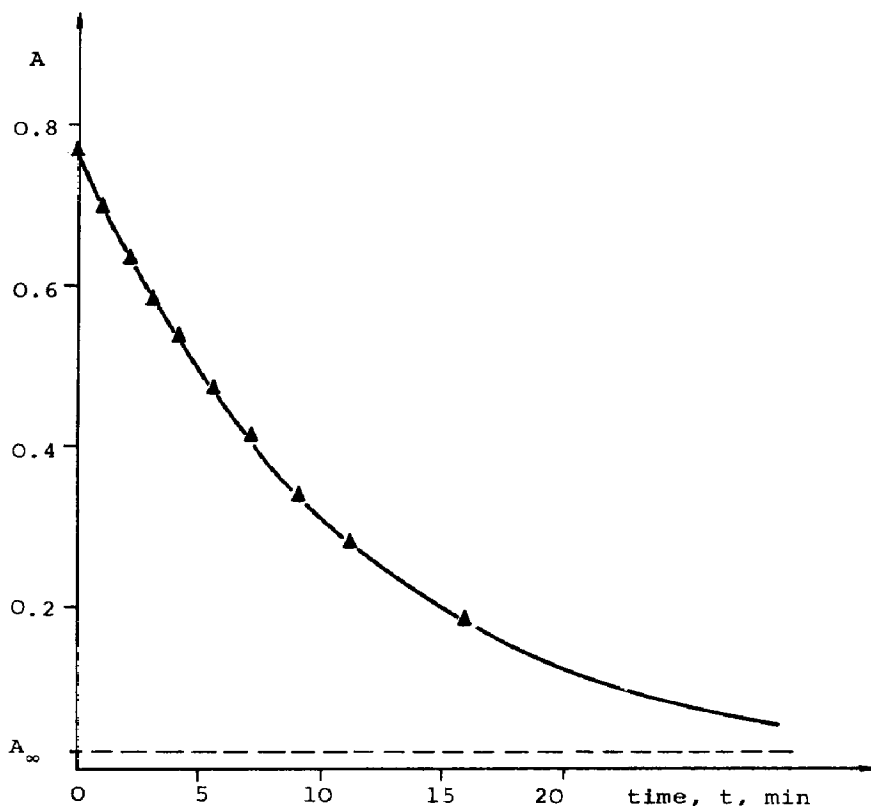


Fig. 2. Decay curve of the intermediate ($[\text{Cl}^-] = 0.2 \text{ M}$; $C_{\text{CuII}} = 0.015 \text{ M}$; $C_{\text{CuI}} = 0.017 \text{ M}$).

between the optical density (*i.e.* the concentration of the transient) and the decay time (A_0 is the optical density at $t = 0$; k is the rate constant), the absorbance A_∞ as $t \rightarrow \infty$ and k can be calculated by a least-squares method from a point series read off the curve ($A_i = A_0 \exp(-kt_i)$; $i = 0, 1, 2, \dots$).

In the case of faster decays ($t_{1/2} < 8 \text{ min}$) the curves could be evaluated by using the Guggenheim method [8] as well. Here in addition to the mentioned point series, another series shifted by $\tau \geq t_{1/2}$ ($A_i'' = A_0 \exp[-k(t_i + \tau)]$) had to be read off. From the relations for the two point series the equation

$$\ln(A_i - A_i'') = \text{const} - kt_i \quad (\text{II})$$

can be obtained by subtraction and by taking the logarithm of both sides. In this case k may be estimated by using a least-squares method also. There were no significant differences in the results obtained by the two different methods.

On plotting the values of k in the form $\lg k$ versus $\lg C_{\text{CuI}}$, lines can be matched on the points with equal chloride or copper(II) concentrations. The values of k from these lines at copper(I) concentrations of $1.1 \times 10^{-2} \text{ M}$ and $9 \times 10^{-3} \text{ M}$ in the middle of the range were plotted as $\lg k$ versus

$\lg C_{\text{Cu}^{II}}$ or $\lg k$ versus $\lg [\text{Cl}^-]$. The apparent orders of the decay rate dependence on $C_{\text{Cu}^{II}}$ and $[\text{Cl}^-]$ can be determined from the slopes of these new lines.

3.3. Effect of hydrogen ion

The values of decay rate constant were not altered significantly on changing C_{H^+} over the range examined (Fig. 3). This result (which differs from the earlier observation [3]) is probably a consequence of the fact that the processes which involve H^+ in the decay are not rate controlled and that the changes produced by them are lower than the errors in the measurements. However, to be safe, in experiments for the investigation of the effects of the other components, the hydrogen ion concentrations were adjusted to 0.5 M.

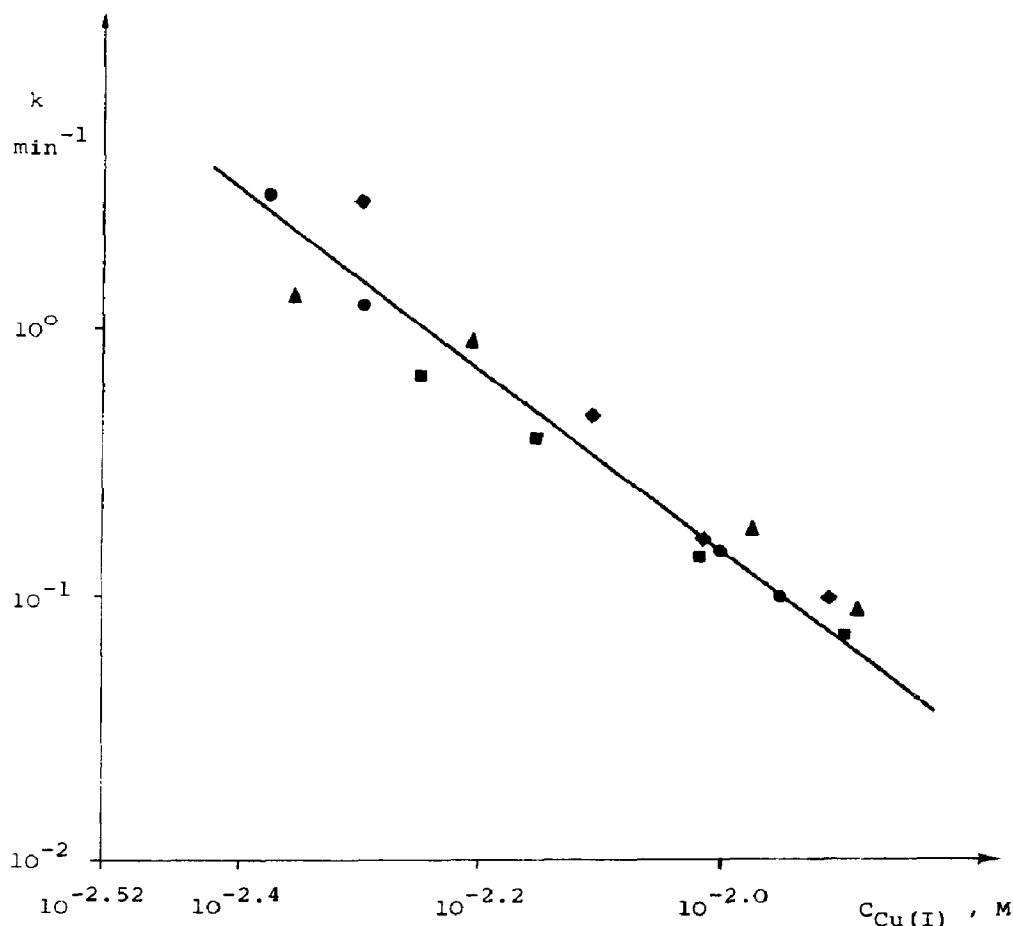


Fig. 3. Effect of hydrogen ion and copper(I) on the decay of the intermediate: \blacktriangle , $C_{\text{H}^+} = 0.3$; \blacklozenge , $C_{\text{H}^+} = 0.5$; \blacksquare , $C_{\text{H}^+} = 0.75$; \bullet , $C_{\text{H}^+} = 1.0$ M.

3.4. Effect of copper(I)

Since four solutions with different $C_{\text{Cu}^{I}}$ had to be examined in the case where the composition of the other components was fixed (for reasons

discussed above) most of the data were obtained on the effect of copper(I). From the slopes of the lines in the plots of $\lg k$ versus $\lg C_{\text{CuI}}$ (Figs. 4 and 5) $n_{\text{CuI}} = 3.8 \pm 0.3$ is obtained for the apparent order of the effect of copper(I) on the decay. This decrease in the decay rate is in accordance with the reversible process (2) assumed by Stevenson *et al.* [3] where the dynamic equilibrium is shifted towards generation of the intermediate on increasing the concentration of copper(I).

3.5. Effect of copper(II)

In view of the above-mentioned equilibrium, an enhancement in the concentration of copper(II) increases the rate of decay, as Figs. 4 and 6 also show. Since during the decay of the intermediate (without irradiation)

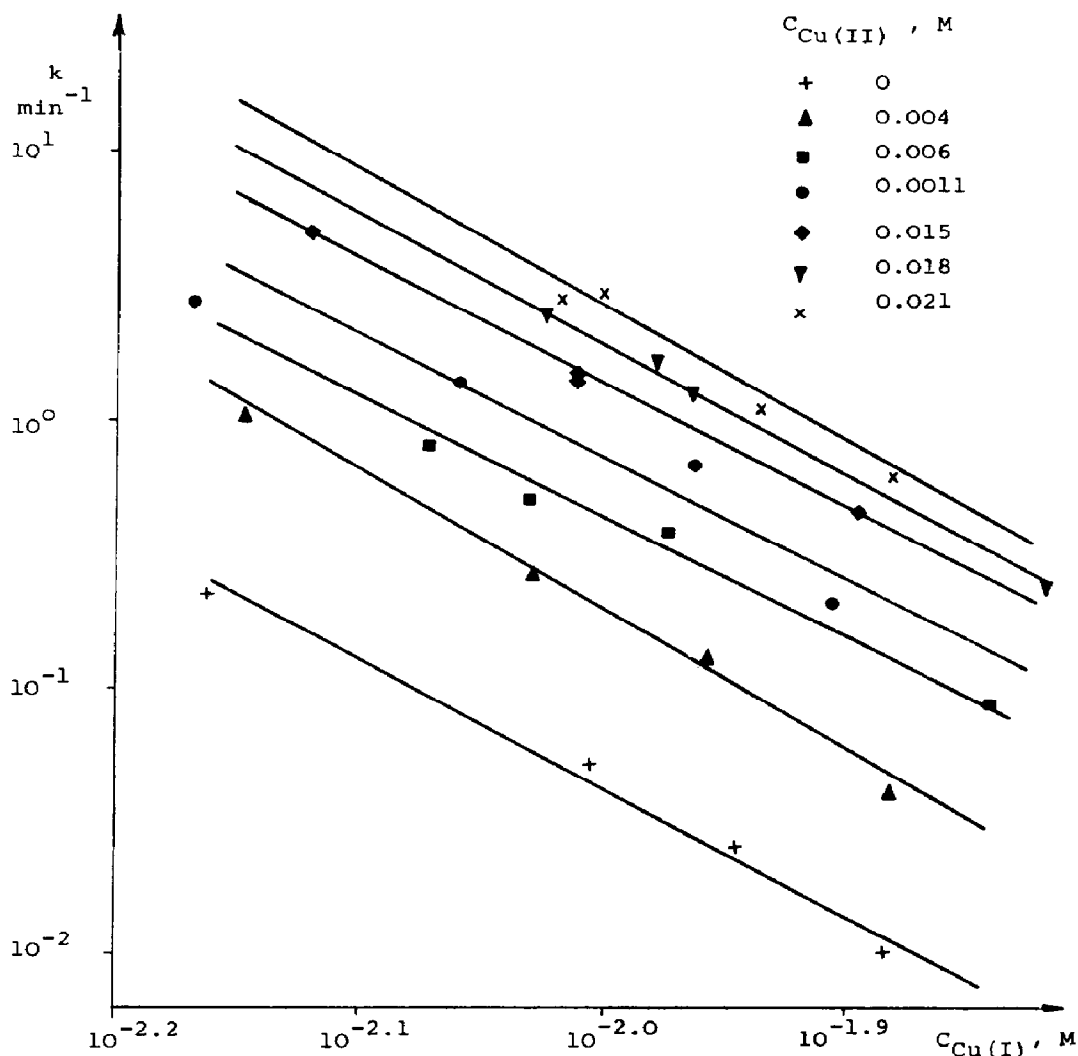


Fig. 4. Effect of copper(II) and copper(I) on the decay of the intermediate ($[\text{Cl}^-] = 0.3 \text{ M}$; $C_{\text{H}^+} = 0.5 \text{ M}$).

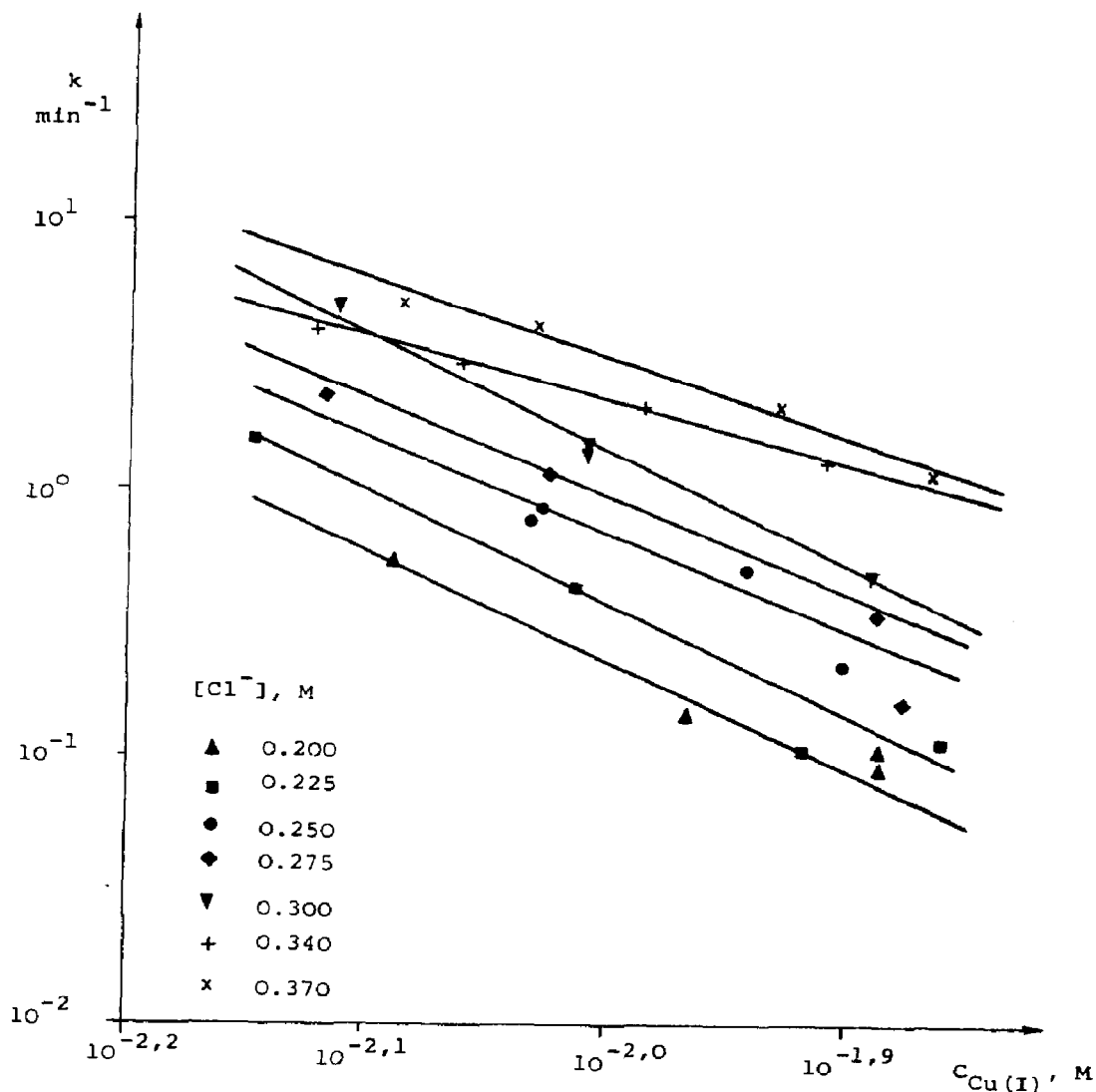


Fig. 5. Effect of chloride ion and copper(I) on the decay of the intermediate ($C_{\text{H}^+} = 0.5 \text{ M}$; $C_{\text{Cu(II)}} = 0.015 \text{ M}$).

the concentration of copper(II) does not change, the continuous lines of Fig. 6 provide an opportunity to determine the concentration of copper(II) in solution after irradiation for 10 min. Projecting the rate constants for decay without the addition of copper(II) on the lines $C_{\text{Cu(II)}} = (1.4 \pm 0.1) \times 10^{-3} \text{ M}$ a value can be read off the abscissa. Taking this value as the starting point for correction by successive approximation, the actual copper(II) concentration after 10 min irradiation may be estimated (about $2.3 \times 10^{-3} \text{ M}$) together with the actual slopes of the (broken) lines ($n_{\text{Cu(II)}} = 1.5 \pm 0.1$). The former value gives the overall quantum yield $\Phi_{\text{Cu(II)}} = 1.3$, taking into account the incident light intensity. This is in accordance with data from previous experiments [1].

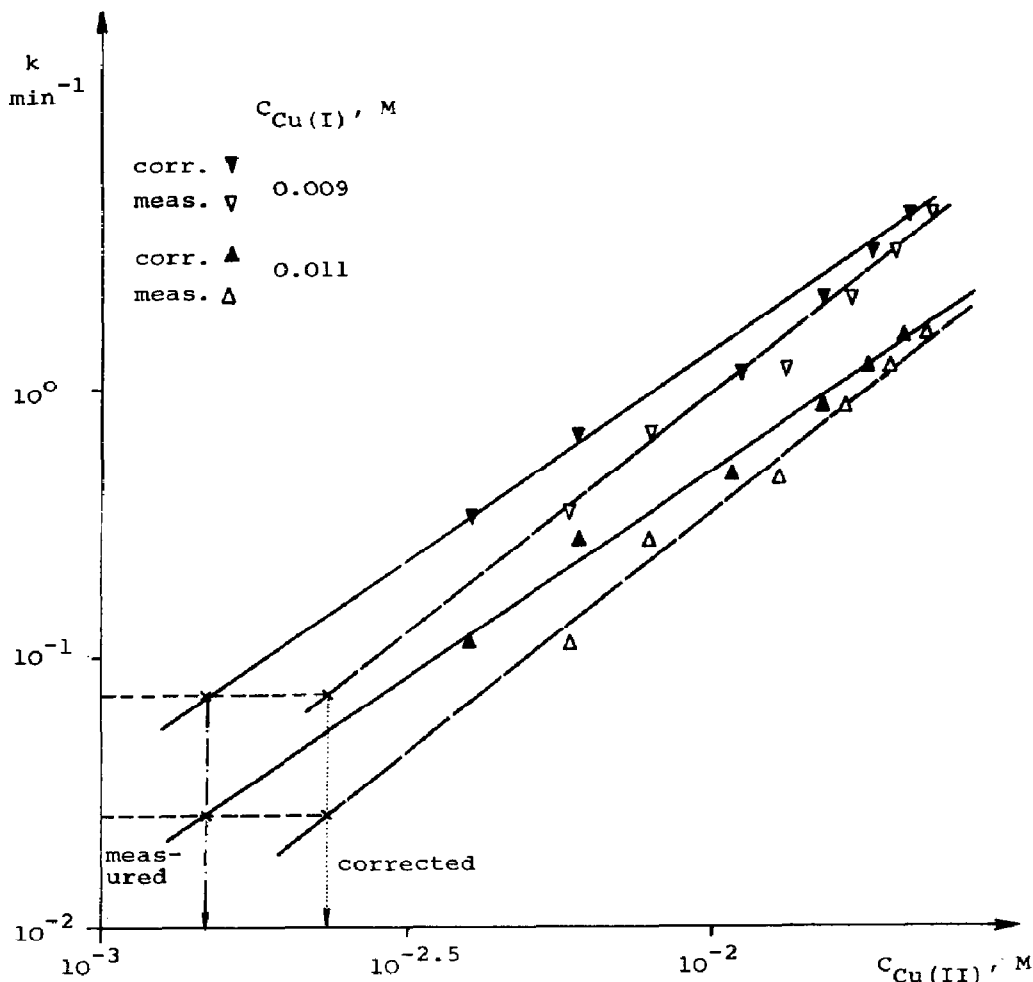


Fig. 6. Effect of copper(II) on the decay of the intermediate ($[Cl^-] = 0.3$ M; $C_{H^+} = 0.5$ M).

3.6. Effect of chloride ion

The diagram for the accumulation of the intermediate (Fig. 1) has already supported the assumption that, in the range 0.2 - 0.4 M, the change of chloride ion concentration strongly affects the generation and disappearance of the yellow species. This is also confirmed by the results for the decay rate constant (Figs. 5 and 7). The apparent order is $n_{Cl^-} = 4.3 \pm 0.3$. This increase in the decay suggests that complexation is one of the processes being examined, *i.e.* complexes (probably dimeric or polymeric) with three or more ligands which are also intermediates with a short lifetime can form during the decay.

The chloride effect does not seem to be related to the existence of monomeric dichloro or trichloro copper(I) complexes because in the examined $[Cl^-]$ range the changes in the mole fraction of these complexes were negligible compared with those in the decay rate [9].

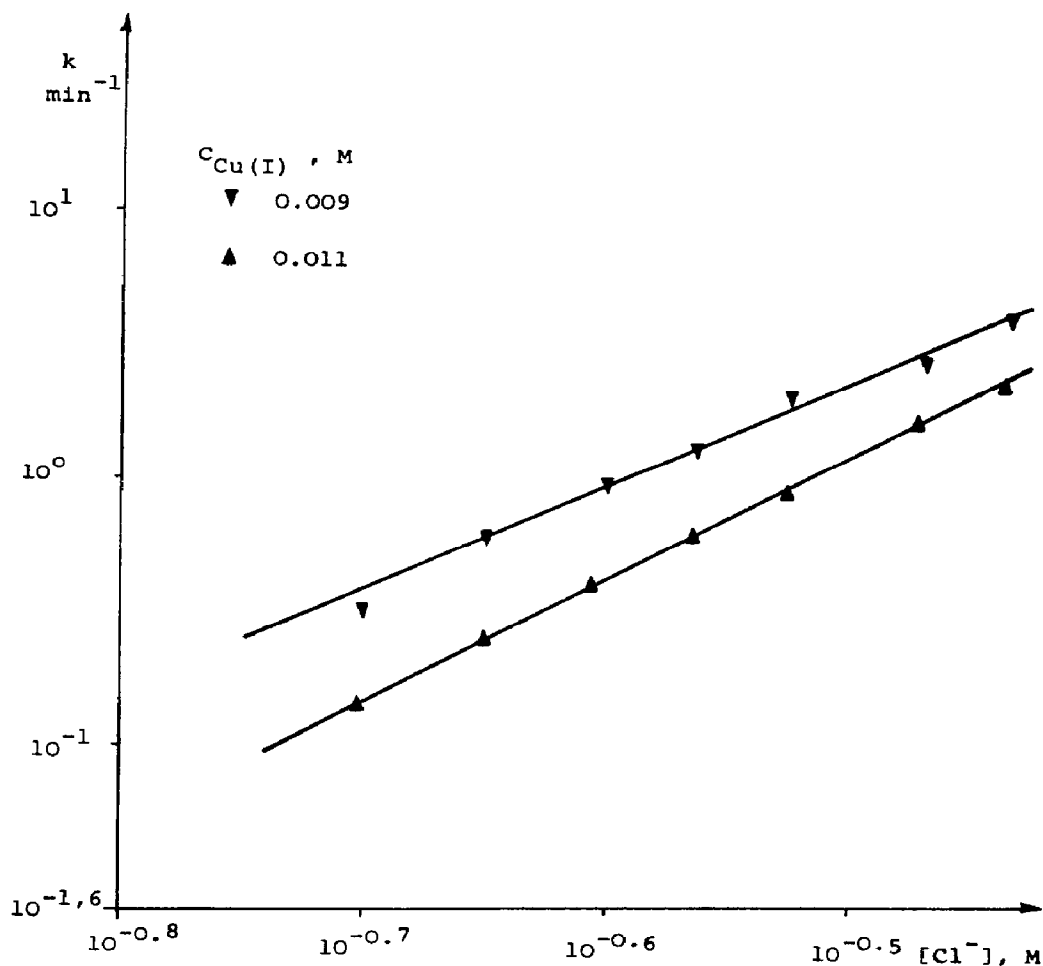
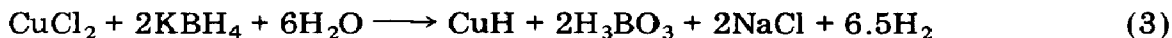


Fig. 7. Effect of chloride ion on the decay of the intermediate ($C_{CuII} = 0.015$ M; $C_{H^+} = 0.5$ M).

3.7. Estimation of the concentration of the intermediate

In the interaction of acidic solutions of copper(I) chloro complexes and $NaBH_4$ a material is formed the visible absorption spectrum of which is identical with that of the examined species. Mixing $CuCl_2$ and KBH_4 solutions in suitable proportions gave a similar result. If we assume that the material formed during the interaction is the same as the species formed in the photo-oxidation, the absolute concentration of the intermediate may be estimated. Considering the reaction between $CuCl_2$ and KBH_4 ($C_{CuCl_2}/C_{KBH_4} > 2$) to be stoichiometric, according to [10]



and accepting that the intermediate is a chloro complex derivative of CuH [3], the value $\epsilon_I \approx 5 \times 10^3$ M⁻¹ cm⁻¹ was obtained for its molar absorption coefficient. So in the chloride ion concentration range 0.1 - 0.3 M, 1.8×10^{-4} M yellow species exist after irradiation of the 8×10^{-3} M $CuCl$ solution

for 10 min. This value is acceptable but the uncertainty due to the above assumptions must be taken into consideration.

4. Conclusions

The results on the effects of the different components may be interpreted as showing that dimeric or perhaps polymeric $\text{Cu}^{\text{I}}\text{-Cu}^{\text{II}}$ chloro complexes form and disappear during the photo-oxidation of chlorocuprate(I) complexes. This is supported by the independent investigations of McConnel *et al.* [11] who noted an optical interaction in solutions of copper(I) and copper(II) chloro complexes; this effect was attributed to the formation of dimeric $\text{Cu}^{\text{I}}\text{-Cu}^{\text{II}}$ chloro complexes with three or more ligands.

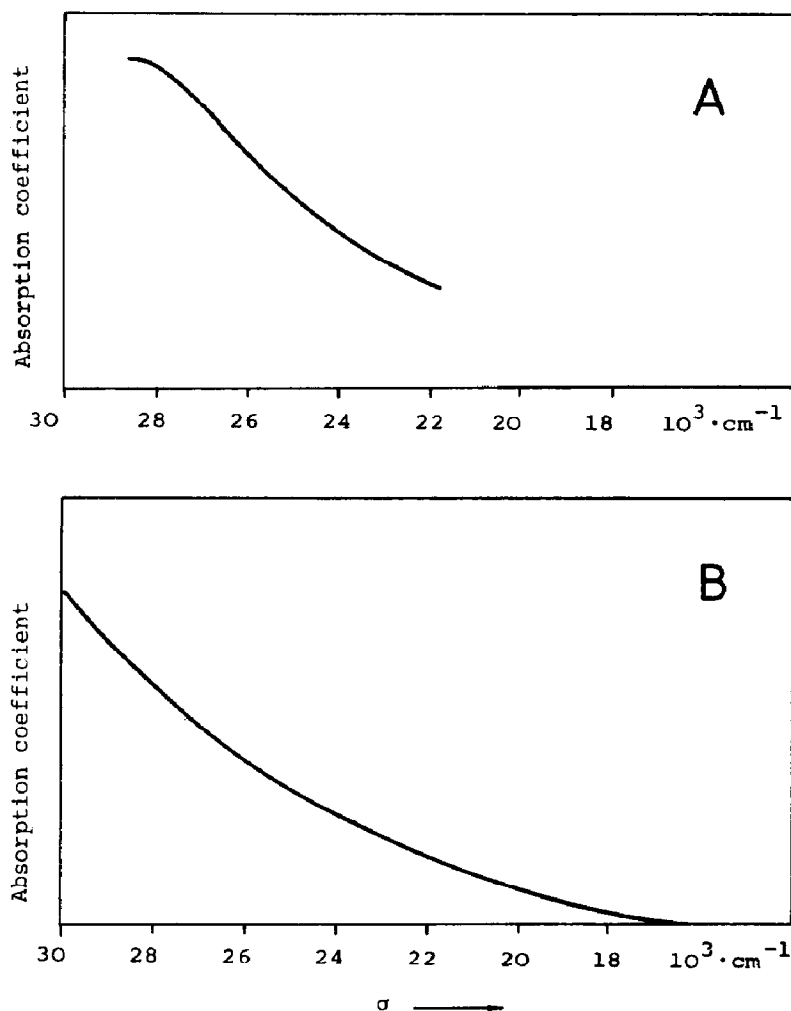


Fig. 8. Absorption spectra of the intermediate observed by Ferraudi (curve A) and in this work (curve B).

Moreover, it is possible that in the second, longer, period of the transient observed by Ferraudi (using flash photolysis) [2] the species examined in this work had disappeared. This hypothesis is confirmed by the coincidence of the visible spectra of these two species (Fig. 8). In the case of these measurements the shorter decay time (millisecond time scale) can be accounted for by the facts that the copper(I) concentration (10^{-3} M) was much lower and the chloride ion concentration (0.5 - 1.0 M) higher than in our experiments. This assumption may be verified by examination of the copper(I) and copper(II) dependences of the decay using flash photolysis in concentration ranges which are unsuitable for the method used in this work.

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