

THE PHOTOCHROMIC PROPERTIES OF THE SYSTEM $\text{CuCl(s)}-\text{H}_2\text{O(l)}$ IN RELATION TO THE COMPOSITION OF THE AQUEOUS SOLUTION

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Summary

The photochromic properties of the system $\text{CuCl(s)}-\text{H}_2\text{O(l)}$ in relation to the composition of the aqueous solution were studied using diffuse reflectance spectroscopy. The photochemical disproportionation of Cu^+ into Cu^{2+} and Cu^0 proved to be essentially independent of pH, ionic strength and the concentrations of Cu^{2+} and Cl^- in the solution. The reverse reaction, *i.e.* thermal fading, takes place in two steps, one initial exponential step followed by a second step of zero order, *i.e.* of constant reaction rate. For both steps the reaction rate is independent of the concentration of metallic copper. The rate of the initial step is proportional to the product of the Cu^{2+} and Cl^- concentrations of the solution. The rate of the second step is independent of the Cu^{2+} concentration and proportional to the Cl^- concentration. The results are consistent with the following mechanism for the bleaching reaction: (I) diffusion of $\text{Cu}^{2+}-\text{Cl}^-$ complexes to reaction sites on the surface; (II) fast chemical reaction between $\text{Cu}^{2+}-\text{Cl}^-$ and Cu^0 at the reaction sites yielding CuCl ; (III) desorption of the product CuCl by complex formation with Cl^- ions.

1. Introduction

An aqueous suspension of CuCl exhibits a photochromic reaction involving a drastic colour change from white to dark green. The dark green colour arises from the formation of extremely small metallic copper particles in CuCl [1].

Previous investigations [2, 3] have shown that the presence of liquid water is necessary for CuCl to exhibit photochromic properties. The composition of the aqueous solution has been found to influence greatly the characteristics of the photochromic phenomenon, in particular the dark reaction, but the data reported have largely been qualitative in nature. In this investigation attempts are made to find quantitative descriptions of how the composition of the aqueous solution determines the reaction. The study

forms part of a larger study towards understanding of the photochromic properties of CuCl [1, 3 - 5].

The heterogeneous system CuCl(s)-H₂O(l) is determined by several complex and redox equilibria. In 1 M HClO₄ and for Cl⁻ and Cu²⁺ concentrations less than 0.25 M and 25 mM respectively the following data apply:



The equilibrium constants K of reactions (1), (2), (4) and (5) have recently been determined spectrophotometrically [6, 7]. The K value given for reaction (3) is calculated from data valid for $I = 0$ according to refs. 8 and 9. All K values refer to a temperature of 25 °C except those of reactions (1) and (2) which hold for 22 °C.

The photochemical reaction in the CuCl(s)-H₂O(l) system has been explained as a disproportionation of CuCl and thus it primarily disturbs equilibrium (3). The investigation was therefore designed to evaluate how the photochromic reactions depend on the Cu²⁺ and Cl⁻ concentrations. For this evaluation to be possible the complex chemistry according the reactions (1), (2), (4) and (5) has to be known and properly considered.

2. Experimental

The photochromic reactions were followed by recording the diffuse reflex attenuation ($A_R = \log 1/R$) with unilluminated CuCl as a reference. The procedure was essentially the same as that described in previous work [4]. Owing to the relatively large amount of CuCl needed for the reflectance measurements, the presence of Cu²⁺ impurities in the solid phase was highly important in determining the Cu²⁺ content of the liquid phase. Therefore, the same CuCl crystals were used throughout an entire series of measurements and the composition of the solution was checked spectrophotometrically before every illumination.

2.1. Sample preparation

The reaction vessel used consisted of a standard 1 mm quartz cuvette connected to a test tube. This made it possible to use the cuvette for absorption measurements on the solution as well as for reflectance measurements on the solid phase. If not otherwise stated in the following text the ionic strength was equivalent to 1 M and the Cl⁻ concentration was set by the addition of HCl in such a way that the sum of the HCl and the HClO₄ concentrations equalled 1 M. The desired Cu²⁺ concentration of the solution was arrived at either by oxidation with air or by addition of metallic copper.

2.2. Spectrophotometry

Solution absorption spectra and reflex attenuance spectra were determined. The sample was activated with unfiltered light from a 450 W xenon lamp. The colour change was followed by reflectance measurements throughout the bleaching reaction. The samples were subjected to repeated cycling for different levels of metallic copper concentration simply by varying the time of exposure to the activating light. The temperature during the experiments was held at 22 ± 1 °C. For kinetic evaluations, the reflex attenuance at 450 nm was used if not otherwise stated.

2.3. Determination of the Cu^{2+} and Cl^- concentrations of the solution

In two previous investigations the complex constants and corresponding absorption spectra have been determined for $\text{CuCl}-\text{Cl}^-$ complexes [7] and for $\text{Cu}^{2+}-\text{Cl}^-$ complexes [6] in 1 M HClO_4 . The complexes show absorption in the wavelength region 210 - 370 nm. For the $\text{CuCl}-\text{Cl}^-$ complexes ($[\text{Cl}^-] < 0.25$ M) the absorbance A' at a given wavelength can be expressed as

$$A' = \epsilon'_1[\text{CuCl}_2^-] + \epsilon'_2[\text{CuCl}_3^{2-}] = g([\text{Cl}^-]) \quad (6)$$

Thus in the case of solutions saturated with CuCl(s) the absorbance from these complexes will only depend on $[\text{Cl}^-]$. For the $\text{Cu}^{2+}-\text{Cl}^-$ complexes ($[\text{Cl}^-] < 0.25$ M, $[\text{Cu}^{2+}]_{\text{tot}} < 25$ mM) a corresponding expression can be written:

$$\begin{aligned} A'' &= \epsilon''_0[\text{Cu}^{2+}] + \epsilon''_1[\text{CuCl}^+] + \epsilon''_2[\text{CuCl}_2] \\ &= [\text{Cu}^{2+}]_{\text{tot}} f([\text{Cl}^-]) \end{aligned} \quad (7)$$

The absorbance A'' is in this case proportional to the total concentration of Cu^{2+} with a proportionality constant which depends only on $[\text{Cl}^-]$.

In the relevant concentration range there is no spectral evidence for the occurrence of complexes between Cu^+ and Cu^{2+} [6]. Using the absorbance at two wavelengths it is thus possible to determine the total Cu^{2+} concentration and the "free" Cl^- concentration for the solutions. As the functions g and f are relatively complicated, the following solution seemed preferable.

The total absorbance A can be expressed as

$$A = g([\text{Cl}^-]) + [\text{Cu}^{2+}]_{\text{tot}} f([\text{Cl}^-]) \quad (8)$$

Combining the absorbance at two wavelengths 1 and 2 yields

$$\frac{A_1 - g_1}{A_2 - g_2} = \frac{f_1}{f_2} \quad (9)$$

From eqn. (9) $[\text{Cl}^-]$ was determined by an iterative procedure using plots of g_1 , g_2 and f_1/f_2 versus $[\text{Cl}^-]$. The total Cu^{2+} concentration $[\text{Cu}^{2+}]_{\text{tot}}$ followed from eqn. (8). In these calculations the wavelengths of 250 and 274 nm were used in order to exploit best the spectral difference between the $\text{Cu}^{2+}-\text{Cl}^-$ and $\text{CuCl}-\text{Cl}^-$ complexes. The precision in the determination can be estimated to be about 2% in $[\text{Cl}^-]$ and 5% in $[\text{Cu}^{2+}]$. Negligible error arises from the fact that the f values used refer to 25 °C.

3. Results

3.1. The photochemical disproportionation reaction

The reflex attenuance $A_R (= K_R [Cu^0]$ [4]) at the end of the illumination period was determined through extrapolation from curves of the bleaching reaction. As seen from Tables 1 - 3 the extent of conversion in the photochemical reaction, *i.e.* the forward reaction, shows no significant dependence on the Cu^{2+} and Cl^- concentrations. The slight decrease in yield observed at very high Cl^- concentrations (Table 2) may not be significant. (At extremely high $[Cl^-]$ (> 2 M), however, the observed photochromic sensitivity gradually disappears with increasing $[Cl^-]$.)

TABLE 1

Yield of the photochemical reaction in relation to the Cu^{2+} and Cl^- content of the aqueous solution

Illumination time (s)	$[Cl^-]$ (M)	$[Cu^{2+}]_{tot}$ (mM)	$A_R (t = 0)$ (450 nm)
6	0.055	7.3	0.412
6	0.072	8.5	0.448
6	0.111	17.1	0.470
6	0.123	29.1	0.444
6	0.159	20.1	0.446
18	0.066	15.7	0.717
18	0.079	17.4	0.689
18	0.123	29.1	0.744

TABLE 2

Yield of the photochemical reaction at a given light dose in relation to the $[Cl^-]$ of the solution

$[Cl^-]$ (M)	$A_R (t = 0)$ (450 nm)
not added	0.518
	0.505
0.05	0.507
0.25	0.499
0.50	0.492

The effect of changes in pH and ionic strength also seems to be negligible (see Table 3). In addition it should be noted that the $CuCl$ surface is partly converted to Cu_2O in 1 M $NaClO_4$.

TABLE 3

Yield of the photochemical reaction at a given light dose in relation to the pH and ionic strength of the solution

Solution	$A_R (t = 0)$ (600 nm)
1 M HClO ₄	0.350
0.01 M HClO ₄ + 1 M NaClO ₄	0.319
0.01 M HClO ₄	0.330
1 M NaClO ₄	0.322

In this series the reflex attenuation at 600 nm is a better measure of the copper concentration as Cu₂O is formed in the 1 M NaClO₄ sample and absorbs at 450 nm.

3.2. The reverse reaction

Numerous attempts were made to find a numerical expression for the reverse reaction in terms of a relation between the reflex attenuation A_R and the time t . However, plots of $-\Delta A_R/\Delta t$ (determined from two consecutive points) versus time were found to be largely independent of A_R . This is illustrated in Fig. 1 for one series of experiments in which the composition of the solution was held constant in all the measurements. The reaction appears to consist of two steps: an initial step which decays exponentially

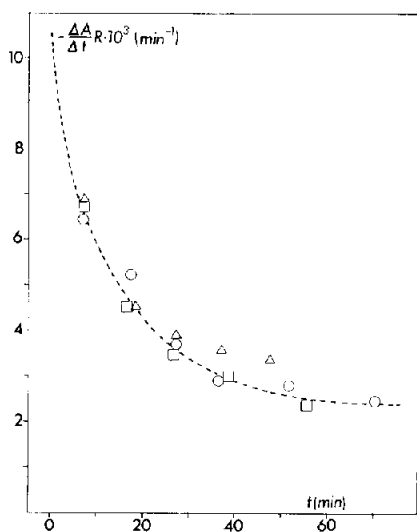


Fig. 1. The influence of metallic copper on the bleaching reaction illustrated by plots of $-\Delta A_R/\Delta t$ vs. time t for a sample of $[Cl^-] = 0.218$ M and $[Cu^{2+}] = 20.6$ mM at $A_R (t = 0)$ values of 0.384 (\square), 0.571 (\circ) and 0.702 (\triangle).

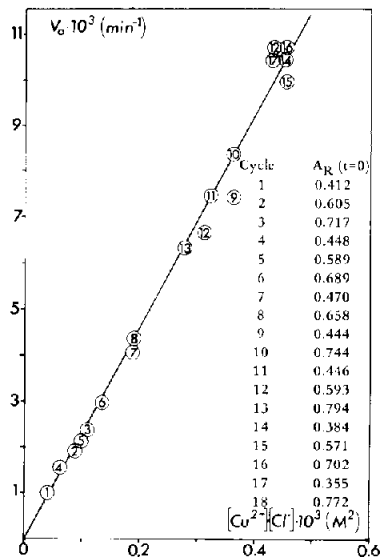


Fig. 2. Influence of Cu^{2+} and Cl^- on the bleaching reaction: the parameter V_0 vs. $[Cu^{2+}]_{tot}[Cl^-]$ (see eqn. (18)).

into a subsequent step of zero order, *i.e.* of constant rate. Two parameters V_0 and V_c can be used to describe numerically the reaction, where V_0 is the initial rate $(-\Delta A_R/\Delta t)_0$ and V_c the constant rate $(-\Delta A_R/\Delta t)_\infty$. V_0 was determined as the intercept of the straight line

$$\log \left\{ - \left(\frac{\Delta A_R}{\Delta t} \right)_t - V_c \right\} = \log(V_0 - V_c) - kt$$

Owing to the relatively low numerical precision in $\Delta A_R/\Delta t$, the determination of the two parameters V_c and V_0 becomes rather uncertain. However, as the reverse reaction shows a strong dependence on $[\text{Cu}^{2+}]$ and $[\text{Cl}^-]$ the lack of precision in the determination of V_0 and V_c proved not to be critical.

In order to identify a specific cycle in Figs. 2 - 4, the cycles have been numbered in order of increasing Cl^- concentration. The value of the reflex attenuation for 450 nm at the end of the illumination is given in Fig. 2.

V_c shows no significant dependence on the Cu^{2+} content of the solution but varies linearly with $[\text{Cl}^-]$ (see Fig. 3). V_0 depends on $[\text{Cu}^{2+}]_{\text{tot}}$ and on $[\text{Cl}^-]$. A plot of V_0 versus $[\text{Cu}^{2+}]_{\text{tot}}[\text{Cl}^-]$ can be represented by a straight line (see Fig. 4). It should be noted that deviations from the general appearance of the reverse reaction, *i.e.* Fig. 1, occur at high $[\text{Cl}^-]$ (more than 0.25 M). The short wavelength region of the reflex attenuation spectrum stays essentially the same during the bleaching reaction. However, for wavelengths longer than about 650 nm there is a faster decrease in A_R than for shorter wavelengths. The occurrence of this spectral change during the bleaching is probably associated with a change in the average particle size of Cu^0 [1].

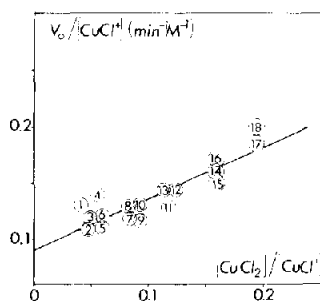
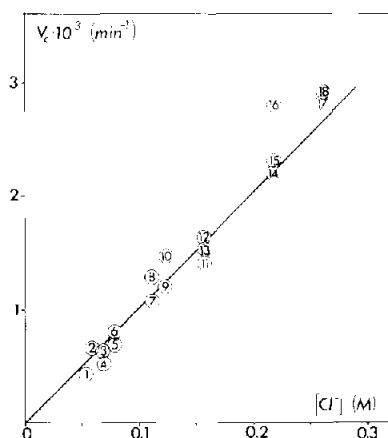


Fig. 3. The influence of Cu^{2+} and Cl^- on the bleaching reaction: the parameter V_c vs. $[\text{Cl}^-]$ (see eqn. (19)).

Fig. 4. Correlation between the parameter V_0 and the concentrations of CuCl^+ and CuCl_2 according to eqn. (21).

4. Discussion

4.1. The photochemical disproportionation reaction

The results from this investigation show that the composition of the solution has very little if any influence on the photochemical disproportionation of CuCl. This concurs with the mechanism proposed in previous work [4]. It is believed that electron-hole pairs are formed in CuCl through the action of light. The holes migrate to the surface where they are trapped by Cu^+ , which are oxidized to Cu^{2+} ions. These ions are then hydrated and diffuse into the solution. The electrons are trapped just below the surface in areas of a high concentration of interstitial Cu^+ . The electron trapping is followed by nucleation of the Cu^0 atoms formed, which results in the formation of small metallic copper particles.

According to this mechanism the reduction step is a subsurface process and the oxidation a surface process. Any influence on the reaction from the composition of the solution must therefore take place in the oxidation stage. The critical step in the oxidation is the dissolution of Cu^{2+} . The variations in $[\text{Cu}^{2+}]$, $[\text{Cl}^-]$, pH and ionic strength of the solution proved not to change the photochemical disproportionation reaction. These results therefore are consistent with the mechanism given earlier.

Previous reported studies of the photochromic system of CuCl by other authors have not been analysed in the same way as here. Hecht and Müller [2] used reflectance measurements but did not separate the photochemical and the reverse reactions. This makes their results difficult to interpret. Galecki and Wojtczak [10], however, report that the addition of Fe^{2+} and Mg^{2+} to the solution increases the light sensitivity. As Fe^{2+} can act as an effective hole trap this is consistent with the proposed mechanism but the action of Mg^{2+} is not understood.

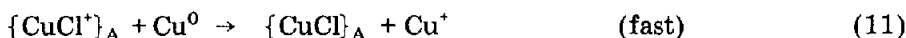
4.2. The reverse action

Previous work [4] has indicated that A_R is proportional to the concentration of metallic copper. The observation that $-\Delta A_R/\Delta t$ is independent of A_R suggests therefore that the reverse reaction is independent of the metallic copper concentration and that the rate is limited by the size of the crystal surface.

The observation that the initial bleaching rate is proportional to $[\text{Cu}^{2+}]_{\text{tot}}$ and to $[\text{Cl}^-]$ suggests that the initial step is determined by the diffusion of $\text{Cu}^{2+}-\text{Cl}^-$ complexes to the surface. The change observed in the character of the bleaching as the reaction moves to a dependence on $[\text{Cl}^-]$ alone agrees with the idea that the available surface sites gradually become highly populated, *i.e.* desorption of the reaction product CuCl through complex formation with Cl^- ions becomes the rate-limiting step.

4.3. The mechanism of the reverse reaction

Assuming the reverse reaction to take place at certain reaction sites (A) on the crystal surface, the bleaching process can be described by the following net reactions (CuCl^+ is the predominant $\text{Cu}^{2+}-\text{Cl}^-$ complex):



A rough quantitative description of the kinetics is obtained by assuming that the total number of reaction sites per unit volume equals a given number N of moles. Then

$$-\frac{d[\text{CuCl}^{+}]}{dt} = k_1[\text{CuCl}^{+}](N - \{\text{CuCl}\}_{\text{A}}) = a(N - D) \quad (14)$$

where $a = k_1[\text{CuCl}^{+}]$ and $D = \{\text{CuCl}\}_{\text{A}}$.

$$\frac{d[\text{Cu}^0]}{dt} = \frac{d[\text{CuCl}^{+}]}{dt} \quad (15)$$

$$\begin{aligned} \frac{d\{\text{CuCl}\}_{\text{A}}}{dt} &= -\frac{d[\text{CuCl}^{+}]}{dt} - k_2\{\text{CuCl}\}_{\text{A}}[\text{Cl}^{-}] \\ &= a(N - D) - bD \end{aligned} \quad (16)$$

where $b = k_2[\text{Cl}^{-}]$. Combining these equations yields

$$-\frac{d[\text{Cu}^0]}{dt} = \frac{aN}{a+b} [b + a \exp\{-(a+b)t\}] \quad (17)$$

With $A_{\text{R}} = K_{\text{R}}[\text{Cu}^0]$ it is evident that the proposed mechanism yields a mathematical expression that is consistent with the observations made.

The initial rate V_0 and the constant rate V_c can be expressed as

$$V_0 = -\left(\frac{dA_{\text{R}}}{dt}\right)_{t=0} = K_{\text{R}}Na = K_{\text{R}}Nk_1[\text{CuCl}^{+}] \quad (18)$$

and

$$V_c = -\left(\frac{dA_{\text{R}}}{dt}\right)_{t \rightarrow \infty} = K_{\text{R}}N \frac{ab}{a+b} \quad (19)$$

Experimentally V_0 was found to be essentially proportional to the product $[\text{Cu}^{2+}]_{\text{tot}}[\text{Cl}^{-}]$ (Fig. 2). This product gives a good approximation of $[\text{CuCl}^{+}]$ at low Cl^{-} and Cu^{2+} concentrations; see the equilibrium constants (1) - (5). However, the interpretation of the initial rate as consisting of only reaction (10) is probably an oversimplification. It may instead be assumed that Cu^{2+} diffuses to the surface both in the form of CuCl^{+} and CuCl_2 . A more accurate expression for reaction (10) should thus be



and the expression for the initial rate becomes

$$V_0 = K_R N(k_1 [\text{CuCl}^+] + k'_1 [\text{CuCl}_2]) \quad (21)$$

Using the equilibrium constants of eqns. (4) and (5) $[\text{CuCl}^+]$ and $[\text{CuCl}_2]$ were calculated. According to eqn. (21) the ratio of V_0 to $[\text{CuCl}^+]$ was plotted against the ratio of $[\text{CuCl}_2]$ to $[\text{CuCl}^+]$. This is illustrated in Fig. 4. The ratio of the slope to the intercept of the straight line in this figure indicates that k'_1 is about five times larger than k_1 .

The constant reaction rate V_c can be obtained by combining eqns. (18) and (19):

$$V_c = \left(1 - \frac{V_c}{V_0}\right) K_R N b = \left(1 - \frac{V_c}{V_0}\right) K_R N k_2 [\text{Cl}^-] \quad (22)$$

Experimentally, V_c was found to be roughly independent of $[\text{Cu}^{2+}]$ but proportional to $[\text{Cl}^-]$. From eqn. (22) it is evident that the proposed model meets these two requirements only approximately. However, the precision in the experimental data does not allow for a more detailed analysis. The variations in the factor $1 - V_c/V_0$ are too small in comparison with the deviations from the linear dependence of V_c on $[\text{Cl}^-]$ as can be seen by comparing Figs. 3 and 5.

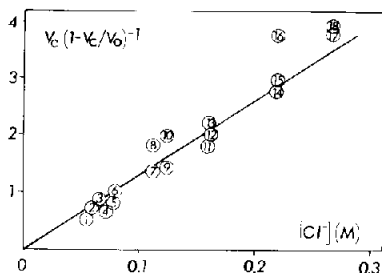


Fig. 5. Correlation between $V_c (1 - V_c/V_0)^{-1}$ and the Cl^- concentration according to eqn. (22).

4.4. Comparison with other investigations of the reverse reaction

The bleaching reaction for the photochromic system $\text{CuCl}(s) - \text{H}_2\text{O}(l)$ has been studied by Hecht and Müller [2]. They report their observations in terms of the percentage reflection relative to a BaSO_4 surface without any numerical or kinetic evaluations. However, the results do give valuable qualitative information. Thus it was found that the addition of Cl^- and Br^- to the solution is necessary for the bleaching to take place. The role of these ions in the reverse reaction is suggested to be due to a necessary complex formation of CuCl but this idea was not further developed. Any effect of variation in the $[\text{Cu}^{2+}]$ of the solution was not reported. By varying the relative amounts of liquid to solid phase it was observed that a large excess of the liquid phase decreased the fading reaction rate. It was also found that

smaller crystals gave an increased reaction rate. Hecht and Müller also observed a hysteresis phenomenon in the photochromic cycle with a slower reaction rate in the first cycle as compared with the subsequent cycles. This hysteresis could be overcome by keeping the sample for a longer time before the next exposure.

The observations by Hecht and Müller are consistent with the theory for bleaching given here. The observed decrease of the rate when the relative amount of liquid phase is large is thus explained as a dilution effect on the photochemically formed $\text{Cu}_{\text{aq}}^{2+}$. The reported crystal size dependence is understood in terms of a variation of the reaction surface. The observed hysteresis was not found in the present study and this suggests that the effect may have been due to variations in the composition of the solution.

The present results precisely parallel those from a study of the reaction between metallic copper and Cu^{2+} [11]. A flow system was used in this study, the flow reactor being filled with metallic copper and fed with a solution of CaCl_2 and Cu^{2+} . It was concluded that the rate-determining step in the reaction is the diffusion of Cu^{2+} into the grain boundaries of the metallic copper. The chemical reaction between Cu^{2+} and Cu^0 was found to be fast and irreversible and the CuCl(s) produced in the reaction forms complexes with CaCl_2 .

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