KINETICS OF THE PHOTOAQUATION OF HEXACYANOFERRATE(II) ION
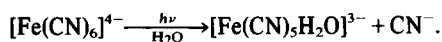
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Abstract—Kinetics of the photoaquation of hexacyanoferrate(II) ion in aqueous solution were studied potentiometrically and spectrophotometrically. Supposing the simplest mechanism (see Fig. 3. in text), the photoaquation in alkaline medium can be well described. The value of the constants at pH = 11.0 are: $\phi = 0.8$–1.0, $k_6 = (3.0 \pm 0.5) \times 10^{-8}$ s^{-1} and $k_{-6} = 1.5 \pm 0.2$ mol^{-1} dm^3 s^{-1}. To describe the photoaquation in neutral medium the scheme was extended ($k' = 3.33 \times 10^2$ mol^{-1} dm^{3}s^{-1}). The quantum yield in acidic medium can be calculated by combination of ϕ values of different protonated complexes. The reversibility of photoaquation in alkaline medium is also explained by the scheme.

The photosensitivity of different cyanocomplexes is well known. The kinetics and mechanism of these photochemical reactions have been intensively studied for a long time.[1] Nevertheless, the reversible photoaquation of hexacyanoferrate(II) ion is still an unsolved problem. The following primary photoprocess was established:

$$[Fe(CN)_6]^{4-} \xrightarrow[H_2O]{h\nu} [Fe(CN)_5H_2O]^{3-} + CN^-.$$

On illumination the concentration of aquapentacyanoferrate(II) ion reaches to a well-defined value, but after interrupting the illumination the concentration decreases.[2] Illuminating an alkaline or a neutral solution of the complex, the pH increases due to the hydrolysis of cyanide ion formed. In the next dark period the pH decreases. According to Asperger[3] the characteristic changes in the concentration of complex and in pH are totally reversible while MacDiarmid and Hall[4] found only partial reversibility.

Asperger followed the changes of pH and established some qualitative conclusions, namely:

—the initial rate of photoprocess and the maximum concentration of free cyanide ion increased with increasing initial concentration of complex,

—the initial rate of reversible dark (thermal) reaction decreased with increasing total concentration of complex.

Different quantum yields (ϕ) were determined with different methods (Table 1). Explanation of the dependence of ϕ on the pH has not yet been given.

The reasons for the contradictions are as follows:

(a) *The light was not monochromatic.* The authors should have taken into account the disturbing effect of photooxidation. On illumination with light of shorter wavelength than 330 nm, only the photooxidation occurs according to Stein.[5] The photoaquation takes place on illumination with longer wavelength light.

(b) *The atmosphere was not inert,* and the effect of thermal oxidation was not eliminated. Toma[7] found that trace amounts of iron(II) ion strongly catalysed the oxidation of aquapentacyanoferrate(II) ion even in the dark.

(c) *The reagents used* (sodium azide,[7] nitrosobenzene,[2] 2,2'-dipyridyl and 1,10-phenanthroline[8]) *considerably*

influenced the studied systems since they react with the components of them.

Under such experimental conditions the kinetic data calculated from the concentration versus time curves are contestable. One cannot separate the effects of different reactions such as thermal dissociation, thermal and photochemical oxidation, photoaquation, reversible thermal reaction between the products and the substitution reactions with reagents.

Sodium aquapentacyanoferrate(II) monohydrate (the so-called Hofmann salt) is the reference compound for spectrophotometric determination of the concentration of primary product. The preparation and purification of the complex are further problems since it is not very stable in the solid state.[7] In an inert atmosphere, sodium azide cannot be used as a reagent according to the results of Jaselkis[9] and Swinehart.[10] They indicated that the reaction between azide ion and aquapentacyanoferrate(II) ion does not occur in the absence of oxygen.

Nitrosobenzene is not a suitable reagent, either. In the standard procedure, mercuric chloride is used as a catalyst since the mercuric ion accelerates and reaction between the primary product and nitrosobenzene. The problem here is that the velocity of the catalysed reaction depends on pH and the negative effect of chloride ion must also be considered according to Hadjiioannou.[11] Moreover, some investigations[12] indicated that the uncatalysed reaction between the aquapentacyanoferrate(II) ion and the reagent strongly depends on pH and there is also a slow reaction between hexacyanoferrate(II) ion and nitrosobenzene.

By the use of monochromatic irradiation (365 nm), an inert atmosphere (argon) and potentiometric monitoring of pCN$^-$ and pH, the reaction could be followed in alkaline medium without perturbing the system. In nearly neutral solutions the processes were followed by a pH potentiometric method since the cyanide ion-selective electrode shows anomalous behaviour at lower pH[13]. In acidic medium the reaction was followed by measuring the absorbance of primary product.

EXPERIMENTAL

The light source was a HANOVIA 6515–36–A type medium-pressure mercury lamp (preheated for 15 min). The light was filtered with a solution filter system containing two solutions such as 0.31 mol dm^{-3} copper sulphate and 3.1×10^{-4} mol dm^{-3} tris-phenanthrolineiron(II) ion in acetate buffer at pH = 4.0. The two solutions were divided by a glass wall as in the presence of

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Table 1. Different quantum yields (ϕ)determined by different methods for the photoaquation reaction of hexacyanoferrate(II) ion in aqueous solution. (a) V. Carassiti and V. Balzani, *Ann. Chim. Rome* 1960, **50**, 782. (b) G. Emschwiller and J. Legros, *Compt. rend.* 1965, **261**, 1533. (c) G. Emschwiller, *Compt. rend.* 1954, **239**, 1491. (d) S. Ohno, *Bull. Chem. Soc. Japan*, 1967, **40**, 1765

No.	Wavelength (nm)	pH-range	method	ϕ	Ref.
1.	365	7–10	pH-potentiometric	0.1	a.
2.	365	7–10	spectrophotometric determination of the concentration of aqua-pentacyanoferrate(II) ion using nitrosobenzene	0.4	b,c.
3.	365	below 7	spectrophotometric determination of the concentration of aqua-pentacyanoferrate(II) ion using sodium azide	0.5–0.9 (pH dependent)	d.
4.	313	10	the same method as in entry 2.	0.4	b.

copper(II) ion the iron(II) complex decomposes on illumination. The transmission of the filter system has a maximum at 365 nm. The intensity of light was measured by the ferrioxalate method.[14] Its value was 5.0×10^{-11} mole of photons (365 nm)/cm^{2}s^1.

The solutions were kept under argon atmosphere in a dark glass cuvette ($5 \times 3.7 \times 9.8$ cm) that was thermostatted (298 ± 0.1 K). A magnetic stirrer was used. The volume of irradiated solutions was constant (120 cm^3). The distance between the lamp and the cuvette was 13 cm.

Before following the photoaquation in alkaline medium, the pH values of the nearly neutral aqueous solutions were set to 10.5–11.0 by adding a few drops of 1.0 mol dm^{-3} carbonate-free sodium hydroxide solution. The free cyanide concentration was monitored potentiometrically by using an OP–711–D–I Radelkis ion-selective electrode and radiometer Type K 401 saturated calomel electrode with an OP–205 Radelkis mV-meter (reproducibility was ± 0.5 mV). The pH was measured by a combined glass electrode (GK 2301 B Radiometer) and PHM 51 Radiometer mV-meter (reproducibility was ± 0.1 pH).

The solutions were prepared in acetate buffer (pH = 4.0) for following the photoaquation in acidic medium. A Hitachi–Perkin-Elmer 139 single beam spectrophotometer was used for actinometry and determination of the concentration of primary product ($\epsilon_{440nm} = 640$ mol^{-1}dm^3). The optical length of the flow cell was 0.51 cm.

RESULTS AND DISCUSSION

In aqueous solution of hexacyanoferrate(II) at pH values from 10 to 12, there is a slow aquation reaction even in the dark. On illumination the rate of aquation increases. If the illumination period is short, the increase of cyanide ion concentration continues in the dark until the equilibrium state is attained. If the illumination period is long enough, the concentration of cyanide reaches a higher value than that which corresponds to the dark equilibrium (Fig. 1). The system returns to the equilibrium state when the illumination is interrupted. This alternating increase and decrease of cyanide concentration can be repeated several times.

The pH changes similarly in nearly neutral solution (pH = 7–7.5) of hexacyanoferrate(II) ion on illumination (Fig. 2). If the dark period is long enough, after illumination the pH decreases to the initial value. If the system was in thermal equilibrium before illumination, the change of pH is completely reversible.

The behaviour of this system can be quantitatively

described by the following scheme (Fig. 3): where I_c is the average number of moles of photons (365 nm) absorbed by the complex per unit volume and unit time. In our experiments it amounts to 1.5×10^{-8},* as the excited complex ion, k_6, k_{-6} is the reaction rate constants (rrc) of thermal reactions, k_r is the rrc of the recombination reaction, k_f is the rrc of the products forming reaction, K_d is the dissociation constant of hydrogen cyanide at a certain ionic strength.[13]

Introducing the quantum yield as $\phi = k_f/(k_f + k_r)$ and applying the steady-state approximation for the concentration of the excited complex, the following rate equation is obtained:

$$-\frac{d[Fe(CN)_6]^{4-}}{dt} = \frac{d[Fe(CN)_5H_2O]^{3-}}{dt} = \phi I_c + k_6[Fe(CN)_6]^{4-} - k_{-6}[Fe(CN)_5H_2O]^{3-}[CN^-].$$

If the total concentration of cyanide (T_{CN}) is known at a certain time, the concentrations of hydrogen cyanide, cyanide ion, hydroxide ion and proton can be calculated as the components of an acid-base equilibrium system. T_{CN} is always equal to the concentration of aquapentacyanoferrate(II) ion.

On illumination, the system approaches the photostationary state when the following equation is valid:

$$\phi I_c + k_6[Fe(CN)_6]^{4-} = k_{-6}[Fe(CN)_5H_2O]^{3-}[CN^-].$$

In the dark, changes occur towards thermal equilibrium.

The exact values of the constants (ϕ, k_6, k_{-6}) were calculated by a least-squares method from the linear algebraic system of equations given for the parameters. The calculation of kinetic curves was based on the required combination of the fourth-order Runge–Kutta and the Newton-Raphson numberical methods.[15]

As shown in Fig. 4, there is excellent agreement between the experimental (full circles) and calculated (line) concentrations of cyanide ion, when ϕ, k_6 and k_{-6} are 0.8–1.0, 1.5 ± 0.2 mol^{-1}dm^{3}s^{-1} and $(3.0 \pm 0.5) \times 10^{-8}$ s^{-1}, respectively.

To characterize the conversion of the aquation process it is convenient to introduce the kinetic mean coor-

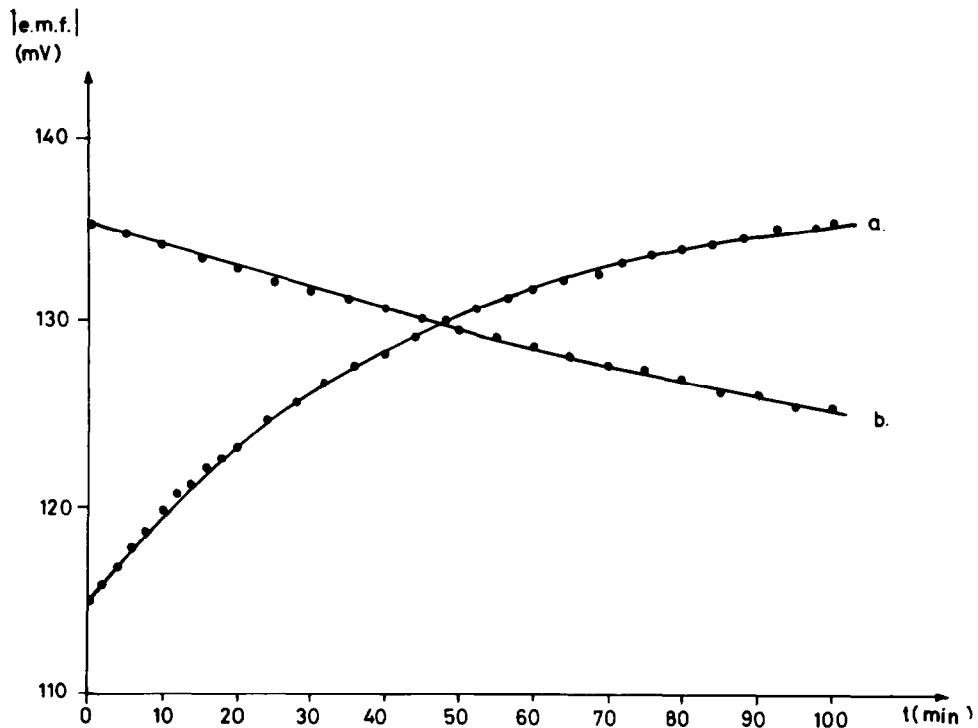Fig. 1. The change of e.m.f. in hexacyanoferrate(II) solution C: 0.1 mol dm^{-3}, pH$_0$ = 10.75, (a) on irradiation (365 nm), (b) after interrupting the illumination.

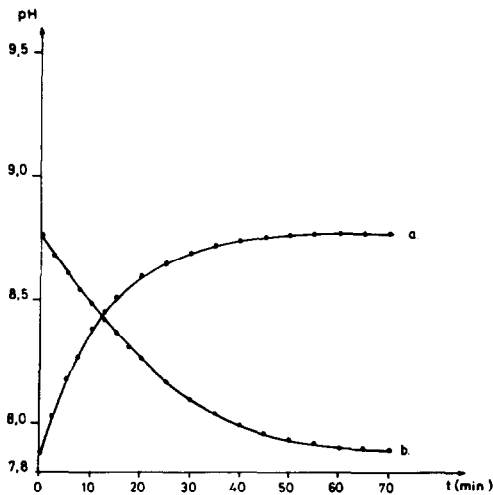Fig. 2. The change of pH of hexacyanoferrate(II) solution. C: 0.1 mol dm^{-3}, pH$_0$ = 7.85, (a) on irradiation (365 nm), (b) in the dark reaction, after illumination.

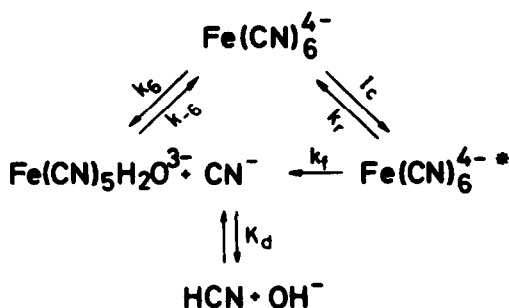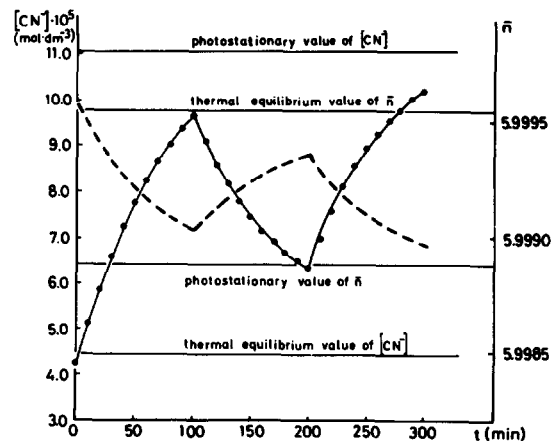Fig. 4. Experimental (●) and calculated (line) cyanide ion concentrations in 0.1 mol dm^{-3} hexacyanoferrate(II) solution at pH$_0$ = 10.75 on illumination and in the next dark period. Dashed line: the change of the kinetic mean coordination number ($\bar{n}_t$). Values of ϕ, k_6 and k_{-6} are 1.0, 3.0 × 10^{-8} s^{-1} and 1.5 mol^{-1} dm^{3}s^{-1}, respectively.

Fig. 3. The scheme of photaquation reaction.

dination number ($\bar{n}_t$):

$$\bar{n}_t = \frac{T'_{CN} - CN_t^-}{T_{Fe}},$$

where T'_{CN} and T_{Fe} are analytical concentrations and CN_t^- is the free cyanide concentration at a certain moment.

The conversion both of the photo and the thermal (dark) reaction is extremely small (0.112 and 0.045%, respectively). Nevertheless, these very small changes of $\bar{n}_t$ can be quite exactly determined because of the high sensitivity of the cyanide ion-selective electrode and the
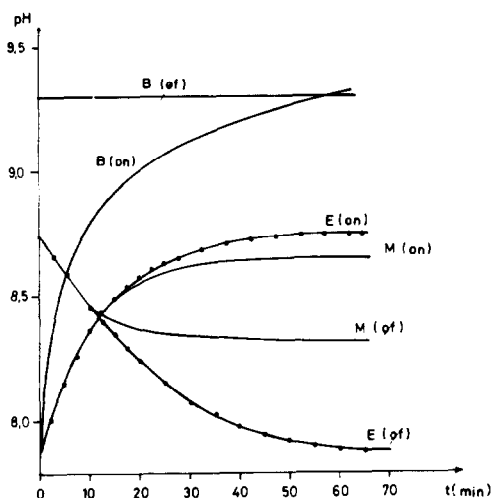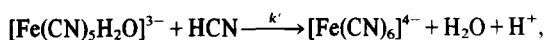
Fig. 5. The change of pH of hexacyanoferrate(II) solution. C: 0.1 mol dm^{-3}, pH$_0$ = 7.0 *on*: on illumination, *off*: after illumination E: experimental, B: calculated curve using the constants determined in alkaline medium (Fig. 4), M: calculated by the extended scheme.

large total concentration of the complex. The very small value of conversion is responsible for the fact that no satisfactory kinetic investigation was made earlier. It follows from the kinetic data that the stability constant of the sixth complex (K_6) is $(5.2 \pm 1.5) \times 10^7$ mol^{-1} dm^3. This value differs somewhat from that predicted theoretically (1.41×10^6)[16] or earlier determined experimentally (2×10^9).[18]

Because of the differences between the experimental and calculated (based on the constants determined in alkaline medium) curves in nearly neutral medium, the scheme should be extended by the following reaction:

$$[Fe(CN)_5H_2O]^{3-} + HCN \xrightarrow{\ k'\ } [Fe(CN)_6]^{4-} + H_2O + H^+,$$

$k' = 3.33 \times 10^{-2}$ mol^{-1} dm^3 s^{-1}. The correlation between the experimental and calculated photostationary pH-values is good. The quantum yield of hydroxide production (0.17) agrees with the literature value.[1]

When illuminating an acidic solution (pH = 4.0) of the complex, a photostationary state was not reached. After interrupting the illumination, the absorbance of primary product did not decrease but slowly increased. The reason for this situation is the continuous formation of hydrogen cyanide that is continuously taken away by the bubbled argon gas.

Figure 6 shows a typical absorbance versus time curve at 0.01 mol dm^{-3} complex concentration. Assuming zero order photodecomposition, the calculated ϕ value is 0.85–0.95 at pH = 4.0 and, in the range of complex concentration 0.01–0.015 mol dm^{-3}, in good agreement with Ohno.[7]

From a comparison of the curve relating quantum yield in acidic medium (ϕ_a) to pH with the distribution curves of the different protonated hexacyanoferrate(II) complexes,[17] it seems possible that the decrease of ϕ_s with decreasing pH is connected with the occurence of differently protonated complexes.

Introducing the $\bar{n}_H/\bar{n}_{H,max}$ ratio to characterize the degree of protonation, the ϕ_a values can be calculated by the following expression:

$$\phi_a = \phi_b \left(1 - \frac{\bar{n}_H}{\bar{n}_{H,max}}\right)$$

where ϕ_b is the quantum yield determined in alkaline solution at the same concentration of complex, and $\bar{n}_{H,max}$ equals 4.

The calculated and determined values agree, considering the experimental error of measuring the protonation constants and ϕ (Fig. 7).

Comparing the ϕ_s vs pH curve with the distribution curves it follows that $\phi_{H_1} \sim 0.8$, $\phi_{H_2} \sim 0.6$, $\phi_{H_3} \sim 0.5$ and $\phi_{H_4} \sim 0$.

The ϕ_a value at a certain pH is the weighted average of the ϕ_{H_i} values ($i = 1,.., 4$).
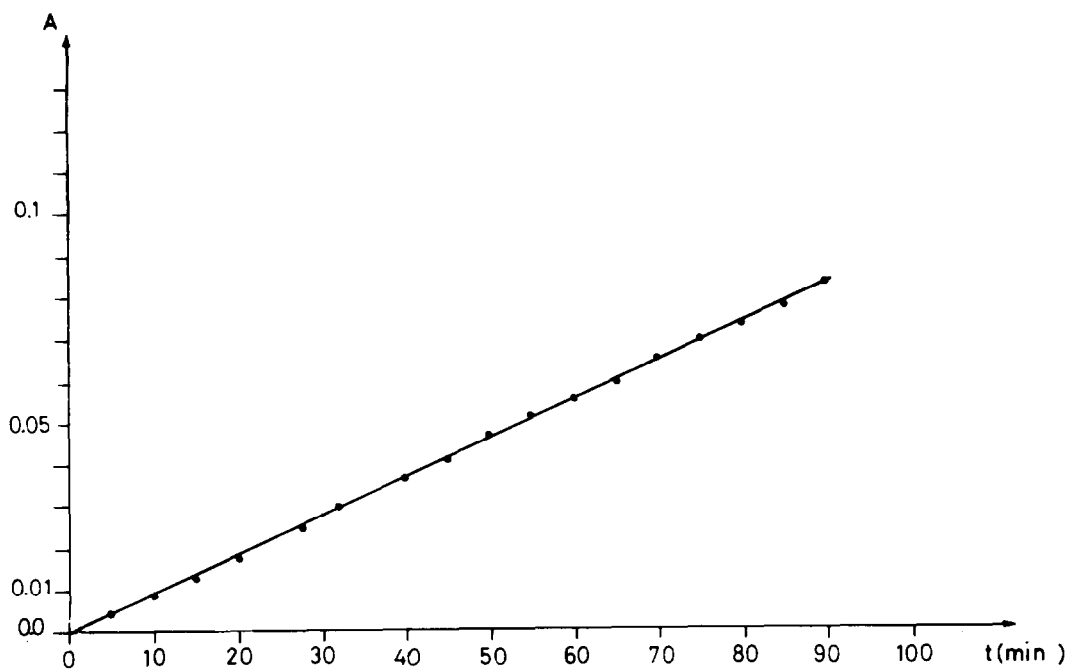

Fig. 6. The change of absorbance at 440 nm on illumination. C: 0.01 mol dm^{-3}, pH = 4.0 (acetate buffer).

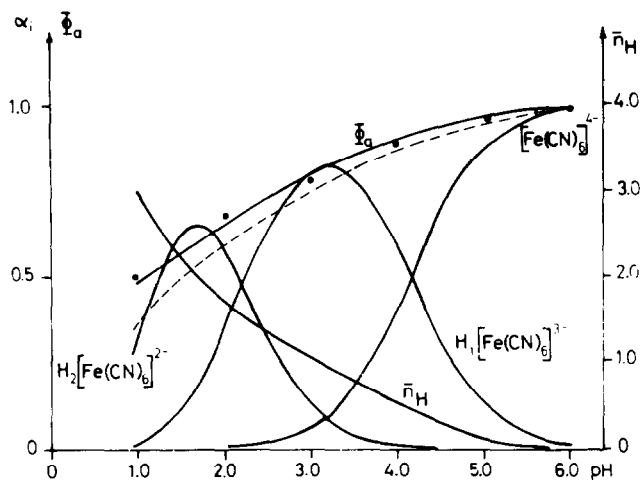Fig. 7. Distribution curves of different protonated hexacyanoferrate(II) complexes[17] and ϕ_a vs pH curve:
($\bullet$): experimental,[7] dashed line: calculated.

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