

## FORMATION OF AQUATED ELECTRONS AND THE INDIVIDUAL QUANTUM YIELDS FOR PHOTOACTIVE SPECIES IN THE Cu(I)-KCN-H<sub>2</sub>O SYSTEM

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(Received July 15, 1983; in revised form September 22, 1983)

### Summary

The photoredox behaviour of the Cu(I)-CN system in aqueous solutions was studied. The cyanide content decreased on irradiation at 253.7 nm and the quantum yield  $\Phi_{\text{CN}}$  for cyanide conversion was determined at various pH values. The individual quantum yields for  $[\text{Cu}(\text{CN})_2]^-$  and  $[\text{Cu}(\text{CN})_3]^{2-}$  were calculated. The results give an indication of the photoactivity of the tri-coordinated complex. The aquated electron was identified as a product of the primary photochemical reaction by scavengers and flash photolysis. The quantum yield  $\Phi_e$  of this reaction is 0.06.

### 1. Introduction

Copper complexes can play an important role as labile intermediates in redox processes and therefore it is believed that their photoredox reactions are also worthy of attention. The photo-oxidation of copper(I) halogeno complexes has been studied in detail for the conversion of solar energy into chemical energy [1 - 3] and to elucidate the connection between the photoredox behaviour and the mutual influence of ligands [4, 5]. Evidence has been provided for the formation of solvated electrons in the primary process of cuprous halides by Ferraudi [6]. It is well known that aquated electrons are produced on UV irradiation of various complex cyanides ( $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Ru}(\text{CN})_6]^{4-}$ ,  $[\text{Mo}(\text{CN})_8]^{4-}$ ,  $[\text{W}(\text{CN})_8]^{4-}$ ) [7 - 11], and therefore it is surprising that the photoredox reactions of copper(I) cyano complexes have not been investigated. In this paper the redox photochemistry of these compounds is presented briefly.

### 2. Experimental details

$\text{K}_2[\text{Cu}(\text{CN})_3]$  was prepared by the method of Barber [12] and was identified by elemental analysis and IR spectroscopy.

The concentrations of copper(I) and cyanide ions of the deaerated solutions were changed from  $2 \times 10^{-5}$  to  $10^{-3}$  M and from  $10^{-3}$  to  $10^{-1}$  M respectively. The pH was adjusted to 7.1 or 9.2 by K-71 and K-92 Reanal reagents respectively.

The  $\text{NO}_3^-$  ion was used to scavenge the aquated electron formed in the primary photochemical reaction and its concentration was  $10^{-2}$  M during continuous irradiation and  $10^{-5}$  -  $10^{-4}$  M in the flash photolysis experiments.

A quartz cell with a path length of 5 or 10 mm was utilized for photolysis. The continuous irradiations were carried out with a low pressure mercury lamp. The lines with a wavelength shorter than 253.7 nm were filtered out by a  $10^{-2}$  M  $\text{KNO}_3$  solution of 10 mm optical path. The light input intensity was determined by ferrioxalate [13].

The UV spectra of the solutions were recorded on a double-beam UV-visible Zeiss spectrophotometer before and after irradiation. The concentration of the cyanide ions was measured with an ion-selective electrode (Radelkis OP-CN-0711). The concentration of the  $\text{NO}_2^-$  ions formed after the electron scavenging reaction was determined by spectrophotometry [14].

To complete the experiments some samples were evaporated carefully and IR spectra of the solid residues were recorded on a UR-10 Zeiss spectrophotometer in KBr.

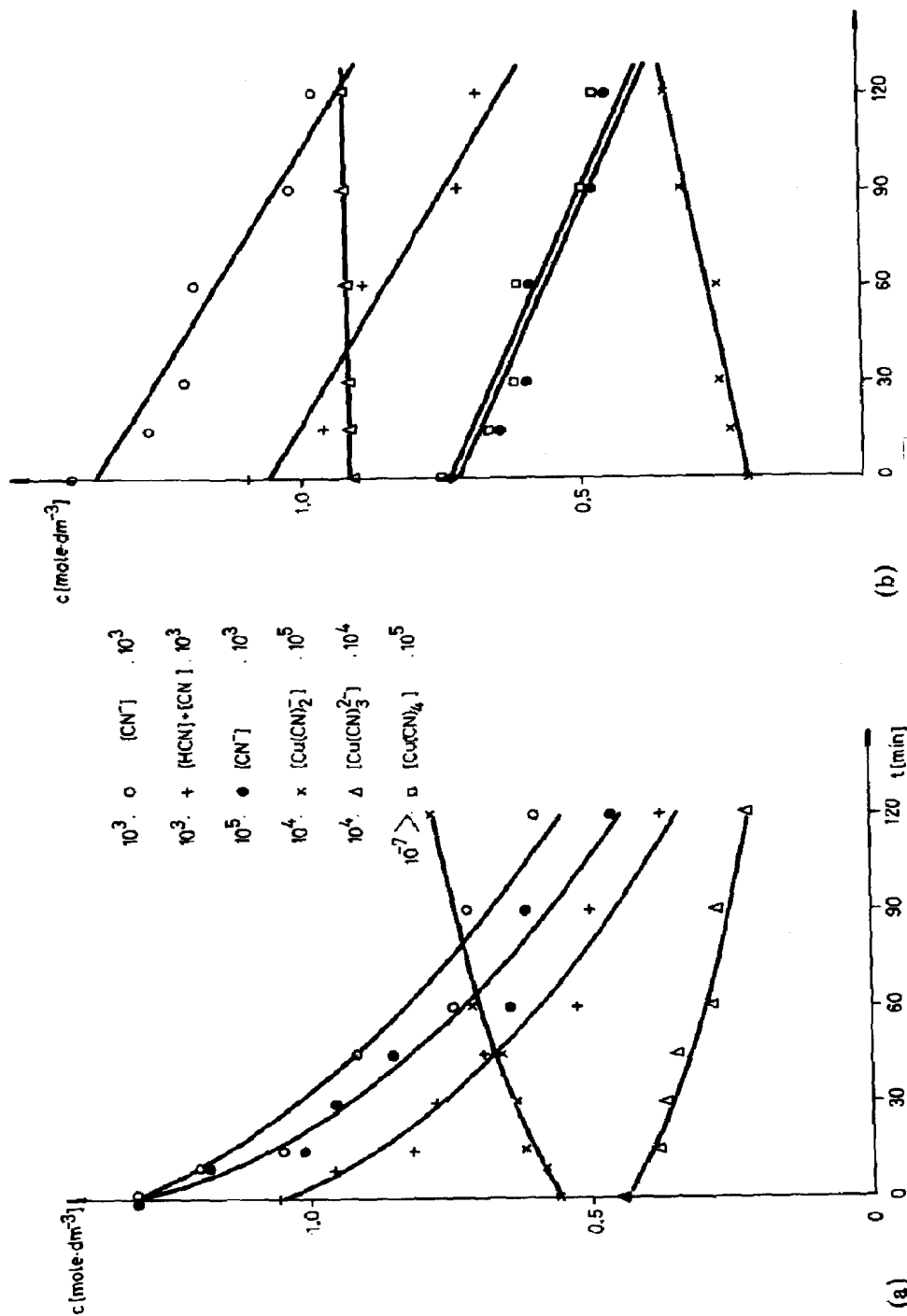
Conventional equipment [15] was used for flash photolysis. The mass spectroscopy investigations were carried out with a JEOL JMS-01SG-2 spectrometer.

### 3. Results and discussion

From the concentration of copper determined by analysis and the measured concentration of cyanide ions the mole fractions of  $[\text{Cu}(\text{CN})_2]^-$ ,  $[\text{Cu}(\text{CN})_3]^{2-}$  and  $[\text{Cu}(\text{CN})_4]^{3-}$  were calculated using stability constants from the literature [16, 17], taking into account the effect of the ionic strength.

As is presented in Fig. 1(a) the cyanide content of the neutral solutions decreases at a decreasing rate on continuous irradiation, while the mole fraction of  $[\text{Cu}(\text{CN})_2]^-$ , in contrast with that of  $[\text{Cu}(\text{CN})_3]^{2-}$ , increases. These trends can also be observed by comparing the UV spectra of an illuminated solution with the spectra of  $[\text{Cu}(\text{CN})_2]^-$  and  $[\text{Cu}(\text{CN})_3]^{2-}$  reported by Baxandale and Westcott [18] (Figs. 2(a) and 3(a)). According to the calculation, the concentration of the tetracyano compound is very low (less than  $10^{-7}$  M) and therefore its effect can be neglected in these solutions.

Figure 3(b) shows the spectra of an alkaline solution before and after irradiation. There is little difference between them, and therefore comparing Fig. 3(b) with Fig. 2 we can only state that the tricyano copper(I) complex remains the dominant species on irradiation. The calculation from the measured cyanide concentration gives similar results; although the cyanide content decreases linearly with time, the mole fraction of  $[\text{Cu}(\text{CN})_3]^{2-}$  is



(a) (b)  
Fig. 1. Change in concentrations of the components during irradiation of the Cu(I)-CN systems.

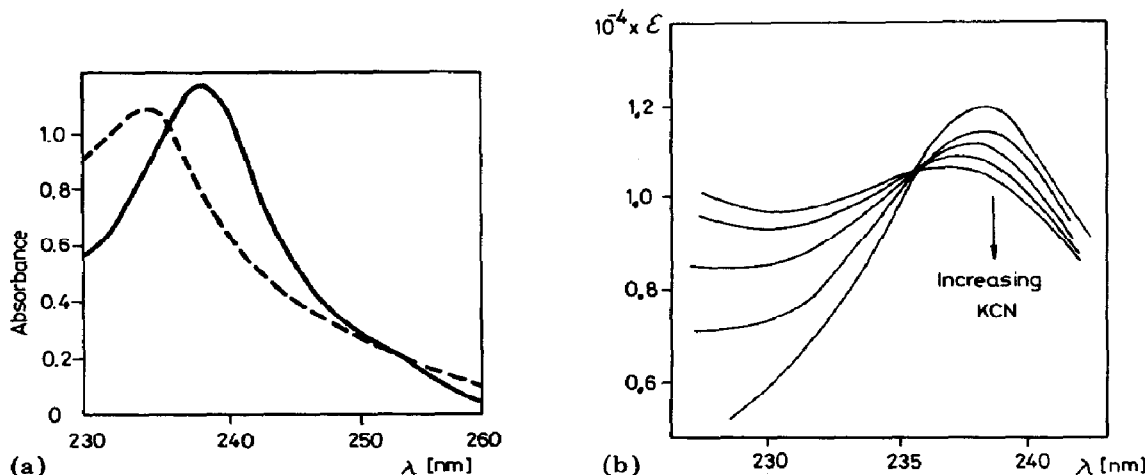


Fig. 2. (a) Electronic spectra of  $[\text{Cu}(\text{CN})_2]^-$  (---) and  $[\text{Cu}(\text{CN})_3]^{2-}$  (—) ions and (b) absorbance spectra of  $\text{Cu}(\text{I})\text{-CN}$  in  $0.01 \text{ M KOH}$  ( $10^{-6} \text{ M K}_3[\text{Cu}(\text{CN})_4]$ ) at  $\text{KCN}$  concentrations of  $10^{-3}$ ,  $2 \times 10^{-3}$ ,  $5 \times 10^{-3}$ ,  $15 \times 10^{-3}$  and  $20 \times 10^{-3} \text{ M}$  (from ref. 18).

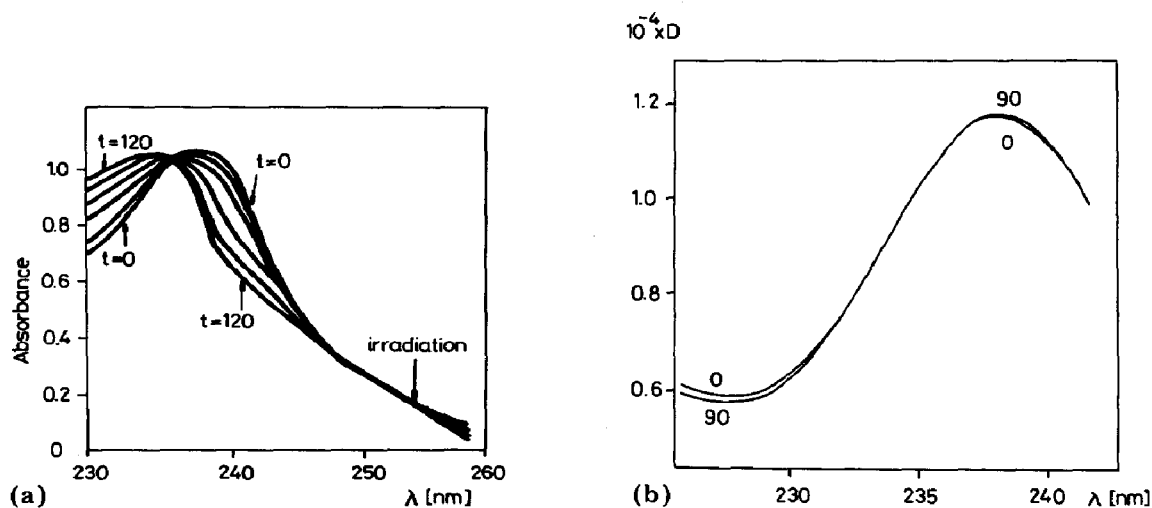


Fig. 3. Electronic spectra of solutions containing  $10^{-4} \text{ M K}_2[\text{Cu}(\text{CN})_3]$  and  $10^{-3} \text{ M KCN}$  during illumination at (a)  $\text{pH } 7.1$  and (b)  $\text{pH } 9.2$  (numerals on curves refer to irradiation times).

essentially constant, while the concentrations of  $[\text{Cu}(\text{CN})_2]^-$  and  $[\text{Cu}(\text{CN})_4]^{3-}$  increase and decrease respectively during illumination (Fig. 1(b)).

### 3.1. The experimental quantum yield for cyanide conversion

The quantum yield  $\Phi_{\text{CN}}$  for cyanide conversion was determined from

$$-\frac{dC_{\text{CN}}}{dt} = I_a \Phi_{\text{CN}} \quad (1)$$

TABLE 1

Dependence of the experimental quantum yield  $\Phi_{\text{CN}}$  on the mole fractions  $\alpha_2$ ,  $\alpha_3$  and  $\alpha_4$  of the dicyano, tricyano and tetracyano copper(I) complexes and the pH

$\alpha_2$	$\alpha_3$	$\alpha_4$	$\Phi_{\text{CN}}$
pH 7.1			
0.55	0.45	—	0.11
0.58	0.42	—	0.12
0.60	0.40	—	0.12
0.60	0.40	—	0.10
0.63	0.37	—	0.08
0.64	0.36	—	0.10
0.66	0.34	—	0.09
0.68	0.32	—	0.09
0.69	0.31	—	0.08
0.72	0.28	—	0.07
0.74	0.26	—	0.06
pH 9.2			
0.02	0.91	0.07	0.055
0.03	0.92	0.05	0.055
0.035	0.92	0.045	0.055

where  $I_a$  (mol photons  $\text{dm}^{-3} \text{s}^{-1}$ ) is the amount of light absorbed by the complex cyanides of copper and  $C_{\text{CN}}$  (mol  $\text{dm}^{-3}$ ) is the cyanide concentration of the solution determined by analysis.

It is found that  $\Phi_{\text{CN}}$  depends on both the relative amounts of the dicyano and tricyano copper(I) complexes and the pH as Table 1 shows.

### 3.2. Calculation of the individual quantum yields

The relationship between the experimental quantum yield  $\Phi_{\text{CN}}$  and the individual quantum yields of the photoactive species in the equilibrium system is [19, 20]

$$\Phi_{\text{CN}} = \frac{\Phi_i \alpha_i \epsilon_i}{\alpha_i \epsilon_i} \quad (2)$$

where  $\Phi_i$  are the individual quantum yields of the absorbing species,  $\alpha_i$  are their mole fractions and  $\epsilon_i$  are the molar absorbances. When eqn. (2) is applied to neutral solutions (where the concentration of tetracyano copper(I) is almost zero) the expression is

$$\Phi_{\text{CN}} = \frac{\Phi_2 K_2 \epsilon_2 [\text{CN}^-]^2 + \Phi_3 K_2 K_3 \epsilon_3 [\text{CN}^-]^3}{K_2 \epsilon_2 [\text{CN}^-]^2 + K_2 K_3 \epsilon_3 [\text{CN}^-]^3} \quad (3)$$

where  $K_2$  and  $K_3$  are the stability constants of the dicyano and tricyano complexes respectively.

Since the absorbance of the reaction mixtures at 253.7 nm does not show a considerable change during irradiation (Figs. 2(a) and 3(a)), i.e.  $\epsilon_2 \approx \epsilon_3$ , eqn. (3) can be simplified to

$$\Phi_{\text{CN}} = \frac{\Phi_2 + \Phi_3 K_3 [\text{CN}^-]}{1 + K_3 [\text{CN}^-]} \quad (4)$$

Rearranging, we obtain

$$\Phi_{\text{CN}}(1 + K_3 [\text{CN}^-]) = \Phi_2 + \Phi_3 K_3 [\text{CN}^-] \quad (5)$$

Figure 4 shows a linear representation of the measured data according to eqn. (5). The intercept ( $\Phi_2$ ) and the slope ( $\Phi_3$ ) of the straight line are zero and 0.26 respectively. This means that (i) no photoactivity is detected for the dicyano copper(I) complex at 254 nm and (ii) the tricyano copper(I) complex is photoactive in the neutral solution at 254 nm. These results are in accordance with those reported by Stevenson and Davis [1], whereas the  $[\text{CuX}_3]^{2-}$  complexes show photoactivity during photolysis of the copper(I) halogeno complexes. The  $\Phi_3$  value obtained in the alkaline solutions is only 0.06.

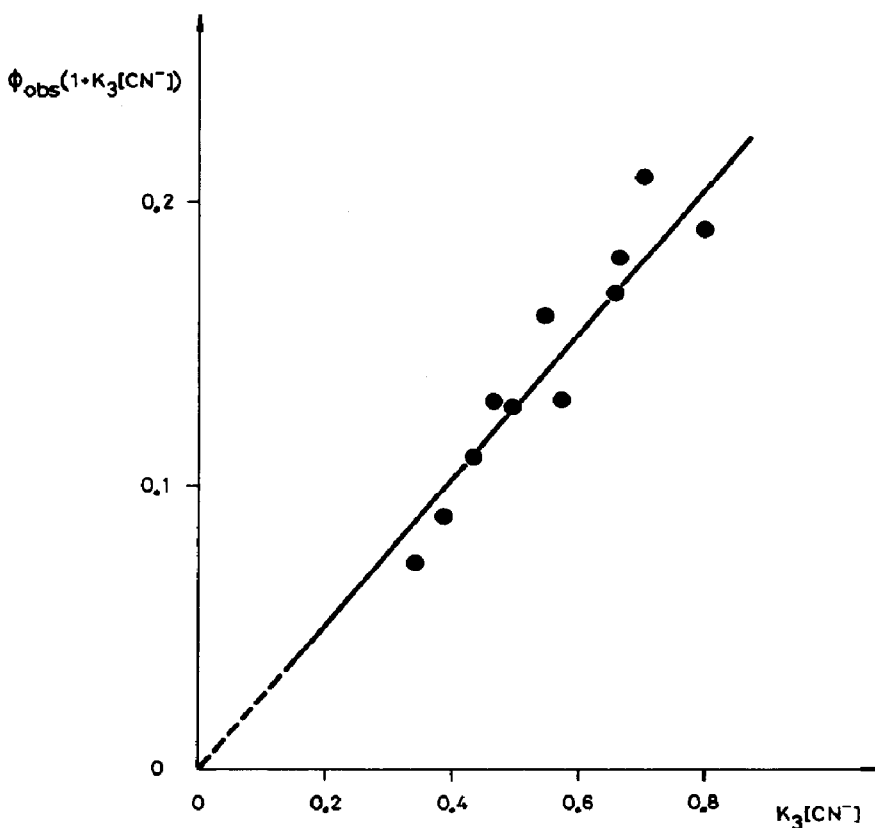
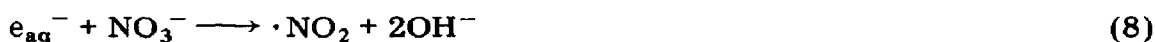


Fig. 4. Determination of  $\Phi_2$  ( $\approx 0$ ) and  $\Phi_3$  ( $\approx 0.26 \pm 0.04$ ) from the observed quantum yields at pH 7.1.

### 3.3. Identification of the aquated electron and the quantum yield $\Phi_e$ of the primary photochemical reaction

As the production of solvated electrons from UV excited cyanometallates, e.g.  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Ru}(\text{CN})_6]^{4-}$ ,  $[\text{Mo}(\text{CN})_8]^{4-}$  and  $[\text{W}(\text{CN})_8]^{4-}$ , is well known [7 - 11] it was supposed that aquated electrons are produced in the primary photochemical reaction of the copper(I) complexes as well. Steady state irradiations were carried out in the presence of  $\text{NO}_3^-$  ions as electron scavengers to indicate the electron ejection.  $\text{NO}_2^-$  ions were detected during photolysis and their formation was attributed to the following processes [8, 21]:



All the reactions of the reactive  $\cdot\text{NO}_2$  radical that are possible in this system (disproportionation of  $\cdot\text{NO}_2$  and oxidation of copper(I) or  $\text{CN}^-$  ions) give  $\text{NO}_2^-$  ions but the oxidation of  $\text{CN}^-$  ions is favoured according to the redox potentials ( $E^\circ_{\text{CN}|\text{CN}^-} = 0.37 \text{ V}$ ;  $E^\circ_{\text{Cu}(\text{CN})_2|\text{Cu}(\text{CN})_2^-} = 1.103 \text{ V}$ ). A value of  $0.06 \pm 0.01$  was calculated for the quantum yield  $\Phi_e$  of the primary photochemical process from the concentration of  $\text{NO}_2^-$  formed during photolysis of the solutions containing  $\text{K}_2[\text{Cu}(\text{CN})_3]$  ( $10^{-3} \text{ M}$ ),  $\text{KCN}$  ( $10^{-2} \text{ M}$ ) and  $\text{KNO}_3$  ( $10^{-2} \text{ M}$ ).

The formation of aquated electrons was also supported by flash photolysis experiments. Oscillograms of deaerated solutions of copper(I) cyanides after flashing show rapidly decaying transients (about  $50 \mu\text{s}$ ) in the range of electron absorption. The wavelength dependence of the intensity of the absorption corresponds to the spectrum of the solvated electron (Fig. 5). We can exclude the possibility that the transient spectrum is due to the absorption of a copper(II) complex because the absorption maximum of copper(II) cyanides at about  $550 \text{ nm}$  [23, 24] was not observed. Figure 6

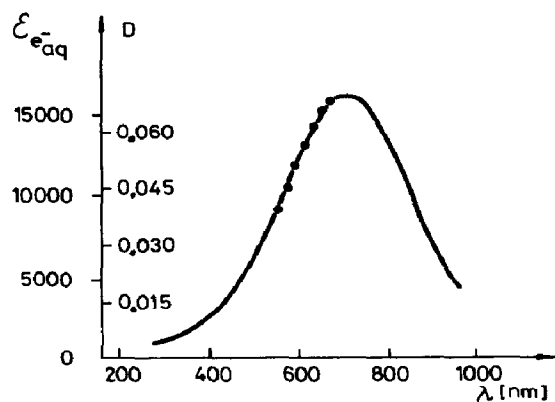


Fig. 5. Transient absorbance  $D$  observed in flash irradiation of  $5 \times 10^{-4} \text{ M}$   $\text{K}_2[\text{Cu}(\text{CN})_3]$  (●) and the spectrum of the aquated electron from refs. 21 and 22.

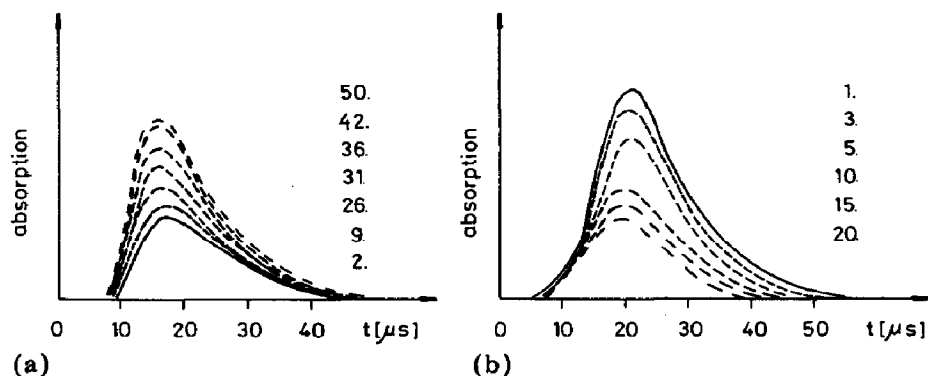
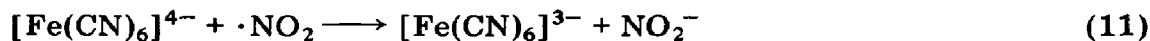
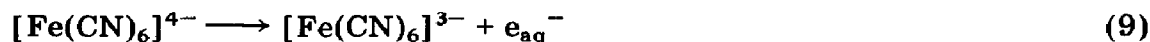


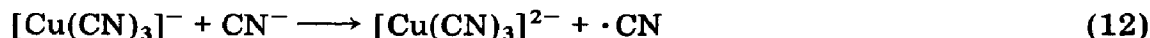
Fig. 6. The change in the aquated electron transient spectrum during repeated flashing of (a)  $[\text{Cu}(\text{CN})_3]^{2-}$  solutions and (b)  $[\text{Fe}(\text{CN})_6]^{4-}$  solutions in the presence of  $\text{KNO}_3$  as a scavenger. (The numerals on the curves indicate the number of flashes.)

represents the transients detected during repeated flashing of  $[\text{Cu}(\text{CN})_3]^{2-}$  and  $[\text{Fe}(\text{CN})_6]^{4-}$  solutions containing  $\text{NO}_3^-$  ions as electron scavengers. The intensity of decay decreases gradually for the iron compound, which can be explained by the following reaction sequence proved by Ohno [8] and Ottolenghi and Rabani [25]:

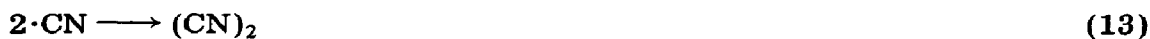


According to these reactions the concentration of ferrocyanide decreases and two good scavengers ( $\text{NO}_2^-$  and  $[\text{Fe}(\text{CN})_6]^{3-}$ ) are formed simultaneously instead of one ( $\text{NO}_3^-$ ). Both these scavengers decrease the concentration of aquated electrons in a solution after flashing.

The tendency is exactly the opposite for the copper complex. This result may be interpreted by the well-known thermal redox reaction which occurs in addition to reactions (6) - (8):



Consequently the photoactive copper(I) complex is reproduced. The concentration of the scavenger decreases gradually when the excitation is repeated so many times that even the different nitrogen oxides formed in the secondary processes decompose to nitrogen in their reaction with the aquated electron [26, 27]. The fact that  $\text{OCN}^-$  produced by



was identified by IR spectroscopy of the solid residue of irradiated solutions of  $[\text{Cu}(\text{CN})_3]^{2-}$  indirectly proves the formation of the  $\cdot\text{CN}$  radical.



In the absence of  $\text{NO}_3^-$  ions different reaction pathways may exist.

(i) The aquated electrons can be scavenged by protons, giving hydrogen radicals and then hydrogen. In this case the decrease in the concentration of the  $\text{CN}^-$  ions is the consequence of reactions (13) and (14) following processes (6) and (7).

(ii) The aquated electrons can initiate the base-catalysed polymerization of HCN, producing various HCN oligomers and their hydrolysis products [28]. The relatively large molecules detected by mass spectroscopy of the irradiated neutral solutions indicate the important role of the second reaction route. Experiments to identify the main products and to determine the reaction pathway are in progress.

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