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PHOTO-OXIDATION OF COPPER(I) CHLORO COMPLEXES: INDIVIDUAL QUANTUM YIELDS OF $[CuCl_2]^-$ AND $[CuCl_3]^{2-}$

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Summary

The effects of the chloride and hydrogen ion concentrations on the photo-induced oxidation of copper(I) chloro complexes were investigated under continuous irradiation ($\lambda = 253.7$ nm). The spectrophotometric experimental method combined with computerized evaluation of the data gave results similar to those of experiments carried out earlier using the gas volumetric technique.

The characteristics of the Φ *versus* $C_{H^+}{}^{1/2}$ plots, *i.e.* the linearity at $0.1\ M \leqslant C_{H^+} < 1.0\ M$ and the levelling off (saturation) at $1.0\ M \leqslant C_{H^+} \leqslant 3.0\ M$, at each chloride concentration examined indicate a Noyes geminate-pair scavenging mechanism where the electron formed in the photo-induced redox reaction undergoes competitive recombination and scavenging processes.

The individual quantum yields of the copper(I) chloro complexes $[CuCl_2]^-$ and $[CuCl_3]^{2-}$ were determined from their resolved spectra and the dependence of Φ on the chloride ion concentration. In the saturation region $\Phi_2/\Phi_3 \approx 2$, *i.e.* the individual quantum yields for the electrons escaping primary recombination are $\Phi_2 = 0.60$ and $\Phi_3 = 0.29$.

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1. Introduction

The photochemical properties of inorganic copper(I) complexes have recently been thoroughly studied [1]. Most of the investigations were performed using the halogeno, pseudohalogeno and amino complexes, as copper(I) forms comparatively few stable complexes with inorganic ligands [2]. Initially the copper(I) complexes were studied together with other metal ions. McMillin *et al.* [3] and Farr *et al.* [4] observed light-induced redox reactions between complexes of cobalt(III) and copper(I), and Davis and Stevenson [5] reported that copper(I) had a catalytic effect on the photo-induced oxidation of titanium(III) in HCl solution. These results suggested that inorganic copper(I) complexes, like some other transition metal complexes, might be suitable for the generation of hydrogen from

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acidic solutions using radiation sources of appropriate wavelengths [6]. Therefore, as part of investigations of processes for the conversion and storage of solar energy, the photochemical behaviour of copper(I) bromo and chloro complexes (mainly the dependence of the quantum yield of hydrogen on the ionic strength, the temperature and the irradiation wavelength) was examined in detail. The variation in the total quantum yield Φ with the chloride and hydrogen ion concentrations were determined [7, 8], and the intermediates formed in the photo-induced oxidation of copper(I) complexes were investigated [9, 10].

Most of the continuous irradiation experiments carried out to date have been based on volumetric measurement of the hydrogen gas evolved in the photoreaction. The simultaneous dependence of the total quantum yield on the chloride and hydrogen ion concentrations has been examined over a relatively narrow range, and no efforts have been made to estimate the individual quantum yields of copper(I) halogeno complexes. The main purposes of the further examination of the photochemical properties of copper(I) chloro complexes reported here were as follows: (1) to investigate the dependence of Φ on the chloride and hydrogen ion concentrations C_{Cl^-} and C_{H^+} over a relatively wide range; (2) to determine the individual quantum yields of each photoactive copper(I) chloro complex by using the total quantum yields and the individual absorption coefficients; (3) to apply a spectrophotometric experimental technique which is completely different from the gas volumetric method used in previous studies of copper(I) chloro complexes and to compare the results of the two independent procedures.

2. Experimental details

The copper(I) chloride was prepared by reducing $CuSO_4$ with SO_2 gas in NaCl solution [11].

The solutions for irradiation and calibration contained the following reagent grade chemicals: HCl, NaCl, $HClO_4$ and $NaClO_4$. Traces of copper(II) in the copper(I) solutions were reduced by stirring with copper turnings under an inert atmosphere. Therefore the copper(I) concentration calculated on the basis of the amount of solid copper(I) chloride used to prepare the solution was inaccurate, and hence the precise copper(I) concentration in the standard solutions for calibration was determined using the following indirect method. After recording the spectra the copper(I) was transformed into copper(II) by stirring the solutions in air; the spectra of these solutions were then recorded again. The copper(II) concentration, which was equal to the original copper(I) concentration, was determined using the calibration spectra of copper(II) solutions with the same values of C_{H^+}, C_{Cl^-} and ionic strength μ. The concentration of the $CuCl_2$ stock solution was determined by complexometric titration with ethylenediaminetetraacetic acid [12].

A Specord UV–visible spectrophotometer was used to record the absorption spectra. The photochemical oxidation of the copper(I) solutions was performed by continuous irradiation at room temperature. 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 trioxalatoferrate(III) actinometer [13].

The irradiations were performed in a quartz cuvette with a volume of 3 cm^3 and an optical pathway of 1 cm. The irradiated solutions were kept under a nitrogen atmosphere. An experimental series generally consisted of irradiations lasting for 5, 10, 15, 20, 30 and 50 min.

Since the copper(II) chloro complexes $[CuCl_x]^{(x-2)-}$ show only fairly weak absorption in the visible range and the molar absorption coefficients of the copper(I) chloro complexes $[CuCl_x]^{(1-x)-}$ in the UV range are at least as great as those of $[CuCl_x]^{(x-2)-}$ at almost all wavelengths, photooxidation is followed by a change in the copper(I) concentration in the UV range at wavelengths where the absorption coefficient of copper(II) is relatively low. A wavelength of 276 nm was suitable for this purpose (*e.g.* $\epsilon_{Cu^I} = 1637\ cm^{-1}\ M^{-1}$ and $\epsilon_{Cu^{II}} = 556\ cm^{-1}\ M^{-1}$ in 1 M HCl ($\mu = 3$ M)).

3. Results and discussion

3.1. Spectra of solutions of copper(I) and copper(II) chloro complexes

In order to evaluate properly the changes induced by irradiation of the copper(I) solutions, it was necessary to know the accurate absorption coefficients of both copper(I) and copper(II) in solutions with different values of C_{Cl^-} and C_{H^+}. As the absorption coefficients of the copper(II) species are relatively high at the irradiation wavelength, the inner filter effect became increasingly significant on increasing the irradiation time. Since the values of the absorption coefficients are strongly affected by the hydrogen ion concentration, we recorded the calibration spectra for each C_{Cl^-}–C_{H^+} concentration pair. It was found that on increasing C_{H^+} the absorption coefficients increased in the copper(II) solutions and decreased in the copper(I) solutions. The absorption of both kinds of solution increased on increasing C_{Cl^-} but the increase was stronger for copper(II). The results are shown in Fig. 1. On increasing the chloride concentration the spectra of the two types of solution approached and touched each other ($C_{Cl^-} = 0.5$ M; $C_{H^+} = 0.5$ M), and then the two isosbestic points formed where the spectra crossed moved away from each other. A similar, but weaker, phenomenon was found when C_{H^+} was increased. These observations are not in total agreement with the results of earlier studies [5, 8].

It is known that only $[CuCl_2]^-$ and $[CuCl_3]^{2-}$ species exist in the Cu^I–Cl^- system in equilibrium in the concentration range 0.1 M $\leqslant C_{Cl^-} \leqslant$ 3 M [8, 14]. The complex stability constant K for the process

$$[CuCl_2]^- + Cl^- \rightleftharpoons [CuCl_3]^{2-} \qquad (1)$$

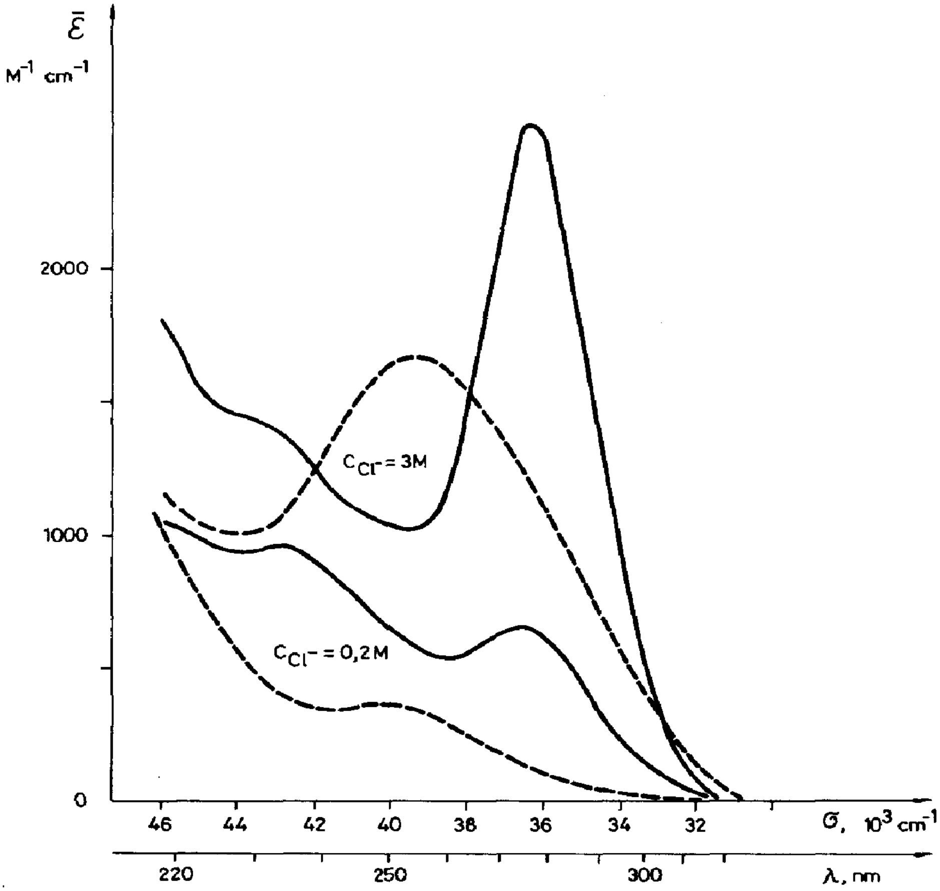

Fig. 1. UV spectra of copper(I) (——) and copper(II) (— — —) at C_{Cl^-} values of 0.2 and 0.3 M, C_{H^+} = 1.0 M and $\mu = 3.0$ M.

determined by Davis *et al.* [8] is 1.1 ± 0.1 mol^{-1} dm^3 at $\mu = 3$ M. (Our measurements gave a similar result.)

The molar absorption coefficients ϵ_2 and ϵ_3 of $[CuCl_2]^-$ and $[CuCl_3]^{2-}$ respectively can be calculated from the ϵ values at various chloride concentrations by means of the least-squares method using the relation

$$\bar{\epsilon} = \epsilon_2 + \frac{\epsilon_3 - \epsilon_2}{1 + K[Cl^-]} \tag{2}$$

which is derived from the well-known relationship

$$\bar{\epsilon} = \left(\epsilon_0 + \sum_{i=1}^{n} \epsilon_i c^i \beta_i\right)\left(1 + \sum_{i=1}^{n} c^i \beta_i\right)^{-1} \tag{3}$$

The results are given in Table 1 and Fig. 2. They show good agreement with the values of ϵ_2 and ϵ_3 reported earlier.

TABLE 1

Data for the resolved spectra of $[CuCl_2]^-$ and $[CuCl_3]^{2-}$ ($\mu = 3.0$ M)

λ (nm)	220	227	233	241	250	254	260	268	276	284	298	313
$C_{H^+} = 0.10\ M$												
ϵ_3	2083	1721	1538	1306	1224	1258	1734	2870	3674	2869	749	84.3
ϵ_2	835	838	890	734	522	472	337	225	89.6	52.4	—	—
$C_{H^+} = 0.30\ M$												
ϵ_3	2026	1695	1520	1309	1210	1247	1701	2755	3567	2791	738	81.3
ϵ_2	827	822	876	719	511	461	335	201	68.4	—	—	—
$C_{H^+} = 0.50\ M$												
ϵ_3	1983	1685	1512	1299	1196	1237	1687	2682	3480	2724	730	78.4
ϵ_2	822	802	868	716	505	448	318	192	43.6	—	—	—
$C_{H^+} = 1.0\ M$												
ϵ_3	1915	1645	1490	1279	1190	1256	1653	2572	3336	2616	717	72.5
ϵ_2	810	785	855	767	488	451	287	160	15.5	—	—	—
$C_{H^+} = 2.0\ M$												
ϵ_3	1834	1609	1475	1249	1152	1192	1587	2444	3199	2480	700	69.6
ϵ_2	815	780	839	709	486	417	279	133	—	—	—	—
$C_{H^+} = 3.0\ M$												
ϵ_3	1773	1592	1467	1237	1119	1179	1544	2366	3167	2451	695	67.5
ϵ_2	828	770	827	697	490	414	258	93.6	—	—	—	—

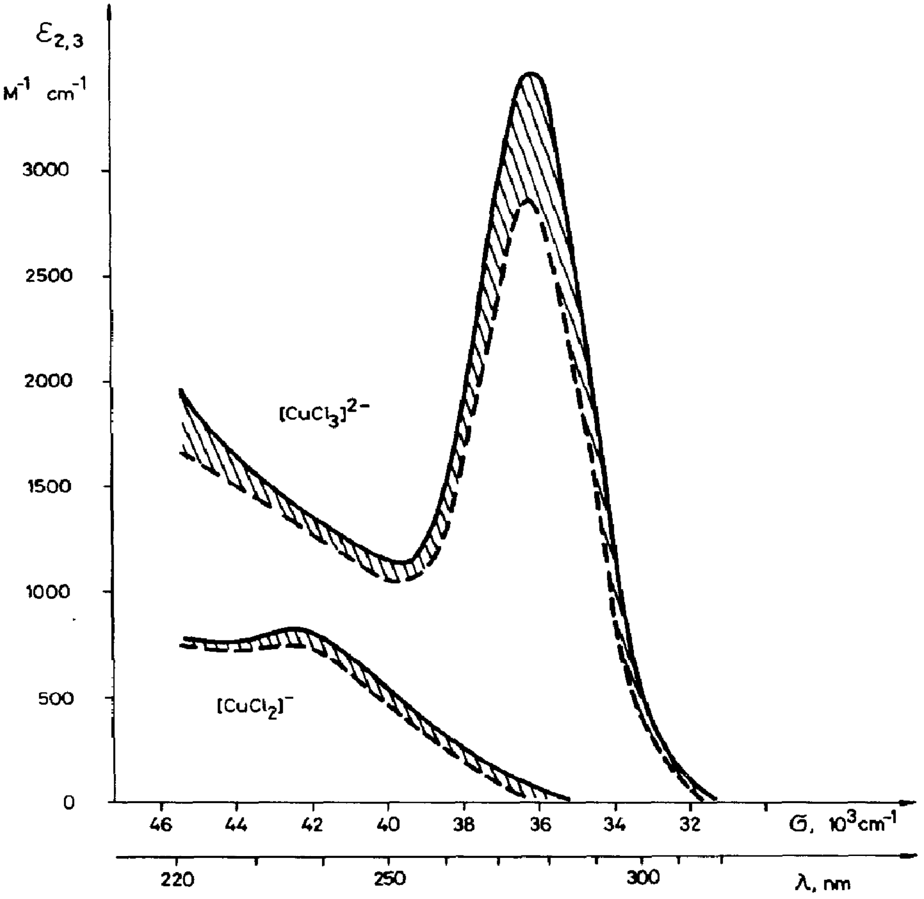

Fig. 2. Resolved UV spectra of $[CuCl_2]^-$ and $[CuCl_3]^{2-}$ at C_{H^+} values of 0.1 M (———) and 3.0 M (— — —) and μ = 3.0 M.

3.2. Evaluation of the results of the photochemical oxidation

Since the exciting light is monochromatic, the rate of photo-oxidation is proportional to the number of light quanta absorbed by the photoactive species $[CuCl_2]^-$ and $[CuCl_3]^{2-}$ and there is no significant back reaction in the system examined, the kinetics of the photochemical reaction are described by

$$-\frac{d[Cu^I]}{dt} = I_0\Phi(1-10^{-A})\frac{A'}{A} \qquad (4)$$

where I_0 is the intensity of the incident light in einsteins per cubic decimetre per second, Φ is the total quantum yield in moles of oxidized copper(I) per einsteins absorbed, A is the total absorption of the solution and A' is the absorption of the photoactive species at the irradiation wavelength.

As the decrease in the copper(I) concentration was followed at 276 nm (for the reasons given above), the absorption at this wavelength of the copper(II) formed had to be taken into consideration. The total absorption of the solution is

$$A = A' + l \sum_{j} c_j \epsilon_j \tag{5}$$

where c_j and ϵ_j are the absorption coefficients and concentrations respectively of the photoactive species, l is the optical path length and

$$A' = l \sum_{i} c_i \epsilon_i \tag{6}$$

where c_i and ϵ_i are the concentrations and absorption coefficients respectively of the non-photoactive species in the system. Equation (6) represents the inner filter effect.

The increase in photochemical oxidation with irradiation time in a solution with a given composition is shown in Fig. 3. The recorded spectra were obtained from independent experiments in which the solutions were irradiated for times of 5, 10, 15, 20, 30 and 50 min. A least-squares method

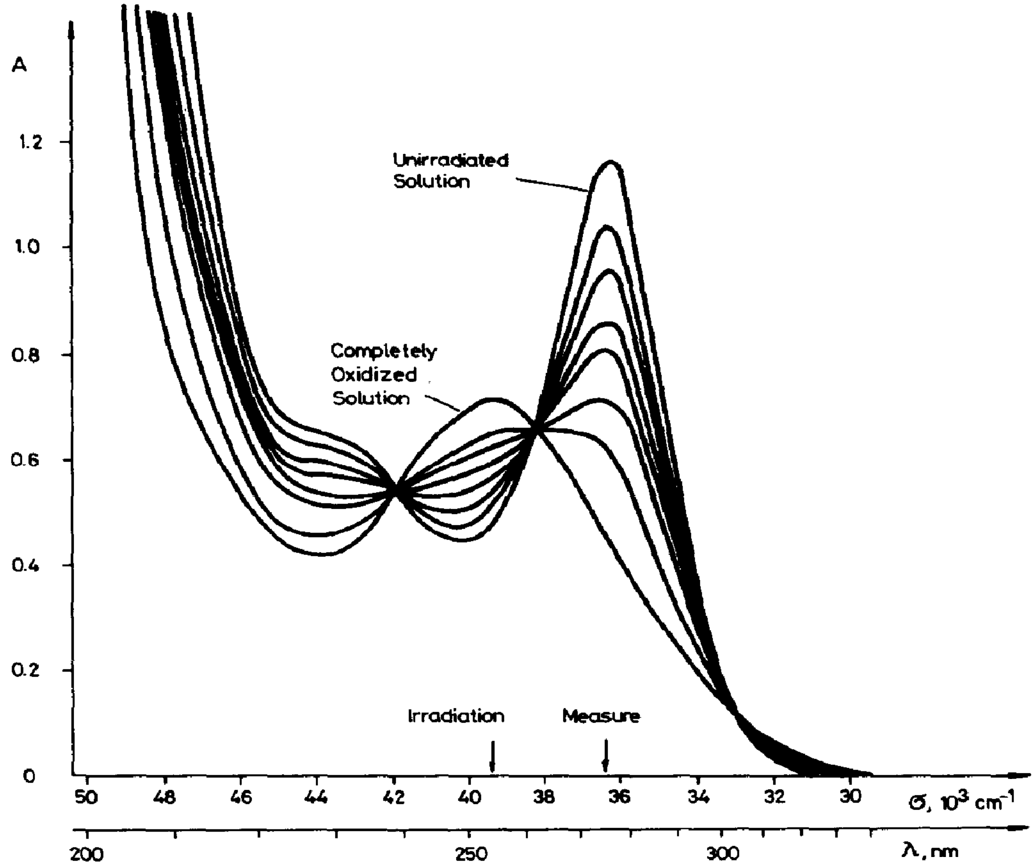

Fig. 3. UV spectra of a 2.4×10^{-3} M CuCl solution (C_{Cl^-} = 2.0 M, C_{H^+} = 0.5 M and μ = 3.0 M) during illumination (λ = 253.7 nm) for times of 5, 10, 15, 20, 30 and 50 min.

using eqns. (4), (5) and (6) such that the sum of the squares of the differences between the calculated and measured absorption data was a minimum was employed to fit curves to the experimental absorption values. Since the relation between [Cu^{I}] and the time t could not be described using elementary functions, as was also the case for the relation between [Cu^{II}] and t, the absorption at each measuring point for a given Φ could only be calculated by changing t in steps Δt ($\Delta t = 1$ min was found to provide sufficient accuracy for the calculations). Figure 4 shows the measured absorption values at 276 nm together with the values calculated using the data of Fig. 3.

The total quantum yield values obtained using the experimental and calculation techniques described above are summarized in Table 2 for all chloride and hydrogen ion concentrations investigated.

3.3. The effect of the hydrogen ion concentration on the total quantum yield

It was found that the quantum yield strongly depends on the ionic strength [8], and the system behaves according to the Noyes scavenging mechanism [15, 16], *i.e.* at concentrations in the range $0.1 \leqslant C_{H^+} \leqslant 3$ M

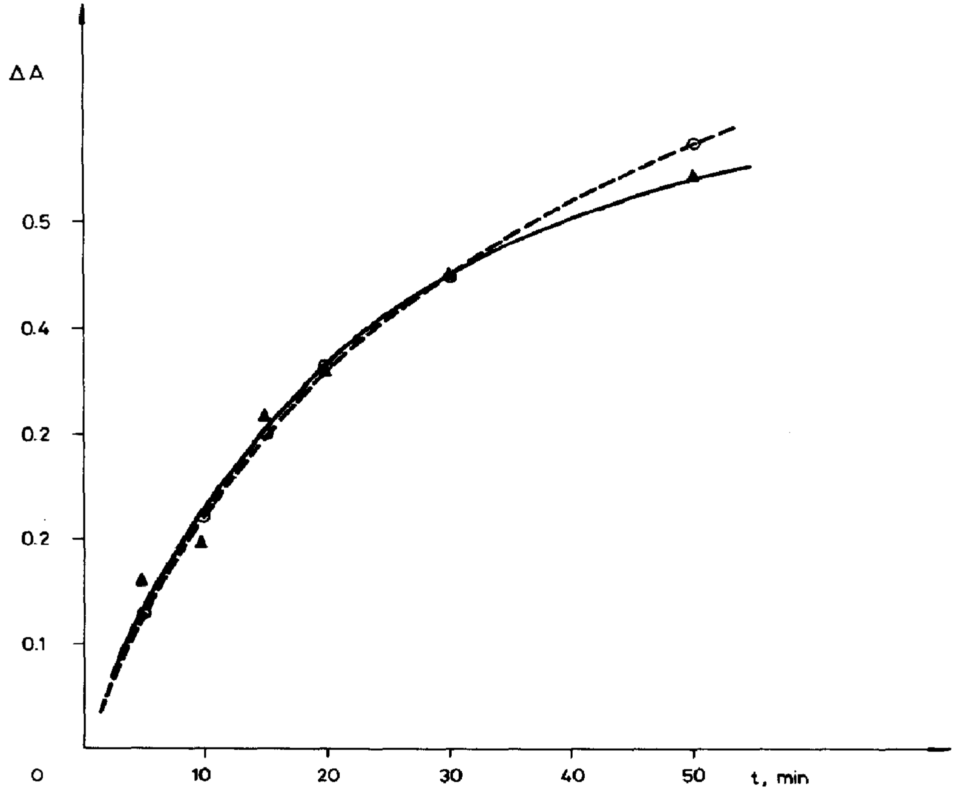

Fig. 4. Measured (▲) and calculated (○) absorption changes $\Delta A(t) = A(0) - A(t)$ in CuCl solution at 276 nm (see Fig. 3): $\Phi = 0.57$; $\Sigma_i\{\Delta A_{exp}(t_i) - \Delta A_{cal}(t_i)\}^2 = 3.2 \times 10^{-3}$.

TABLE 2

Total quantum yields Φ obtained by computerized evaluation of data from the irradiation of CuCl solutions (μ = 3.0 M) at λ = 253.7 nm

C_{Cl^-} (M)	Φ					
	C_{H^+} = *0.10 M*	C_{H^+} = *0.30 M*	C_{H^+} = *0.50 M*	C_{H^+} = *1.0 M*	C_{H^+} = *2.0 M*	C_{H^+} = *3.0 M*
0.20	0.48	0.64	0.70	0.96	1.11	0.91
0.50	0.41	0.71	0.71	0.89	0.87	0.80
1.0	0.24	0.60	0.59	0.72	0.73	0.67
2.0	0.25	0.49	0.57	0.70	0.70	0.50
3.0	0.27	0.43	0.51	0.97	0.59	0.61

electron scavenging by H^+ competes with secondary recombination. The following photo-oxidation mechanism is assumed [8]:

primary pair

$$[CuCl_x]^{(x-1)-} \underset{k_1}{\overset{h\nu}{\rightleftharpoons}} \overline{[CuCl_x]^{(x-2)-}\cdot e^-} \qquad (7)$$

secondary pair

$$\overline{[CuCl_x]^{(x-2)-}\cdot e^-} \xrightarrow{k_d} \overline{[CuCl_x]^{(x-2)-}} + \overline{e^-} \qquad (8)$$

secondary recombination

$$\overline{[CuCl_x]^{(x-2)-}} + \overline{e^-} \xrightarrow{k_r} [CuCl_x]^{(x-1)-} \qquad (9)$$

reactive scavenging

$$\overline{[CuCl_x]^{(x-2)-}} + \overline{e^-} + H^+ \xrightarrow{k_s} [CuCl_x]^{(x-2)-} + H\cdot \qquad (10)$$

hydrogen formation

$$H\cdot + H^+ + [CuCl_x]^{(x-1)-} \xrightarrow{k_p} H_2 + [CuCl_x]^{(x-2)-} \qquad (11)$$

If the secondary pair consists of two different radicals and only one of them can be scavenged (as in the case of the oxidized complex electron pair in these experiments), the relationship between the quantum yield and the scavenger concentration is described by [15, 16]

$$\frac{d\Phi}{d[S]^{1/2}} = 2a(\pi k_s)^{1/2} \qquad (12)$$

where S is the reactive scavenger (H^+ in our case), k_s is the bimolecular scavenging rate constant and a is a diffusion parameter, the value of which is 1.6×10^{-6} $s^{1/2}$ [15].

To check the validity of eqn. (12) for our results, curves of total quantum yield *versus* $C_{H^+}{}^{1/2}$ were drawn. Figure 5 shows the curves obtained at various chloride concentrations. The systems examined undoubtedly behave according to the Noyes relation (eqn. (12)). k_s can be estimated

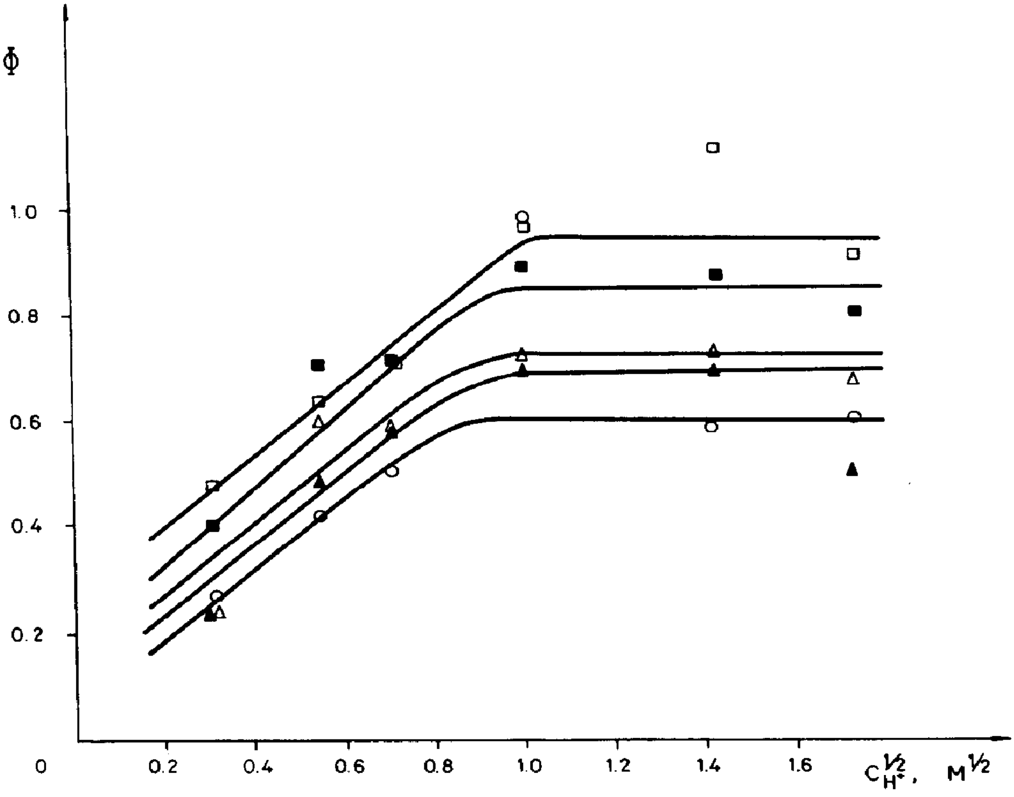

Fig. 5. Dependence of the total quantum yield on $C_{H^+}{}^{1/2}$ for CuCl solutions with various values of C_{Cl^-} (□, 0.2 M; ■, 0.5 M; △, 1.0 M; ▲, 2.0 M; ○, 3.0 M) irradiated at λ = 253.7 nm (μ = 3.0 M).

from the slope of the curves by using the value of a given above. However, it should be noted that the values of Φ in Fig. 5 and Table 2 involve the effect of the thermal reaction represented by eqn. (11) which doubles the quantum yield of the primary scavenging reaction (eqn. (10)).

According to the Noyes theory, above a certain scavenger concentration all the radicals escaping primary recombination are scavenged and the quantum yields reach a limiting value, *i.e.* the Φ *versus* $[S]^{1/2}$ curves level off. This effect can clearly be seen in our curves.

To compare our results with those reported earlier [8] we calculated the k_s values using the Jortner–Ottolenghi–Stein (JOS) relation [17]

$$\Phi = \Phi_0 + \alpha\Gamma[S]^{1/2} \qquad (13)$$

where Φ is the residual quantum yield in the absence of an efficient scavenger, $\alpha = 2a(\pi k_s)^{1/2}$ and Γ is the maximum quantum yield for the radicals escaping primary recombination in the presence of a scavenger. The values of Φ_0 were estimated by extrapolation of Φ to $C_{H^+} = 0$ and the Γ were taken as the Φ_{max} values where the curves levelled off.

To calculate the rate constant of the primary scavenging reaction we had to halve the slopes as well as the Φ_0 and $\Gamma \approx \Phi_{max}$ values obtained from Fig. 5. Therefore the numerical values obtained using eqn. (13) do not involve the doubling effect of the thermal reaction. This must be emphasized because the thermal effect was not taken into consideration in earlier calculations [8] and the Noyes relation for two identical radicals [15] was used. Therefore the results obtained were twice as large as the correct values. However, when the JOS equation is used the two opposing factors counterbalance each other and the calculations give the correct results.

The slopes of the Φ *versus* $C_{\mathrm{H}^+}{}^{1/2}$ plots for different chloride concentrations and the primary scavenging rate constants are summarized in Table 3 which also contains the results reported in ref. 8 for $\mu = 3$ M and $\lambda = 274$ nm. The half k_s values found in the literature are also included for comparison.

The values of Noyes' k_s were selected for analysis because the values calculated using the JOS method are more inaccurate owing to the use of approximations. It was found that the rate constant was almost independent of the chloride concentration: all except one had the same value within the limits of accuracy of the experiments ($k_s = (3.2 \pm 0.4) \times 10^9$ M^{-1} s^{-1}). This value is three times greater than earlier results (accordingly the k_s values calculated using the JOS method are also larger).

Since the k_s values do not differ substantially from the value of 2.2×10^{10} M^{-1} s^{-1} obtained [18] for the rate constant of the reaction

$$\mathrm{H}^+ + e_{aq}{}^- \longrightarrow \mathrm{H}\cdot \qquad (14)$$

our results indirectly support the proposal that hydrated electrons are produced during the photoinduced oxidation of copper(I) and that these electrons are scavenged by hydrogen ions, forming hydrogen radicals. The formation of hydrated electrons in this reaction was also directly observed by Davis *et al.* [8] in flash photolysis experiments. The lifetime of the hydrated electrons in solutions with compositions similar to those examined here, but in the absence of a scavenger, was about 10^{-7} s.

TABLE 3

Characteristic data for the Φ *versus* $C_{\mathrm{H}^+}{}^{1/2}$ curves (Fig. 5) and the rate constants for primary scavenging ($\mu = 3.0$ M)

C_{Cl^-} (M)	*Slope* (M$^{-1/2}$)		$\Phi_{\max}$		k_s ($\times 10^{10}$ M^{-1} s^{-1})			
					Noyes		*JOS*	
	This work	*Reference 8*	*This work*	*Reference 8*	*This work*	*Reference 8*	*This work*	*Reference 8*
0.20	0.67		0.94		0.35		1.6	
0.50	0.77		0.85		0.47		2.6	
1.0	0.62	0.37	0.72	0.60	0.30	0.10	2.3	1.1
2.0	0.66		0.70		0.34		2.8	
3.0	0.60		0.60		0.28		3.1	

In systems containing copper(I) chloro complexes saturation (levelling off of Φ) occurred only at $C_{H^+} \geqslant 1$ M, which is in agreement with the behaviour of systems containing $[Fe(CN)_6]^{4-}$. In this case the lifetime of the hydrated electron was about 10^{-5} s [19] even in the presence of an NO_3^- scavenger. Saturation occurred at N_2O scavenger concentrations of 2×10^{-3} M [20]. This further supports the proposed mechanism as the electron scavenging rate constant of N_2O is 5.6×10^9 M^{-1} s^{-1} [18], which is less than that of reaction (14).

These results show that the rate of secondary recombination for copper(I) chloro complexes (reaction (9)) is much higher than that of a similar process in systems containing $[Fe(CN)_6]^{4-}$ or $[Fe(CN)_3]^{3-}$.

3.4. Determination of the individual quantum yields

The data given in Table 2 show that the total quantum yield decreases markedly with increasing chloride concentration, and this can also be seen in Fig. 6. Davis *et al.* [8] explained this phenomenon in terms of a salt effect, and they considered that the $[CuCl_3]^{2-}$ species was photoactive in view of the dependence of the total quantum yield on the irradiation wavelength. We assumed that both the $[CuCl_2]^-$ and the $[CuCl_3]^{2-}$ species were photoactive at 253.7 nm, which is not unlikely in view of the resolved

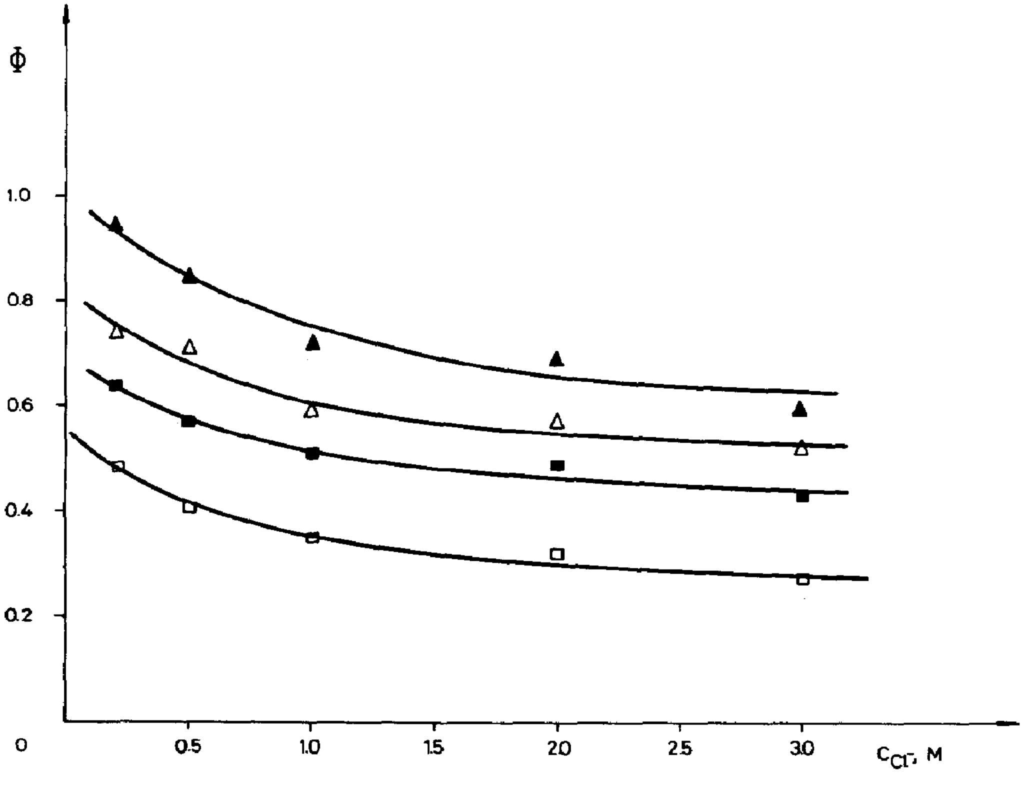

Fig. 6. Dependence of the total quantum yield on C_{Cl^-} at various values of C_{H^+} (μ = 3.0 M): □, 0.1 M; ■, 0.3 M; △, 0.5 M; ▲, 1.0 - 3.0 M.

spectra (Fig. 2) and seems to be supported by the hyperbolic character of the Φ *versus* C_{Cl^-} curves.

If it is assumed that the individual quantum yields of the $[CuCl_2]^-$ and $[CuCl_3]^{2-}$ species are Φ_2 and Φ_3 respectively, the following relationship should be valid [19, 21]:

$$\Phi = \frac{\Phi_2\epsilon_2 + \Phi_3\epsilon_3K[Cl^-]}{\epsilon_2 + \epsilon_3K[Cl^-]} \tag{15}$$

where Φ is the measured total quantum yield and ϵ_2 and ϵ_3 are the absorption coefficients of the two species at the irradiation wavelength. For convenience eqn. (15) can be rewritten in the following form:

$$\Phi = \Phi_3 + \frac{(\Phi_2 - \Phi_3)\epsilon_2}{\epsilon_2 + \epsilon_3K[Cl^-]} \tag{16}$$

Since the total quantum yield at a given wavelength decreased on increasing the chloride concentration, we assumed that both copper(I) chloro complexes were photoactive and that Φ_2 was greater than Φ_3.

If the total quantum yield values are plotted against $\epsilon_2/(\epsilon_2 + \epsilon_3K[Cl^-])$, a straight line with slope $\Phi_2 - \Phi_3$ and intersection Φ_3 should be obtained if eqn. (16) is valid. Refined data from Fig. 5 were used for the graph and calculations. The results obtained are shown in Fig. 7 and Table 4. Figure 8

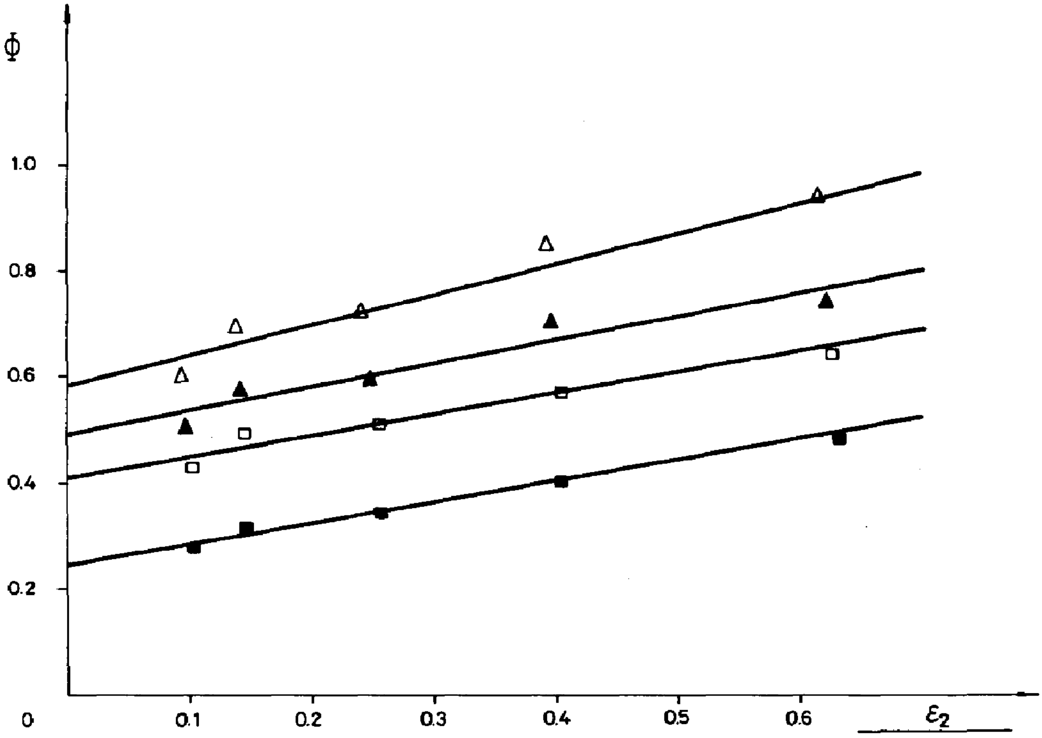

Fig. 7. Curves of Φ *vs.* $\epsilon_2/(\epsilon_2 + \epsilon_3K[Cl^-])$ for the determination of the individual quantum yields of $[CuCl_2]^-$ and $[CuCl_3]^{2-}$ at various values of C_{H^+} (μ = 3.0 M): ■, 0.1 M; □, 0.3 M; ▲, 0.5 M; △, 1.0 - 3.0 M.

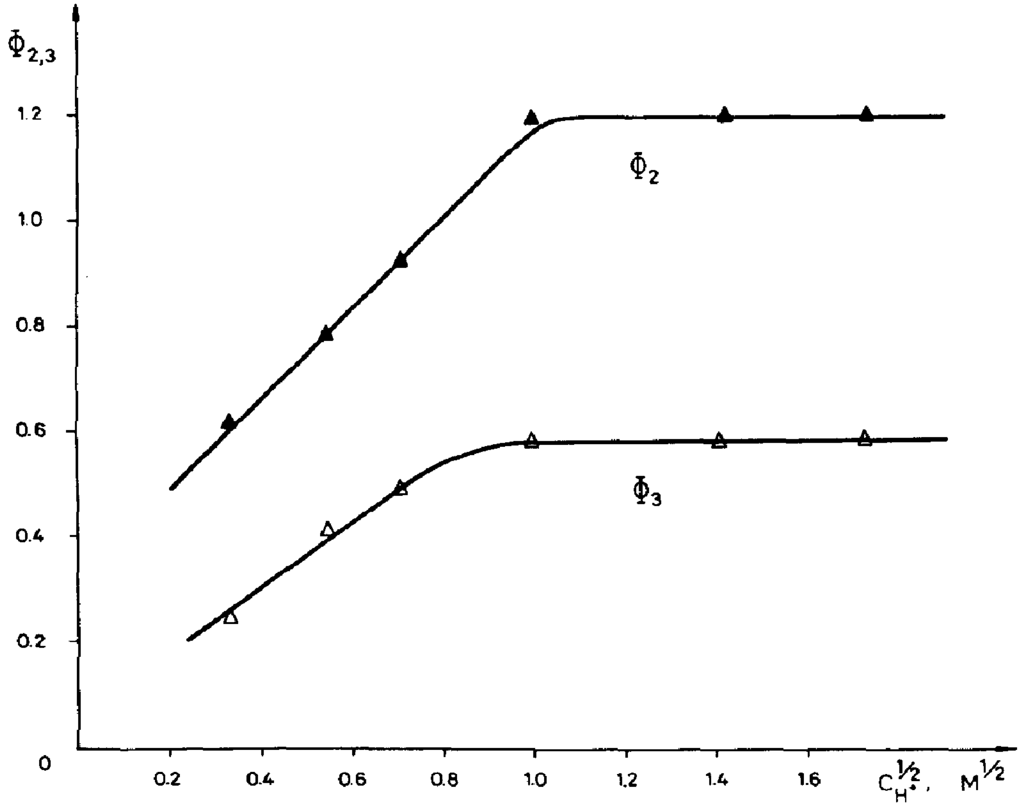

Fig. 8. Dependence of the individual quantum yields Φ_2 and Φ_3 on $C_{H^+}{}^{1/2}$.

TABLE 4

Individual quantum yields of $[CuCl_2]^-$ (Φ_2) and $[CuCl_3]^{2-}$ (Φ_3)

C_{H^+} (M)	Φ_2	Φ_3
0.10	0.62	0.25
0.30	0.78	0.41
0.50	0.93	0.49
1.0 - 3.0	1.20	0.58

shows the Φ_i *versus* $C_{H^+}{}^{1/2}$ plot; the shapes of the curves indicate that the Noyes geminate pair scavenging mechanism is operating. The number of hydrated electrons escaping recombination to $[CuCl_2]^-$ in the saturation region is twice as large as that in the photo-oxidation of the $[CuCl_3]^{2-}$ species. A possible explanation of this behaviour is that the electron departing from the metal centre may be more able to form a secondary pair despite the fact that the charge density produced by two ligands is less negative than that produced by three ligands.

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