

THE PHOTOCHEMICAL DISPROPORTIONATION REACTION IN THE SYSTEM $\text{CuCl(s)}-\text{H}_2\text{O(l)}$

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(Received March 1, 1976)

Summary

The photochemical production of Cu^0 in the system $\text{CuCl(s)}-\text{H}_2\text{O(l)}$ was investigated using reflectance spectroscopy. For u.v. light activation the spectral sensitivity follows the excitonic absorption band of CuCl . The system may also be activated with visible light (after an induction period) through a sensitized process with the photoproduct Cu^0 as the sensitizer. The experimental data, including the time-course of the reaction, are consistent with the following mechanism: Cu^0 aggregates are formed close to the phase boundary. Continued exposure increases the depth of the Cu^0 containing layer but the local concentration of Cu^0 stays essentially constant. With u.v. light there is a continued increase in the number of Cu^0 aggregates but visible light activation has in addition the effect of enlarging the aggregates. As the depth of the layer increases the reaction is slowed down due to an inner filter effect from Cu^0 ; the Hurter equation, usually employed to characterize the photographic process in silver halide systems, is obeyed.

Introduction

It is known that a heterogeneous system of CuCl(s) and water exhibits photochromic properties [1 - 3]. The reactions causing the photochromism involve a disproportionation of Cu^+ into Cu^0 and Cu^{2+} . Cu^0 is formed in the CuCl crystals as very small particles (sizes on the order of 3 nm in diameter) and it produces a deep green colour [2]. The Cu^{2+} produced is observed as an increase in the Cu^{2+} concentration of the solution [3].

This paper presents a model for the forward reaction. The production of the coloured species, Cu^0 , is studied using reflectance spectroscopy.

Experimental

Samples

Small CuCl crystals (Merck, p.a.) were recrystallized from HCl, washed with absolute EtOH, and dried. All preparations were carried out in a nitrogen atmosphere to prevent Cu⁺ oxidation. They were stored dry. Dry crystals are not particularly sensitive to oxidation and can therefore be stored over long periods of time.

For the present experiment, a water suspension was prepared by adding about 0.75 g of CuCl crystals to a 1 mm standard quartz cuvette filled with 1 M HClO₄ in water. The amount of CuCl added was enough to completely fill the cuvette and yielded a suitable surface for the reflectance measurements. The area exposed to the activating light was about 1 cm². In 1 M HClO₄, the reverse photochromic reaction is sufficiently slow to be negligible and hydrolysis of CuCl to Cu₂O does not occur. Moreover changes in the concentrations of Cu²⁺ and Cl⁻ of the aqueous solution do not affect the photolysis reaction [3].

Photolysis equipment

Samples were illuminated with a high pressure xenon lamp (XBO 450 W). To prevent heating during photolysis a water filter was used. A grating monochromator (Jarrel Ash, 0.25 m Ebert monochromator) provided monochromatic light. A slit width of 3 mm was employed corresponding to a resolution of about 2 nm (313 nm). For the visible region of the spectrum a cut-off filter (Jena, GG 400) was added. A potassium ferrioxalate actinometer [4] was used to determine the light flux into the cuvette at 300 nm. From the value thus obtained the light intensities at other wavelengths were calculated using the energy spectrum of the lamp, efficiency curves for the monochromator, and the transmission spectrum of the filter.

Reflectance measurements

Measurements of the diffuse reflectance were carried out on a Shimadzu MPS 50L spectrophotometer using a reflectance accessory. The light reaches the sample at an angle of 45°. The specularly reflected light (135°) is caught in a light trap (via a reflecting mirror). The diffusely reflected light is recorded on an end-on photomultiplier placed close to the sample.

On non-illuminated and illuminated samples the reflex attenuation spectrum, $A_R = \log(1/R)$, was recorded in the wavelength range 350 - 750 nm. A sample of CaSO₄ crystals suspended in water was used as a reference from 350 to 450 nm. In the wavelength region 450 - 700 nm the non-illuminated sample of CuCl was used as a reference. In the latter wavelength region, the reflectance of the CuCl reference was almost identical to that obtained from the CaSO₄ reference.

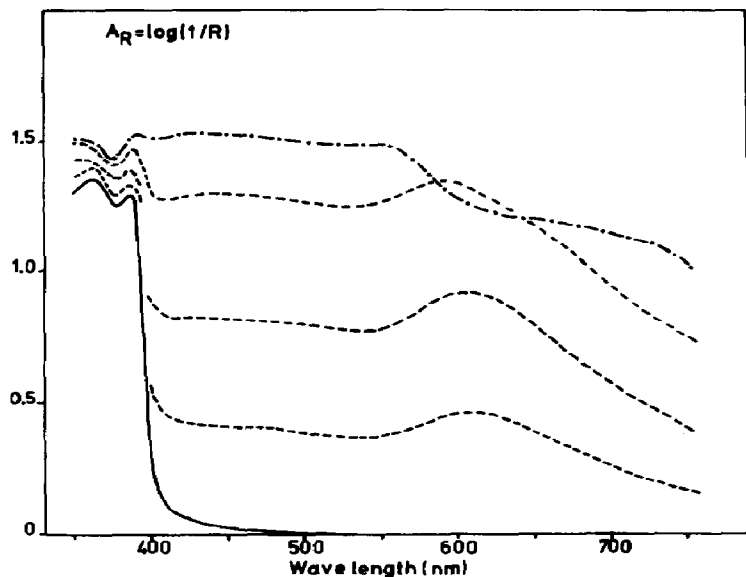


Fig. 1. Illustration of the photochromic phenomenon. I (—) Reflex attenuation spectrum of CuCl(s) (reference CaSO_4), II (- - -) reflex attenuation spectra of the photochromic green species (Cu^0); III (- · - ·) reflex attenuation spectrum obtained at very heavy exposures. Metallic lusted grains of Cu^0 are observed visually (cf. the minimum at about 600 nm).

Results

The spectrum of the photochromic species

The overall photochromic process is favourably illustrated through activation with the full spectrum of the Xe lamp, as this allows very heavy light doses to be delivered within a reasonable time period.

Figure 1 represents data obtained from such exposures (no monochromator, only water filter). For values of A_R up to about 1 (450 nm) the spectrum of the photochromic species (Cu^0) stayed essentially constant. Small deviations occurred at wavelengths longer than 650 nm. Activation with monochromatic u.v. light (in the range 250 - 400 nm) produced Cu^0 having the same reflex attenuation spectrum as obtained with the full spectrum of the lamp [Fig. 2(A)]. Also in this case there was essentially no change in the spectrum when the concentration of Cu^0 increased, the process being followed to attenuances of about 0.7 (450 nm). For visible light activation, the absorption peak of Cu^0 moved to longer wavelengths and there was also a continuous shift in the spectrum towards longer wavelengths during continued exposure. The magnitude of the shift appears to vary inversely with the spectral sensitivity.

The spectrum having the greatest difference from that obtained with u.v. activation is shown in Fig. 2(A) and was recorded after activation with 650 nm light.

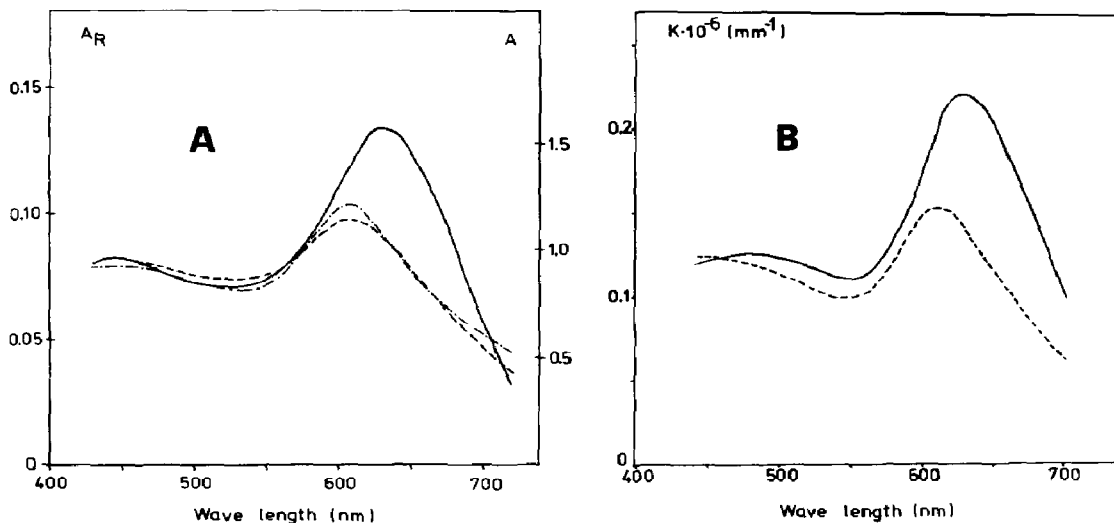


Fig. 2. (A) Reflex attenuation spectra (left scale) obtained by activation with 365 nm (---) and 650 nm (—) light. The two spectra are chosen in such a way that the A_R values are equal at 450 nm. Absorption spectrum (right scale) of single crystals using microspectrophotometry and activation with the full light from a high pressure Hg lamp (.....). (B) Calculated attenuation spectra for small ellipsoids of Cu^0 in CuCl according to an extended Mie theory [2]. The spectra refer to oblate ellipsoids with the rotational axes (b) perpendicular to the surface: I (---) spectrum characterized by the parameters $\bar{P}/4\pi = 0.268$ and $R = 1.3$ nm, and the half axes lengths $a = 1.5$ and $b = 0.9$ nm; II (—) spectrum characterized by $\bar{P}/4\pi = 0.222$ and $R = 1.5$ nm, $a = 1.8$ and $b = 0.9$ nm.

The time-course of the photolysis reaction

Figure 3(A) gives the reflex attenuation at 450 nm plotted *vs.* light dose when a sample was exposed to the entire spectrum of the lamp (no monochromator, no filter). It is noted that there is no intermittence effect, *i.e.* an exposure given in a number of discrete installments leads to the same attenuation as a continuous exposure. The extent of conversion is strictly dose dependent, at least at a ten-fold intensity variation.

The production of Cu^0 as described in Fig. 3(A) may be summarized numerically as:

$$\frac{dA_R}{dt} = \Phi \cdot I_0 \cdot f(A_R) \quad (1)$$

I_0 is the intensity of the incident light and Φ the quantum yield. For wavelengths in the u.v. range (250 - 400 nm) illumination with monochromatic light gave reflex attenuation *vs.* dose curves [Fig. 3(B)] of the same type as shown in Fig. 3(A). For visible light there was a distinct time-lag before a notable conversion took place, *i.e.* the curves displayed an induction period, τ [cf. Fig. 3(B)].

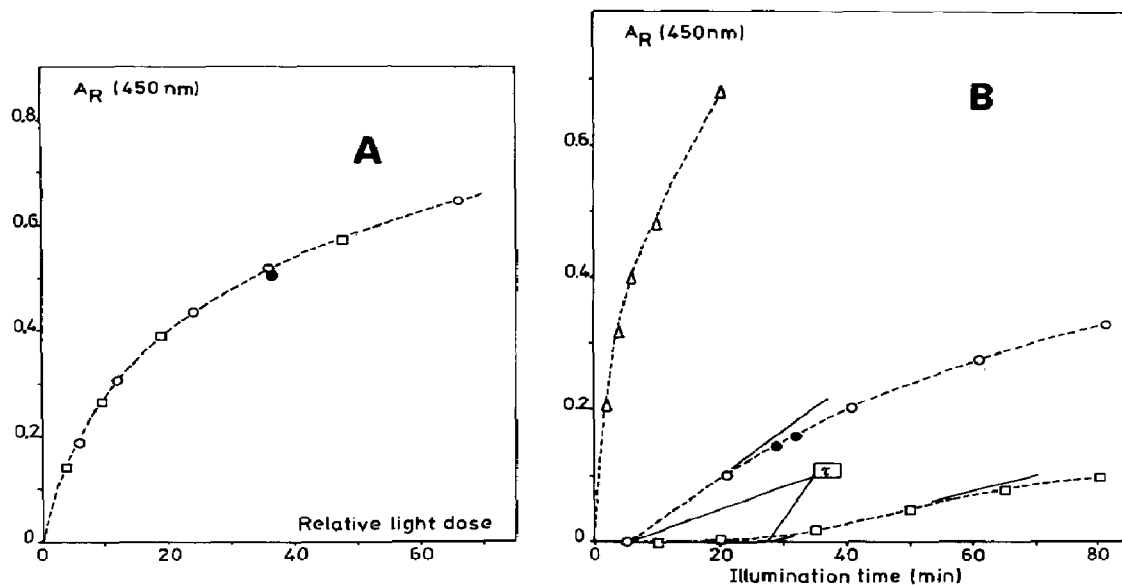


Fig. 3. (A) The photochemical production of Cu^0 represented by A_R vs. light dose (Xe lamp): \circ , points obtained for a consecutive series of exposures; \bullet , point obtained for a continuous exposure; \square , points obtained for a consecutive series of exposures carried out using a lamp intensity six times lower than in \circ and \bullet . (B) Reflex attenuance vs. illumination time curves for activation with light of wavelengths of: 390 nm (\triangle) ($I_0 = 0.114$ mW); 600 nm (\circ) ($I_0 = 0.161$ mW); 650 nm (\square) ($I_0 = 0.147$ mW). \bullet , First point obtained by activation with 365 nm light to $A_R = 0.145$ and inserted at the A_R value on the 600 nm activation curve, second point by a following activation with 600 nm light for 3 min.

Quantitative characterization of the reaction

The molecular interpretation of the diffuse reflectance measurements

The exact molecular meaning of the diffuse reflectance measured in this particular case is not clear. However, by applying a differential equation method valid for ideal diffusing media, *i.e.* the Kubelka Munk theory [5], a useful expression can be obtained.

For a thin superficial layer of Cu^0 and CuCl (1 and 2, respectively) the following equations are considered:

$$\frac{dI_x}{dx} = -(k'_1(x) + k'_2 + s')I_x + s' \cdot J_x \quad (2)$$

$$\frac{dJ_x}{dx} = (k'_1(x) + k'_2 + s')J_x - s' \cdot I_x \quad (3)$$

where I_x is the light intensity in the direction of the incident light beam and J_x the intensity in the opposite direction. The parameters k'_2 and s' denote, respectively, an absorption constant and a scattering constant for CuCl .

The function $k'_1(x)$ describes the light loss due to Cu^0 . With u.v. light activation in this particular case the photolytic beam penetrates the sample only slightly relative to the analyzing visible light (cf. Fig. 1). A reasonable assumption is therefore to assume that the photoproduct (Cu^0) is formed in a layer of thickness d and with a concentration c of Cu^0 located just below the surface of the CuCl crystals. Thus:

$$\begin{aligned} k'_1(x) &= \epsilon'_{\text{Cu}^0} \cdot c = k'_1 \quad (0 \leq x \leq d) \text{ and} \\ k'_1(x) &= 0 \quad (x > d) \end{aligned} \quad (4)$$

The general solution to eqns. (2) - (4) is:

$$R = \frac{J_0}{I_0} = R_g \cdot \left[\frac{\alpha_L - \kappa_L}{\alpha - \kappa} + \frac{(1 - \frac{\alpha_L - \kappa_L}{\alpha - \kappa}) e^{-2\kappa_L \cdot d}}{1 - \frac{(\alpha - \kappa) - (\alpha_L - \kappa_L)}{2\kappa_L} (1 - e^{-2\kappa_L \cdot d})} \right] \quad (5)$$

where $\alpha = k'_2 + s'$, $\alpha_L = k'_1 + \alpha$, $\kappa^2 = \alpha^2 - (s')^2$, $\kappa_L^2 = \alpha_L^2 - (s')^2$ and $R_g = (\alpha - \kappa)/s'$. For $d = 0$, R equals R_g . For an infinitely thick layer, eqn. (5) is reduced to the well known Kubelka Munk expression:

$$R = \frac{\alpha_L - \kappa_L}{s'} \text{ or } \frac{(1 - R)^2}{2R} = \frac{k'_1 + k'_2}{s'} \quad (6)$$

For $k'_1 \gg s'$ and $k'_2 = 0$ ($R_g = 1$), which approximates the conditions for analyzing visible light, eqn. (5) immediately gives:

$$R = e^{-2k'_1 \cdot d} = 10^{-2k_1 \cdot d} \quad (7)$$

or

$$A_R = \log(1/R) = 2k_1 \cdot d \quad (8)$$

i.e. the equation for an absorbing non-scattering layer of thickness d on top of an ideal mirror.

For a scattering layer the extent of approximation made by applying eqn. (8) can be judged from plots of A_R calculated according to eqn. (5) vs. $2k_1 \cdot d$. However, both parameters k_1 and d may vary with the amount of Cu^0 produced during the reaction. Consequently, to simulate the pattern of events during the reaction a model must be assumed.

A reasonable model is to assume that the thickness of the layer is proportional to the total amount of Cu^0 ($[\text{Cu}^0]$) and that the local particle concentration of Cu^0 within the layer stays constant. Assumptions of this kind are necessary to explain the fast saturation effects in the u.v. region where CuCl is responsible for more or less the entire light absorption. In the photographic process the fertilized grains penetrate deeper and deeper into the emulsion as the exposure continues [6] and the corresponding saturation effect in the u.v. region is observed [7].

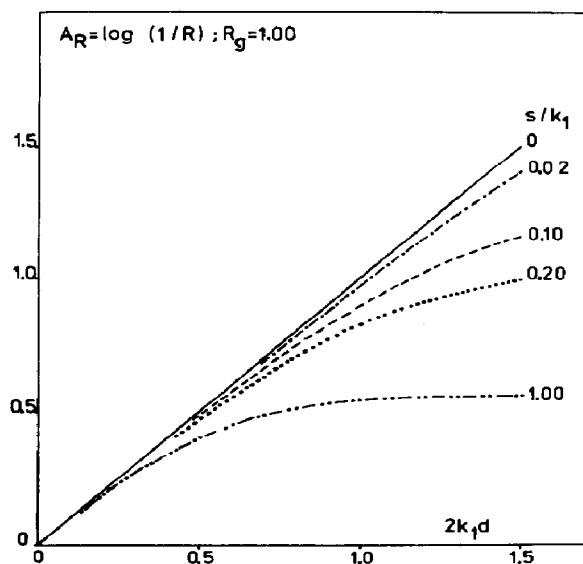


Fig. 4. Interpretation of the reflex attenuation: A_R vs. $2k_1d$ according to eqn. (5) for different values of the parameters s/k_1 ($R_g = 1.00$).

Thus

$$A_R = K_R [\text{Cu}^0] = 2k_1 \cdot d \quad (9)$$

where $d = \text{constant} \cdot [\text{Cu}^0]$ and k_1 is a constant.

The deviation from eqn. (9) can therefore be expressed in terms of s/k_1 ($s = s'/\ln 10$) by using the general equation (5). This is illustrated in Fig. 4 for $R_g = 1.00$ representing the condition when visible analyzing light is used. As is seen from Fig. 4 the reflex attenuation approaches a constant value at sufficiently high values of $2k_1 \cdot d$ in accordance with eqn. (6). For activation with the entire spectrum of a Xe lamp spectrum III in Fig. 1 should thus give the maximal size of s/k_1 when eqn. (6) is applied. For 450 nm, $A_R = 1.53$ ($R \approx 0.03$, $R_g \approx 1$) which means that $s/k_1 \approx 0.06$. It follows that for this activation eqn. (9) is a good approximation for values of A_R lower than about 1 (max deviation $\sim 5\%$ at $A_R = 1$).

The above analyses have proved that it is reasonable to interpret A_R (450 nm) according to eqn. (9) for u.v. light activation. For visible light activation eqn. (9) is applicable at least for small values of A_R (cf. Fig. 4).

Equations (8) and (9) suggest that results from absorption measurements should parallel those obtained from reflex attenuation measurements. The reflex attenuation spectrum obtained by activation with u.v. light or the entire spectrum of a Xe lamp agrees favourably with the absorption spectrum obtained from microspectrophotometry on single crystal specimens [2], [cf. Fig. 2(A)]. In ref. [2] it was shown that the spectrum of the coloured species (Cu^0) stayed constant upon continued exposure with a high pressure Hg lamp. For u.v. activation (or activation with the full spectrum of the Xe lamp) and for values of A_R up to about 1 (450 nm) this is also essentially true in the present case (see above).

The size and shape of the Cu⁰ aggregates as judged from the spectral changes

In previous work with single crystals of CuCl and applying an extended Mie theory it was concluded that the absorption spectrum shown in Fig. 3(A) can be reproduced by assuming Cu⁰ aggregates about 1.3 nm in diameter and oblate in shape with an axis ratio of about 0.6 and oriented perpendicularly to the surface [2]. The fact that the spectrum did not change upon continued exposure with the full spectrum of a high pressure mercury lamp (except for very heavy exposures) was interpreted as an increase in number of particles without affecting their size and shape. In view of the present results it is now concluded that the particle size and shape stays constant upon exposure to u.v. light. Exposure to the full light of the Xe lamp gives the same results because the u.v. effects predominate and mask any effects from the visible light in the spectrum of the lamp.

To obtain a physical interpretation of the observed spectral changes when the sample is exposed to visible light, the same extended Mie theory has been applied to the present data. Closest agreement with the experimental spectra in Fig. 2(A) was obtained for the calculated spectra in Fig. 2(B) characterized by the parameters given in the figure text. The following conclusions can be drawn: (i) the shift towards longer wavelengths followed by a narrowing of the conduction electron band corresponds to an increase in the size of the metallic copper particles; (ii) the growth of the particles tends to take place in a direction parallel to the surface, *i.e.* the particles become more plate-like; (iii) the Mie theory implies that attenuances around 450 nm are almost insensitive to variations in particle size and shape as they are primarily determined by an interband transition. The attenuance at 450 nm is thus a useful measure of the metallic copper concentration.

Numerical evaluation of the time-dependence of the photolysis curves

To characterize the photolysis curves numerically it is appropriate to employ the equations valid for a photochemical reaction where the photo-products are formed in a layer in front of the photoactive system and act as an external light filter. The attenuance A of the filter ($A = \log I_0/I_d$) may roughly be expressed as (see eqn. 2):

$$A = (k_1 + k_2 + s) \cdot d = \epsilon \cdot d \quad (10)$$

The parameter ϵ is the total loss in intensity per unit length and represents the sum of the contributions from the absorption of the metallic copper and the absorption and scattering of the host substance CuCl.

The Cu⁰ reaction rate can accordingly be expressed as:

$$\frac{d[\text{Cu}^0]}{dt} = \Phi \cdot I_d = \Phi \cdot I_0 \cdot 10^{-\epsilon \cdot d} \quad (11)$$

I_d is the intensity of the transmitted light and Φ the quantum yield.

The proportionality between $d[\text{Cu}^0]/dt$ and I_d is easily understood if the photoelectron production in the layer is negligible. However, the propor-

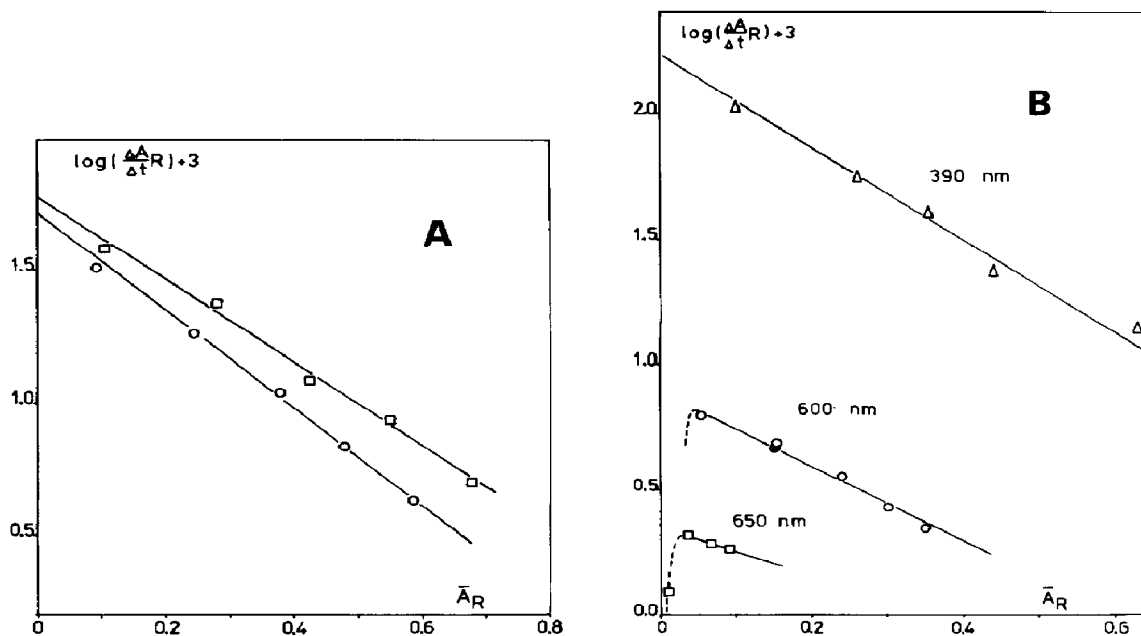


Fig. 5. (A) Equation (12) applied to the experiments illustrated in Fig. 3(A). Activating light: full spectrum of Xe lamp. Plots are made for two wavelengths 450 (○) and 600 nm (□) of the analyzing light. (B) Equation (12) applied to the measurements reported in Fig. 3(B). The sample was activated with monochromatic light at the wavelengths indicated; the wavelength of the analyzing light was 450 nm.

tionality also holds without the above approximation if one assumes that the mean free path of the photoelectrons is very short compared to the thickness of the layer.

Combining eqns. (8), (9) and (11) yields:

$$\log \left(\frac{dA_R}{dt} \right) = \log (\Phi I_0 K_R) - A_R \frac{\epsilon}{2R_1} = \log V - SA_R \quad (12)$$

It should be noted that eqn. (12) is analogous to Hurter's equation for describing the photographic process in a deep emulsion (AgCl, AgBr) in the case of a photon number equal to one [7].

Figure 5(A) shows a plot of the data from Fig. 3(A) using eqn. (12) (for 450 nm) and the corresponding data for another wavelength, 600 nm. The derivative dA_R/dt has been approximated by $\Delta A_R/\Delta t$ and \bar{A}_R is the mean of the two measurements. The good fit indicates that eqn. (12) can be used to represent the photochemical reaction. Thus only two parameters V and S are required to characterize the reaction. An additional test of the validity of eqn. (12) comes from a comparison of the regression lines for the two wavelengths in Fig. 5(A). For 450 nm (1): $V_1 = 0.0519 \text{ s}^{-1}$, $S_1 = 1.84$; for 600 nm (2): $V_2 = 0.0598 \text{ s}^{-1}$, $S_2 = 1.57$. This means: $K_{R2}/K_{R1} = V_2/V_1 = 1.15$; $K_{R2}/K_{R1} = S_1/S_2 = 1.17$, which also should be compared with the average value obtained directly from the reflex attenuance spectra $K_{R2}/K_{R1} = 1.15$.

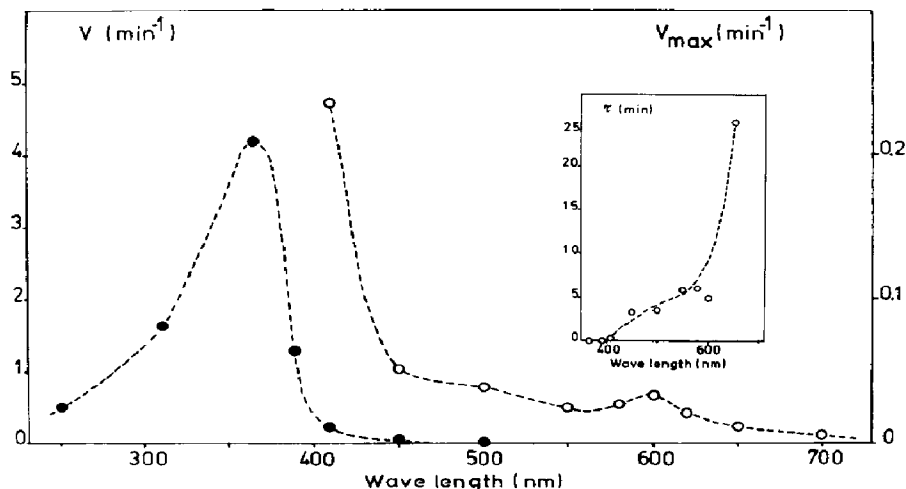


Fig. 6. Action spectrum or the wavelength dependence of the parameters V (initial rate, ●, left scale) and V_{\max} (maximal rate, ○, right scale) for $I_0 = 0.84$ mW. Insert: the induction period, τ , vs. wavelength.

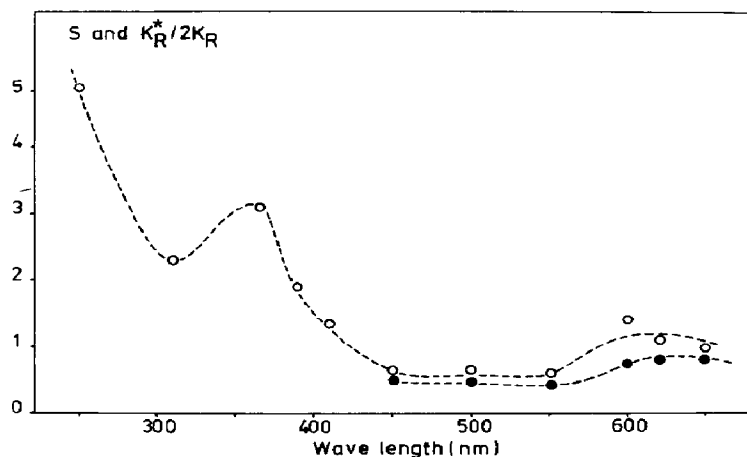


Fig. 7. The wavelength dependence of the parameter S (cf. eqn. 12) (○) and that of $K_R^*/2K_R$ (●).

After the induction period, when present, all curves for monochromatic light activation show the same general appearance as that in Fig. 3(A) and can be represented by eqn. (12) [cf. Fig. 5(B)]. Figures 6 and 7 show the results of analyzing curves into τ , V and S , [cf. eqn. (12)]. They all represent results from measurements of A_R at 450 nm during activation at various wavelengths and are partly based on the data presented in Figs. 3(B) and 5(B)].

The parameter τ has been taken as the intercept between the time-axis ($A_R = 0$) and the tangent at the point in the A_R vs. time curve that possess the maximum slope. The determination of τ has not been the object of a

systematic study in this investigation mainly because of the difficulty in obtaining fully reproducible results and the data inserted in Fig. 6 must be considered as preliminary. For a good determination of τ , extra precautions must be employed in the preparation of the sample to prevent formation of Cu^0 before the actual exposure and for instance avoiding all contact with light. The importance of this is illustrated in Figs. 3(B) and 5(B) where a sample was primarily activated by 365 nm light to $A_R = 0.145$ and later illuminated with 600 nm light. The second change of attenuance falls exactly on the curve for 600 nm activation suggesting that the attenuance (copper concentration) is a parameter determining the reaction rate (but not the history *i.e.* how this attenuance was brought about). The point at 700 nm in Fig. 6 represents a value obtained by using a procedure with preexposure at a different wavelength.

For the curves representing activation with u.v. light (250 - 400 nm) and where no induction period appears, the initial rate V was obtained directly. For the other curves, the parameter V was set equal to the maximal reaction rate (V_{max}) as estimated graphically from plots of the type given in Fig. 3(B). The V values so obtained were all normalized to an incident light flux I_0 of 0.84 mW under the assumption that the proportionally described by eqn. (1) holds, and are given in Fig. 6. As $V = \Phi \cdot I_0 K_R$ and I_0 and K_R are constant, Fig. 6 is proportional to the quantum yield Φ and represents thus an action spectrum. It shows an appearance in the u.v. region, which closely agrees with the excitonic absorption band of CuCl [8]. In the visible region, it seems to be primarily determined by the absorption of Cu^0 , *i.e.* the photochemically produced copper. The cut-off at longer wavelengths is probably due to insufficient energy of the activating photons. The fact that an induction period exists which can be overcome by exposure to u.v. light also suggests that the action of visible light is a sensitized process with Cu^0 acting as a sensitizer.

The values of the parameter $S = \epsilon/2k_1$ are directly obtained from the slope of straight lines drawn as in Fig. 5(B). The spectrum of S (Fig. 7), can be divided into two wavelength regions according to the absorption of the species involved.

For wavelengths less than 400 nm, absorption is almost entirely determined by CuCl . Thus the terms of importance in ϵ are k_2 and s , *i.e.* the absorption and scattering constants of CuCl . From 250 nm to 400 nm the curve can therefore be interpreted as a superposition of Rayleigh scattering and absorption from CuCl .

For wavelengths longer than 400 - 450 nm k_1 , *i.e.* the absorption of metallic copper is the dominating term in ϵ (at 450 nm $s/k_1 \approx 0.06$, see above). In the visible light region the photoproduct also acts as a sensitizer. However, as eqn. (12) holds, except for very low reflex attenuances, it is concluded that the filter effect dominates, and that the mean free path for the photoelectrons is short compared to the depth of the Cu^0 layer (see above). In fact S should be equal to $K_R^*/2K_R$ where K_R^* is the reflex attenuation coefficient for the wavelength of the photolytic light. As is seen from Fig. 7, the correlation between S and $K_R^*/2K_R$ is fairly high.

The mechanism of the photochemical disproportionation

The results from the present investigation have shown that the photochromic disproportionation of CuCl is very similar to the reactions involved in the photographic system (AgBr, AgCl). Chemically, CuCl and AgCl behave very much in the same way and it is thus reasonable to apply results obtained from the well studied AgCl system to the present system.

The CuCl(s)–H₂O(l) interface

A starting point for proposing a detailed mechanism of the photochromic reactions of CuCl is to consider the interface between CuCl and the aqueous solution. It is well known that Cl[−] ions can be adsorbed on the surface of AgCl giving rise to a negative surface charge [9]. This adsorption is associated with the formation of complexes of the type (AgCl–XCl)^{x−}. As CuCl forms complexes of the same type, one expects the surface of CuCl to be negatively charged. The surface charge is partly compensated through the build up of an electric double layer with an outer shell of positively charged mobile ions in the solution. The electrical conductivity of CuCl in the dark is almost entirely determined by the mobility of interstitial Cu⁺ ions [10]. It is therefore reasonable to assume that an electric double layer is also formed inside the crystal just below the crystal surface owing to the presence of mobile interstitial Cu⁺ ions in the same way as proposed for semiconductors [11]. (Impurities of Cu²⁺ turn CuCl into a *p*-type semiconductor and should therefore amplify the effect proposed above).

Photochemical reactions caused by light with wavelengths of less than 400 nm

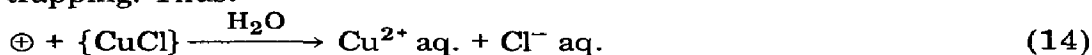
The primary step

The results have shown that the sensitivity maximum corresponds to the excitonic absorption band of CuCl. This implies to that the primary step in the photochemical reaction is the formation of excitons or electron-hole pairs. Thus:



The hole trapping step

The Cu²⁺ formed in the reaction is observed as an increase in the Cu²⁺ concentration of the solution [1, 3]. According to the proposed model for the CuCl–H₂O interface, holes are attracted to the negatively charged surface. This implies that oxidation of Cu⁺ occurs at the surface as a result of hole trapping. Thus:



Another possibility is hole trapping within the crystal (as is assumed to be the case in the photographic system). In this case Cu²⁺ is formed within the crystal and migrates to the surface by way of diffusion or through reactions

with photoexcitons [3]. At the surface, Cu^{2+} is dissolved out. The net reaction will be the same as reaction (14).

The electron trapping step

Cu^0 is assumed to be formed in the CuCl matrix in the form of small particles. According to the interface model, electrons are repelled by the surface, although they are attracted by the area having an excess of interstitial Cu^+ in the layer just below the surface. Thus:



Direct recombination of Cu^0 and holes can be assumed to be prevented by the following reaction:



The particle growth

Reactions (15) and (16) correspond to the first step in the Mitchell theory for the formation of a latent image Ag nucleus [9]. The other corresponding steps can be written as:



This mechanism states that one photoelectron should be capable of creating one copper atom, *i.e.* the upper theoretical limit for the quantum yield = 1. However, in the case of CuCl it is reasonable to believe that disproportionation steps are present leading to higher quantum yields. A chain reaction of disproportionation steps can be written as:



Factors limiting the particle growth

For the photochemical reaction caused by light of wavelengths within the excitonic band of CuCl, the spectrum of the photoproduct remains essentially constant during the reaction. This indicates that a continued reaction involves an increase in the number of particles without affecting their size [2]. The question then arises as to which factors determine the particle size. The mechanisms we have proposed for the particle growth suggest the following factors: (1) the cross-sectional area for electron capture by the particle; (2) the supply of Cu^+ ; (3) the disproportionation equilibrium of Cu^+ into Cu^0 and Cu^{2+} . Factor (1) suggests a termination of the particle size due to an increased negative charge around the particle. However, this implies an initial increase in the cross-sectional area during the build-up process (reaction 17), and such a variation in the cross-section with the particle size does not seem likely. The supply of Cu^+ acting as the limiting

factor is difficult to understand in view of the results obtained with visible light activation. It may therefore be hypothesized that factor 3 is the most crucial. The formation of atomic Cu^0 forms a system that is far from equilibrium, but which can be restored partly by nucleation of Cu^0 , thereby reducing the activity of the metallic species. The nucleation process as it occurs through the reactions described by reactions (17) and (18) will continue until a local equilibrium is reached, *i.e.* when the particles become sufficiently large a disproportionation equilibrium is established through the type of reaction sequences shown in reaction (18).

Photochemical reactions caused by visible light activation

For the photochemical reaction caused by visible light activation the reaction was found to be sensitized by Cu^0 and is also reported to be sensitized by adsorbed dye molecules [12]. The mechanism may formally be written as:



Considering the energy of the photons involved it is not likely that reaction (20) can proceed in only one step. It was previously concluded that particle size increases during the reaction caused by visible light. It was also concluded that particle growth was less for wavelengths of higher spectral sensitivity. This suggests a two step sensitizing reaction where the metallic copper acts both as donor and acceptor for electrons in CuCl . The donor action is confirmed by the creation of new copper particles and the acceptor action by the observed increase in particle size.

Acknowledgement

This work has been supported by the Swedish Natural Research Council.

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