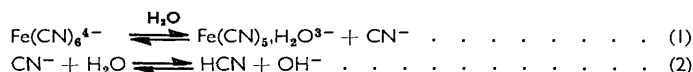


151. *Kinetics and Mechanism of the Decomposition of Complex Cyanides of Iron(II) and Molybdenum(IV).*

By S. AŠPERGER, I. MURATI, and D. PAVLOVIĆ.

The photodecomposition of the hexacyanoferrate(II) ion to aquopentacyanoferrate(II) ion and the analogous reaction involving release of a cyanide group from an octacyanomolybdate(IV) ion are both reversible in darkness. The energy of activation of the decomposition of aquopentacyanoferrate(II) ion in the dark at elevated temperature amounts to 28.2 kcal./mole and is higher by 8.4 kcal./mole than that of the hexacyanoferrate(II) ion. The rate of formation of ferrous ions from the aquopentacyanoferrate(II) ion in the dark at elevated temperature is about 60 times slower than the rate of decomposition of the aquopentacyanoferrate(II) ion under the same conditions. This suggests the presence of an intermediate complex cyanide of iron(II). In ultraviolet light the rates differ only by a factor of two because the proposed complex is unstable in this light.

IN an earlier publication¹ a kinetic study of the photodissociation of potassium hexacyanoferrate(II) ion in aqueous solution was described. It was reported that the pH of such solutions increased on exposure to ultraviolet light and that in darkness the reaction was reversible. The kinetic data obtained supported the reaction scheme:



MacDiarmid and Hall² have also measured the pH effects in solutions of potassium hexacyanoferrate(II). They found that the pH of solutions which had been kept for some time in the light did not decrease in the dark. They observed further that after short exposure to light the reversibility was much smaller than we had found. We therefore repeated some of the previous measurements of the reversibility of the reaction (1) and carried out new measurements under different conditions, using two methods for the determination of aquopentacyanoferrate(II) ion. It was found that the reaction was always reversible when the conditions were such that no appreciable decomposition of the aquopentacyanoferrate(II) ion occurred, as was the case in our previous work.

¹ Ašperger, *Trans. Faraday Soc.*, 1952, **48**, 617.

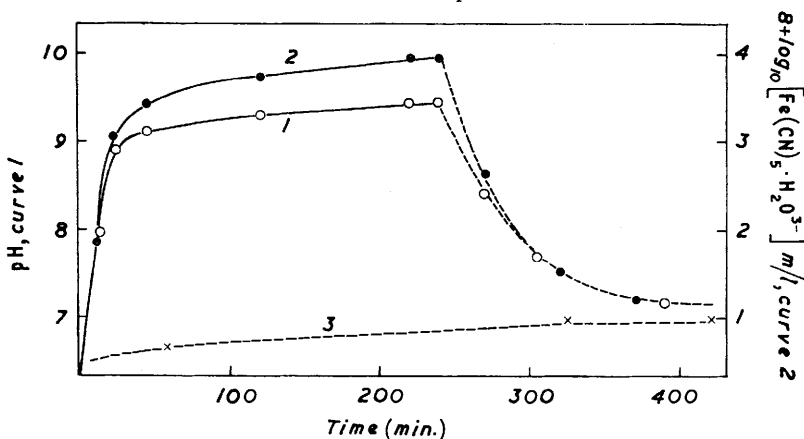
² MacDiarmid and Hall, *J. Amer. Chem. Soc.*, 1953, **75**, 5204.

The kinetics of decomposition of octacyanomolybdate(IV) ion in ultraviolet light, and the kinetics of the reverse reaction in darkness, have been measured and an analogy with the decomposition of hexacyanoferrate(II) has been found.

The rate of decomposition of aquopentacyanoferrate(II) in acid and neutral solution at elevated temperatures and under the influence of ultraviolet light was determined and compared with the rate of formation of ferrous ions. The latter rate was much the smaller. Therefore the presence of an intermediate complex cyanide of iron(II) is postulated.

Decomposition of the Hexacyanoferrate(II) Ion in Ultraviolet Light.—A typical change of pH of a 0.1M-solution of potassium hexacyanoferrate trihydrate (Merck, analytical grade) exposed to ultraviolet light from a Philips Philora HO2000 mercury lamp is shown in Fig. 1, curve 1. The reaction conditions are described in the Experimental part of the paper. It was previously shown¹ by spectrographic measurements that under similar conditions the mercury lines at 365 m μ were the photoactive part of the spectrum. It can be seen from Fig. 1 that on transference of the irradiated solution to darkness the pH reverts to

FIG. 1. Change of pH of a 0.1M-solution of $K_4Fe(CN)_6$ exposed to ultraviolet light (curve 1), and the change of the concentration of $Fe(CN)_5 \cdot H_2O^{3-}$ (curve 2). Broken lines are changes in the dark. Curve 3 represents the slow thermal reaction in the dark. Temp.: 20°.



the value given by slow decomposition in darkness of a non-irradiated solution. When the logarithm of the concentration of aquopentacyanoferrate(II) was plotted against the reaction time the same type of kinetics was obtained (Fig. 1, curve 2). The calculations of the concentrations of aquopentacyanoferrate(II) ion were made as previously described, with the supposition that with only brief irradiation times all side-reactions can be neglected.

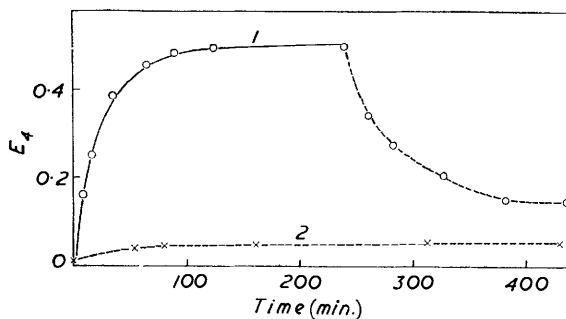
Since aquopentacyanoferrate(II) ion reacts with nitrosobenzene,³ giving the violet complex $Fe(CN)_5 \cdot C_6H_5 \cdot NO^{3-}$, it was possible to follow the light reaction and the reverse reaction in darkness by spectral measurements. The optical density of the violet complex at 528 m μ (maximum of absorption) was determined in the 4th minute ($=E_4$) by means of a Unicam S.P. 500 Quartz Spectrometer. Fig. 2 shows the change of E_4 during reaction in the light and the reverse reaction in the dark (at $20^\circ \pm 0.1^\circ$). The same reaction pattern as in Fig. 1 was obtained. The reversibility was not as complete as in Fig. 1. Undoubtedly the calculations of the concentration of $Fe(CN)_5 \cdot H_2O^{3-}$ on the basis of the pH measurements gave only approximate results.

Experiments were also made by exposing aqueous solutions of potassium hexacyanoferrate(II) to the ultraviolet light of the Philora mercury lamp for several hours. In

³ Baudisch, *Ber.*, 1929, **62**, 2706; Ašperger, Murati, and Cupahin, *J.*, 1953, 1041; Emschwiller, *Compt. rend.*, 1953, **236**, 72.

darkness the pH remained constant for a few hours but then decreased very slowly and returned after two days to almost its initial value. Under such conditions the decrease of pH does not mean that the reaction was reversible since a precipitate of $\text{Fe}(\text{OH})_3$ was also formed. The same happened when the solutions of hexacyanoferrate(II) ion were exposed briefly in a quartz vessel to the ultraviolet light of a mercury quartz lamp or to sunlight for a few minutes only.

FIG. 2. Change of the concentration of $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ during exposure of a 0.1M-solution of $\text{K}_4\text{Fe}(\text{CN})_6$ to ultraviolet light, and the reverse reaction in the dark. Curve 2 represents the slow decomposition of 0.1M- $\text{K}_4\text{Fe}(\text{CN})_6$ in the dark. E_4 is the optical density of $\text{Fe}(\text{CN})_5\text{C}_6\text{H}_5\text{NO}^{3-}$ in the 4th minute at $528\text{ m}\mu$. Temp.: 20°



Decomposition of Octacyanomolybdate(IV) Ion in Ultraviolet Light.—Aqueous solutions of octacyanomolybdate(IV) ion, exposed to ultraviolet light, decompose readily and free cyanide ions are formed. The pH of irradiated solutions will therefore increase. As pointed out by Adamson and Sporer,⁴ a complicated reaction sequence is clearly involved, since the original yellow solution develops a red colour which with prolonged irradiation changes to green and finally to pale blue. The mechanism seems to be analogous to that of the decomposition of the hexacyanoferrate(II) ion. In the first reaction stage a cyanide ion is released. When the conditions were mild enough and no further decomposition took place the reaction was reversible in the dark. This was not the case with the irradiated solutions which acquired a pale blue colour. The pH of these blue solutions remained constant for some time but began to decrease slowly after a couple of days, probably because of the formation of basic cyanides.⁵

A 0.05M-solution was exposed to the ultraviolet light of the Philips Philora HO2000 mercury lamp, the conditions of irradiation being the same as in the measurements reported in the previous section (see also Experimental). The group of mercury lines at $365.5\text{ m}\mu$ was again the main photoactive source. Fig. 3 shows the change of absorption at $580\text{ m}\mu$. At that wavelength the yellow solution absorbs very little while the products absorb appreciably. At intervals aliquot parts were withdrawn and the optical densities measured as quickly as possible: during the measurements the fast reverse reaction took place, so that the measurements were not easily reproducible. However, it can be seen (Fig. 3) that the reaction was reversible in the dark, though not completely so.

Rate of Decomposition of Aqueous Solutions of Sodium Aquopentacyanoferrate(II).—*Influence of pH.* The kinetic measurements were made at $40^\circ \pm 0.1^\circ$. Sodium aquopentacyanoferrate(II) was used as a 0.001M-solution in a phosphate-citric acid buffer at the required pH. At intervals aliquot parts were withdrawn, quickly cooled to 20° , and poured into a 0.004M-solution of nitrosobenzene kept at 20° . The determination of aquopentacyanoferrate(II) was then carried out as described in the Experimental part. First-order rate constants were invariable only up to 40% of decomposition and afterwards

⁴ Adamson and Sporer, *J. Amer. Chem. Soc.*, 1958, **80**, 3865.

⁵ Gmelin's "Handbuch d. anorg. Chem.," Vol. 53, Berlin, 1935, pp. 201-202.

started to decrease, probably because a reversible reaction of lower complex cyanides with cyanide ions re-formed aquopentacyanoferrate(II) ion. The average first-order rate constants were plotted against pH (Fig. 4). Decomposition is fastest at pH 3.55. A

FIG. 3. Change of optical density at 580 μ of a 0.05M-solution of $K_4Mo(CN)_8 \cdot 2H_2O$ in ultraviolet light (full line) and in the dark (broken line) at 20°.

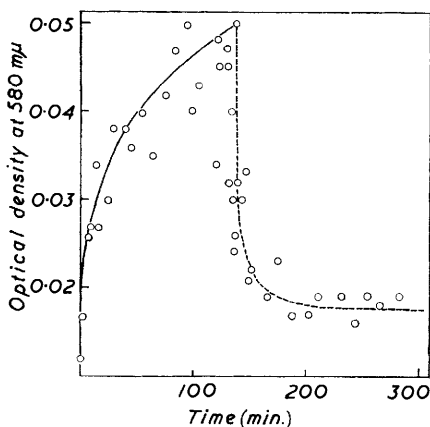
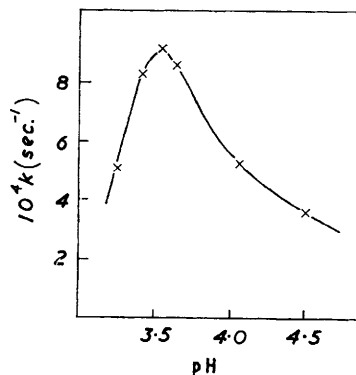
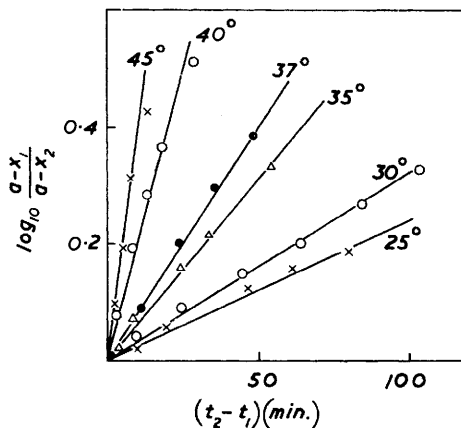


FIG. 4. Dependence of the rate of decomposition of a 0.001M-solution of $Na_5Fe(CN)_5 \cdot H_2O$ (in phosphate-citric acid buffer) on pH at 40°.



similar influence of pH was previously observed in the decomposition of potassium hexacyanoferrate(II) catalysed by mercuric ions.⁶ The slow reaction at pH 4.5 is probably caused by the reverse reaction of lower complex cyanides with hydrogen cyanide. (At that pH all cyanide ions are in the form of hydrogen cyanide.) The action of hydrogen

FIG. 5. Dependence of the rate of decomposition of aquopentacyanoferrate(II) ion (0.001M) on temperature at pH 3.55.



ions is even more complex since in acid solutions $H_2Fe(CN)_5 \cdot H_2O^-$ and $HFe(CN)_5 \cdot H_2O^{2-}$ should predominate. The larger the number of protons in the complex, the smaller is the probability of a cyanide group's leaving the complex ion. The result of all these influences is an optimum pH for the rate of decomposition.

Influence of temperature. The influence of temperature on the rate of decomposition of aquopentacyanoferrate(II) ion was measured at pH 3.55 (maximum velocity). Fig. 5 shows the dependence of $\log_{10} [(a - x_1)/(a - x_2)]$ on $(t_2 - t_1)$, where a is the initial

⁶ Ašperger and Pavlović, *J.*, 1955, 1449.

concentration of aquopentacyanoferrate(II) ion. Straight lines were obtained up to 40% decomposition, the slope being $0.4343k_t$, where k_t is the rate constant. The rate constants were: 8.33×10^{-5} , 1.28×10^{-4} , 2.55×10^{-4} , 4.66×10^{-4} , 9.17×10^{-4} , and $1.58 \times 10^{-3} \text{ sec.}^{-1}$ at 25° , 30° , 35° , 37° , 40° , and 45° , respectively.

An Arrhenius plot was made and the energy of activation calculated to be 28.2 kcal./mole by the method of least squares. The energy of activation previously determined (Ašperger *et al.*³) for the decomposition of hexacyanoferrate(II) ion in neutral solutions was 19.8 kcal./mole.

The rate of formation of ferrous ions. In acid solutions the decomposition of sodium aquopentacyanoferrate(II) leads to ferrous ions. The rate of formation of ferrous ions has been compared with the rate of decrease of the concentration of aquopentacyanoferrate(II) ion reported above.

The formation of ferrous ions was followed by means of the 2,2'-bipyridyl reagent which was added in excess to 0.001M-sodium aquopentacyanoferrate(II) solution in phosphate-citric acid buffer. The first-order rate constants were determined from the expression $\frac{1}{t} \log_e \frac{E_\infty - E_0}{E_\infty - E}$, where E_0 , E , and E_∞ are optical densities at the reaction times t_0 , t , and t_∞ , respectively, at 520 m μ (maximum absorption of the red complex formed with bipyridyl). The extinction coefficient of the red complex was found to be 8450 l. cm.⁻¹ mole⁻¹ at 520 m μ . Calculation of E_∞ gave a measure of the concentration of ferrous ion equivalent to the initial concentration of aquopentacyanoferrate(II) ion.

Kinetic measurements were made at 40° . At pH 4.0 the first-order rate constant was $9.25 \times 10^{-6} \text{ sec.}^{-1}$.

Comparison of this rate constant with that for the disappearance of aquopentacyanoferrate(II) ion at the same pH and temperature ($5.4 \times 10^{-4} \text{ sec.}^{-1}$ at 40° , see Fig. 4) shows the former to be about 60 times slower than the latter. This indicates the existence of an intermediate complex cyanide, probably with four cyanide groups. The existence of such ion has not been reported as yet. According to Kimball⁷ this ion would have the configuration d^{2sp} (irregular tetrahedron).

Rate of decomposition in ultraviolet light. Aqueous solutions of sodium aquopentacyanoferrate(II) (0.001M) were exposed to the ultraviolet light of a Philips Philora HO2000 mercury lamp under the conditions used in irradiation of potassium hexacyanoferrate(II) solutions. The emission spectrum of the mercury lamp was recorded through the glass wall of the thermostat and the cells filled with water and 0.001M-solution of sodium aquopentacyanoferrate(II), respectively; a Zeiss Universal spectrograph was used.* The blackening of the photographic plate showed that the main photoactive source was again the group of lines at 365.5 m μ , because the shorter wavelengths were completely absorbed by the glass of the light source, thermostat, and vessel. The mercury lines at 390.64, 398.40, and 410.81 m μ are of very low intensity and need not be considered. A Unicam S.P. 500 quartz spectrometer was used and the extinction coefficient of the sodium aquopentacyanoferrate(II) solution at 365.5 m μ was found to be 250 l. cm.⁻¹ mole⁻¹; the calculated absorption of a 0.001M-solution ($p = 22 \text{ cm.}$) was 68.3%.

Under the influence of the ultraviolet light decomposition to ferrous ions took place. The rate of decomposition was followed by measuring (a) the rate of disappearance of $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ by the above kinetic method with nitrosobenzene, and (b) the rate of formation of ferrous ions by means of the bipyridyl reagent, which was added to aliquot parts withdrawn from the reaction solution. The absorption of the red complex formed with bipyridyl was then determined at 520 m μ and the concentration of ferrous ions was calculated as already described. The first-order rate constants were calculated from the expression $[\varepsilon p(x_2 - x_1) + \log_{10} A_1/A_2]/(t_2 - t_1)$, valid for medium absorptions. In this

* Spectrograms made by Professor K. Weber in the Institute for Forensic Medicine of the University of Zagreb.

⁷ Kimball, *J. Chem. Phys.*, 1940, **8**, 188.

expression ϵ is the molar extinction coefficient of the aquopentacyanoferrate(II) ion at $365.55 \text{ m}\mu$, A_1 and A_2 are the absorptions at the same wavelength at reaction times t_1 and t_2 , respectively, and $(x_1 - x_2)$ is the change of concentration of aquopentacyanoferrate(II) ion when method (a) was used, or the change of the ferrous ions concentration when method (b) was applied. Unfortunately, the kinetic measurements could be carried only to about 32% of decomposition since ferrous ions with aquopentacyanoferrate(II) ion give a blue-green colour which increasingly interferes with measurements. Further, when the rate was measured on the basis of disappearance of aquopentacyanoferrate(II) ion, then for some unknown reason the reaction rate increased slightly during initial decomposition but soon began to decrease normally. The first-order rate constants were therefore determined between 7% and 32% of decomposition. The tabulated results show that the rate of the decomposition of aquopentacyanoferrate(II) ion is about twice as large as the rate of the formation of ferrous ions. (In the thermal reaction the analogous ratio of rates was 60:1.) It may be concluded that in ultraviolet light an intermediate complex cyanide (presumably with four cyanide groups) is also formed, though in much smaller quantities than in the thermal decomposition.

(a) Rate of decomposition of a 0.001M-solution of $\text{Na}_3\text{Fe}(\text{CN})_5 \cdot \text{H}_2\text{O}$ in ultraviolet light at 20° and pH 6.15. (b) Rate of formation of ferrous ions under the same conditions.

(a) Decompn. of $\text{Fe}(\text{CN})_5 \cdot \text{H}_2\text{O}^{3-}$ (%)	$10^5 k$ (sec. ⁻¹)	(b) Formation of ferrous ions (%)	$10^5 k$ (sec. ⁻¹)
7.0	5.04	8.3	2.62
12.6	5.00	12.7	2.32
19.2	5.00	17.5	2.45
25.6	5.20	21.7	1.94
31.6	5.39		
	Average 5.13		Average 2.33

EXPERIMENTAL

Materials.—Potassium hexacyanoferrate(II) trihydrate was Merck's analytical grade. Potassium octacyanomolybdate(IV) dihydrate was prepared according to "Inorganic Syntheses" ⁸ [Found: Mo, 19.4. Calc. for $\text{K}_4\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$: Mo, 19.35%]. Sodium aquopentacyanoferrate(II) was prepared according to Hofmann,⁹ though the method was somewhat modified. To the sodium nitroprusside, Merck's analytical-grade sodium hydroxide was added, instead of sodium carbonate as required by the procedure, because the subsequent addition of methanol otherwise precipitated sodium carbonate in large quantities together with the sodium aquopentacyanoferrate(II) and we were not able to get a pure product by recrystallization from methanol. When sodium hydroxide was added, a pure product was obtained [Found: Fe, 20.6. Calc. for $\text{Na}_3\text{Fe}(\text{CN})_5 \cdot \text{H}_2\text{O}$: Fe, 20.5%].

Spectrophotometry.—Absorption-intensity measurements were made with a Unicam quartz spectrophotometer S.P. 500, 10 mm. cells being used.

Kinetics in Ultraviolet Light.—A glass cell ($12 \times 12 \times 2$ cm.) containing the solution freshly prepared in the dark was placed in a water-thermostat ($20^\circ \pm 0.1^\circ$), and the solution stirred. Before reaching the cell the light of a Philips Philora HO2000 mercury lamp had to pass through the 6 mm. thick glass of the water thermostat, through 1 cm. of the water layer, and through the 3 mm. thick glass of the cell. Under similar conditions it was previously shown by spectrographic measurements ¹ that for the solutions of potassium hexacyanoferrate(II) the photoactive light was the group of mercury lines at $365.5 \text{ m}\mu$. The same group of lines was the main photoactive source for the solutions of aquopentacyanoferrate(II) ions.

Determination of Aquopentacyanoferrate(II) Ion.—A 0.004M-solution of nitrosobenzene and one of sodium aquopentacyanoferrate(II) of a known concentration (between 10^{-3} and 10^{-5} M), buffered to pH 4.1 by a phosphate-citric acid buffer, were placed in a water-thermostat at $20^\circ \pm 0.1^\circ$ and after thermal equilibrium had been attained they were mixed in equal volumes. The optical density of the violet reaction product $\text{Fe}(\text{CN})_5 \cdot \text{C}_6\text{H}_5 \cdot \text{NO}^{3-}$ was determined in the tenth minute at $600 \text{ m}\mu$ ($=E_{10}$). The maximum absorption of the violet complex is at $528 \text{ m}\mu$, but

⁸ Audrieth, *Inorg. Synth.*, 1950, **8**, 160.

⁹ Hofmann, *Annalen*, 1900, **312**, 1.

at 600 $m\mu$ the absorption is still appreciable and the absorption of the unchanged aquopentacyanoferrate(II) is small. By plotting E_{10} against the initial concentration of aquopentacyanoferrate(II) a calibration curve was obtained which was practically a straight line for the initial concentrations of $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ up to 0.001M. This method permitted determination of aquopentacyanoferrate(II) ion in a couple of minutes and was adequate because the hexacyanoferrate(II) ion, if present, could not interfere since it does not react with nitrosobenzene. The determination of aquopentacyanoferrate(II) ion in presence of other complex cyanides will be reported later.

Determination of Ferrous Ions.—Known quantities of ferrous ions in the form of Mohr's salt were added to the phosphate-citric acid buffer at pH 4—5. 2,2'-Bipyridyl reagent was then added in excess and after 5—8 min. the optical density of the red complex at 520 $m\mu$ was measured. By plotting known concentrations of ferrous ions against optical densities a straight line was obtained, which showed that the solutions obey the Beer-Lambert law. The extinction coefficient was found to be 8450 l. cm^{-1} mole $^{-1}$ at 520 $m\mu$, and was used for determination of the unknown concentration of ferrous ions.

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INSTITUTE OF INORGANIC AND PHYSICAL CHEMISTRY,
FACULTY OF PHARMACY, UNIVERSITY OF ZAGREB.
DEPARTMENT OF PHYSICAL CHEMISTRY, INSTITUTE "RUDJER BOŠKOVIĆ,"
ZAGREB, CROATIA, YUGOSLAVIA.

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