[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Illumination—*p*H Effects in Solutions of Complex Cyanides[1]

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The dissociation of potassium hexacyanoferrate(III), potassium hexacyanocobaltate(III) and potassium octocyanomolybdate(IV) in dilute solution, is shown to be accelerated by visible light. No such photodissociation is noted in solutions of potassium hexacyanochromate(III) or potassium hexacyanomanganate(III). A suitable method of analysis for the latter compound is discussed.

Recently Ašperger[3] has carried out a kinetic study of the photodissociation of potassium hexacyanoferrate(II) in dilute solution. He reported that the *p*H of a solution of this substance increased on exposure to light, and subsequently decreased to its original *p*H when placed in the dark. However, the rate of the reverse reaction apparently depends on the hexacyanoferrate(II) concentration in some obscure way, since he states that it is subject to the "negative catalytic action of $Fe(CN)_6^{-4}$."

The purpose of this investigation was to study the photodissociation effect in other complex cyanides. Measurements on hexacyanoferrate(II) solutions were also carried out under experimental conditions similar to those used for the other complexes.

Experimental

Preparation and Purity of the Complex Salts. Potassium Hexacyanoferrate(II) Trihydrate.—The Merck analytical reagent grade salt was used without further purification.

Potassium Hexacyanoferrate(III).—The analytical reagent grade product was recrystallized from water and air-dried. The iron in the complex was determined iodometrically[4] as Fe(III). The purified salt was shown to be free from traces of free cyanide by the copper sulfide test,[5a] and free from traces of hexacyanoferrate(II) by the uranyl acetate test.[5b]

Anal. Calcd. for $K_3Fe(CN)_6$: Fe, 16.98. Found: Fe, 16.87.

Potassium Hexacyanocobaltate(III).—The commercial salt was recrystallized from water and dried in a vacuum desiccator. The complex was decomposed by hot, concentrated sulfuric acid, and the cobalt determined gravimetrically as the pyridine–thiocyanate complex.[6]

Anal. Calcd. for $K_3Co(CN)_6$: Co, 17.74; C, 21.69; N, 25.30. Found: Co, 17.66, 17.91; C,[7] 21.85; N,[7] 25.76.

Potassium Octacyanomolybdate(IV) Dihydrate.—This compound was prepared from commercial MoO_3.[8] The molybdenum content was determined by titration with standard permanganate.

Anal. Calcd. for $K_4Mo(CN)_8 \cdot 2H_2O$: Mo, 19.35; C, 19.35; N, 22.58. Found: Mo, 19.27, 19.35; C, 19.05; N, 22.73.

Potassium Hexacyanochromate(III).—This was prepared by a modification of the method given in reference 9. Instead of using potassium dichromate as the starting material, in which case it is necessary to reduce the chromium to Cr(III) with SO_2, chromium(III) nitrate was used as the chromium source. In this way, the time needed for the preparation was reduced considerably.

The complex was analyzed for CN by distillation of the hydrocyanic acid, followed by a silver nitrate titration.[9]

Anal. Calcd. for $K_3Cr(CN)_6$: CN, 47.3. Found: CN, 46.8.

Potassium Hexacyanomanganate(III).—This was prepared according to reference 10, but the crude substance was purified by recrystallization from 25% potassium cyanide solution rather than from water. When crystallized from water, the complex appeared to be contaminated by small amounts of hydrolysis products. Traces of free cyanide were removed by washing with large amounts of 70% ethanol, followed by 95% and then absolute ethanol, and finally with ether.

Analysis of the complex was first attempted by the method used by Adamson, Welker and Volpe[11] in which a solution of the complex was acidified and then the liberated hydrogen cyanide distilled into excess potassium hydroxide, the resulting potassium cyanide being determined by titration with standard silver nitrate. Low results were obtained.

Anal. Calcd. for $K_3Mn(CN)_6$: CN, 47.55. Found: CN, 43.5.

A determination of manganese was then carried out using the bismuthate method,[12] the complex being first decomposed by dilute nitric acid.

Anal. Calcd. for $K_3Mn(CN)_6$: Mn, 16.73; C, 21.92; N, 25.61. Found: Mn, 16.90; C, 21.91; N, 25.34.

Preparation of Solutions of Complexes.—All solutions were 0.050 *f* and were prepared in a darkened room. They were used in the experiments within five to ten minutes of first adding water to the solid complex.

***p*H Determination and Illumination Conditions.**—The solutions were placed in identical small glass-stoppered volumetric flasks. The *p*H was determined from time to time by removing a few drops of the solution with an eye-dropper. The measurements were made with a "one drop" glass electrode connected to a line-operated Beckman *p*H meter. When replacing the stoppers in the flasks, a stream of nitrogen was directed into the flask by means of a very thin glass tube.

When solutions were studied in the light, they were in bright diffuse daylight; when in the dark, they were stored in a light-tight cupboard. All runs on any particular compound were carried out simultaneously so that any slight changes in temperature or illumination would be the same for each solution.

Experimental Results

To give some idea of the relative magnitudes of the illumination-*p*H effects, all graphs are plotted on the same scale. Dotted lines refer to times during which the solutions were in the dark; full lines refer to the times during which the solutions were exposed to the light.

Note: The top curve in the potassium hexacyanoferrate(II) graph was obtained using a solution

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[1] Based on portions of a thesis to be submitted by Alan G. MacDiarmid to the Graduate School of the University of Wisconsin, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[3] S. Ašperger, *Trans. Faraday Soc.*, **48** [7], 617 (1952).

[4] A. I. Vogel, "Quantitative Inorganic Analysis," Longmans, Green and Co., New York, N. Y., 1951, p. 356.

[5] (a) A. I. Vogel, "Qualitative Chemical Analysis," Longmans, Green and Co., New York, N. Y., 1945, p. 255; (b) p. 260.

[6] A. I. Vogel, reference 4, p. 463.

[7] All carbon and nitrogen analyses in this investigation were kindly carried out by the Microanalytical Laboratory of the Department of Chemistry, University of Wisconsin.

[8] L. F. Audrieth, "Inorganic Syntheses," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 160.

[9] W. C. Fernelius, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 203.

[10] W. C. Fernelius, *ibid.*, p. 213.

[11] A. W. Adamson, J. P. Welker and M. Volpe, THIS JOURNAL, **72**, 4030 (1950).

[12] A. I. Vogel, reference 4, p. 287.

of hexacyanoferrate(II) which was contained in a stoppered quartz tube instead of a small volumetric flask.

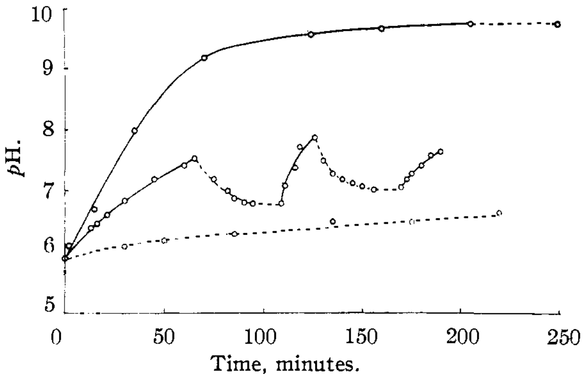

Fig. 1.—Potassium hexacyanoferrate(II); effect of light on *p*H: dotted lines, *p*H in dark; full lines, *p*H in bright daylight.

Potassium Hexacyanoferrate(II).—The results are not in complete agreement with previously published work,[3] in that the *p*H of the solution which had remained for some time in the light after reaching its maximum *p*H value showed no sign of any decrease in *p*H when placed in the dark.

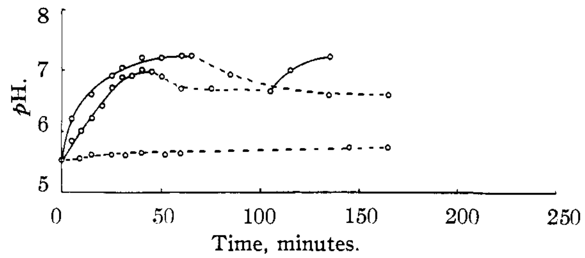

Fig. 2.—Potassium hexacyanoferrate(III), effect of light on *p*H: dotted lines, *p*H in dark; full lines, *p*H in bright daylight.

Potassium Hexacyanoferrate(III).—Similar effects to those noted with the hexacyanoferrate(II) were obtained, except that in all cases the *p*H did decrease somewhat when the solutions were placed in the dark.

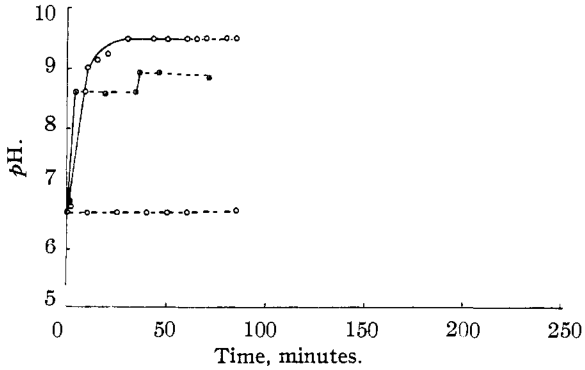

Fig. 3.—Potassium hexacyanocobaltate(III), effect of light on *p*H: dotted lines, *p*H in dark; full lines, *p*H in bright daylight.

Potassium Hexacyanocobaltate(III).—Similar effects were also observed with this compound, but in this case there was no tendency whatever for the *p*H to decrease when the solutions were placed in the dark, even when the exposure to light had been interrupted before the maximum *p*H had been reached.

Potassium Octacyanomolybdate(IV).—The photo-*p*H effect was extremely great with this compound. The *p*H rose by approximately two units within one minute exposure to light. The *p*H also fell rapidly when the solutions were placed in the dark. When placed in the light, the solution acquired a faint orange color which disappeared instantaneously on adding a few drops of potassium cyanide solution, or within half an hour when the tube was placed in the dark.

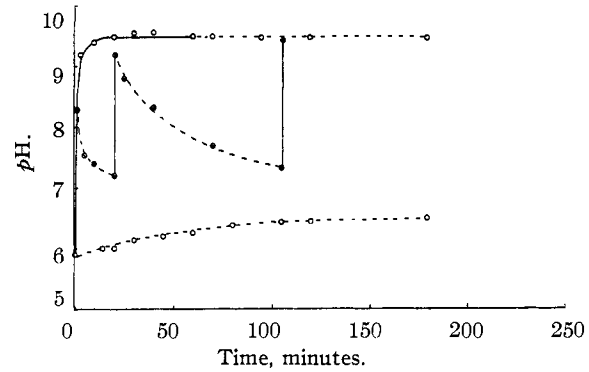

Fig. 4.—Potassium octocyanomolybdate(IV), effect of light on *p*H: dotted lines, *p*H in dark; full lines, *p*H in bright daylight.

Potassium Hexacyanochromate(III).—No change in *p*H was observed under any of the above illumination conditions, even though the solution became very slightly darker in color when exposed to the light. The *p*H remained constant at 9.0.

Potassium Hexacyanomanganate(III).—Even when this solution was prepared using a photographic red lamp as the only source of illumination, the complex rapidly hydrolyzed and a precipitate appeared almost immediately. The *p*H reached a value of 9.1. No further change in *p*H was observed when the solution was allowed to stand in the light or in the dark. If dilute solutions of potassium cyanide instead of water were used to prepare the solution, decomposition of the complex could be prevented, but no change in *p*H of these solutions under any illumination conditions could be observed.

Analytical Methods.—In the case of the potassium hexacyanomanganate(III), it may be noted that the first method of analysis gave a low CN result although the compound was subsequently shown to be pure by the second set of analysis figures. Using the first method of analysis, Adamson, Welker and Volpe[11] also obtained a low result, (43.16%). This was the only analysis carried out by them on the compound and they attributed the low figure to the presence of approximately 8% MnO_2 impurity in the complex. They stated that the presence of 8% MnO_2 in the complex was also supported by magnetic susceptibility measurements. However, this second piece of evidence should be accepted with caution, since theoretical and experimental magnetic susceptibility values frequently do not agree, even if the compound is pure.

It would therefore appear that their preparation was actually pure and that their method of analysis was at fault. During distillation, the Mn(III) complex would very likely oxidize some of the cyanide and consequently lower the analysis figure. In another paper, Adamson, Welker and Wright[13] state that potassium hexacyanomanganate(III) could not be obtained in a pure state by the method of preparation used in this research. Although they did not state their method of analysis, their preparation would naturally appear impure if cyanide distillations were used.

Discussion

The photodissociation of the hexacyanoferrate(II) ion has been discussed fully by Ašperger.[3] It is proposed that the photodissociation of the hexacyanoferrate(III), hexacyanocobaltate(III) and octocyanomolybdate(IV) ions follow a similar type of reaction process, *viz.*

$$\mathrm{M(CN)}_x{}^{-y} + \mathrm{H_2O} \rightleftarrows \mathrm{M(CN)}_{x-1}(\mathrm{H_2O})^{1-y} + \mathrm{CN}^- \qquad \text{(i)}$$

$$\mathrm{M(CN)}_x{}^{-y} + \mathrm{H_3O}^+ \rightleftarrows \mathrm{M(CN)}_{x-1}(\mathrm{H_2O})^{1-y} + \mathrm{HCN} \qquad \text{(ii)}$$

The free cyanide ion formed would hydrolyze instantaneously with a consequent rise in *p*H. The decrease in *p*H of solutions of these complexes when placed in the dark could be explained by a reverse reaction to that shown above. The rate of the reverse reaction may also be increased when the solutions are placed in the light, but if this is the case, the rate of the forward reaction must be increased even more. This reaction hypothesis is also supported by the color change noted with the octacyanomolybdate(IV) when free cyanide was added to the solution. This could be explained by a rapid reversal of the above reaction.

The rate of the "dissociation" reaction appears to be much less than the rate of the "association" reaction, at least in the case of hexacyanoferrate(II). Equal quantities of solutions of 0.05 *f* sodium pentacyanoaquoferrate(II)[14] and 0.05 *f* sodium cyanide were mixed, and the system was tested for the presence of free pentacyanoaquoferrate(II) every few minutes by a sensitive spot test.[15] After three-quarters to one hour all the aquo salt had combined with the cyanide. Therefore, under the above conditions, it combines with free cyanide at the rate of 0.05 mole per hour; but after one hour, a 0.025 *f* solution of hexacyanoferrate(II) has only produced very small amounts of the aquo (II) salt.

It is proposed that the non-reversibility or part-reversibility of the dissociation reaction, as shown by some of the graphs, is caused by a slower secondary reaction between the aquo salt formed and the parent compound. This could account for the lack of decrease in *p*H when the solutions were held in the light at their maximum *p*H value for some time, before being placed in the dark. During this time, equilibrium between all species could be reached. This explanation seems plausible since molecular compounds are known to be formed between some cyanoaquo complex cyanides and fully cyano-substituted complex cyanides.[16,17] Although the results of the hexacyanoferrate(II) experiments differ from those of Ašperger, in that complete reversal of the reaction is not noted, it should be remembered that the conditions of illumination were not the same. It may well be that the reaction by which molecular compounds are formed is also accelerated under the conditions of illumination used in the present research.

It has been stated by Adamson[18] that the first permanent precipitate on titration of potassium cyanide with cobalt(II) chloride occurred at five cyanides per cobalt, and that the stable Co(II) complex cyanide is the penta- and not the hexacyano complex. In the light of the work in this research, it was thought that the equilibrium reaction

$$\mathrm{Co(CN)_5(H_2O)^{-3}} \textit{ or } \mathrm{Co(CN)_5{}^{-3}} + \mathrm{CN}^- \rightleftarrows \mathrm{Co(CN)_6{}^{-4}}$$

might be strongly light-accelerated, and that the $\mathrm{Co(CN)_6{}^{-4}}$ form might be the stable one in the dark. If this were the case, a different titration figure would be obtained, depending on whether the titration was carried out in the light or in the dark. Therefore a 0.10 *f* potassium cyanide solution was titrated with a 0.10 *f* cobalt(II) chloride solution in the dark (using a photographic red lamp as the only source of illumination) and also in a quartz vessel under an ultraviolet lamp. However, no difference in titration figures was observed. Consequently, the pentacyano complex is the stable form of this cobalt complex under all conditions of illumination.

The observations on the potassium hexacyanomanganate(III) solutions are in opposition to those of Adamson, Welker and Wright.[13] They reported that the color of a freshly prepared solution of this complex in dilute potassium cyanide faded from orange-red to pale yellow over a period of 10–15 minutes, and that the *p*H increased at the same time. Meyer[19] and Christensen,[20] they stated, had previously observed the same effects, Christensen supposing that it was due to reduction of the complex by free cyanide, while Meyer supposed that the original orange-red coloration was due to small amounts of $\mathrm{Mn(CN)_3}$. However, the effects observed by Christensen actually referred to the color changes in solutions of the complex when they were heated, diluted, etc., and the effects observed by Meyer related to the difference in color of dilute and concentrated solutions of the complex. The experiments of Christensen, of Meyer, and of Adamson, Welker and Wright were repeated, and results were obtained which agreed with those of the first two workers but not with the latter. It therefore

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(13) A. W. Adamson, J. P. Welker and W. B. Wright, THIS JOURNAL, **73**, 4786 (1951).

(14) K. A. Hofmann, *Ann.*, I **321**, **I** (1900).

(15) H. E. Williams, *J. Chem. Soc.*, 224 (1943).

(16) S. H. C. Briggs, *ibid.*, **117** (II), 1026 (1920).

(17) O. Baudisch, *Ber.*, **62**, 2706 (1929).

(18) A. W. Adamson, THIS JOURNAL, **73**, 5710 (1951).

(19) J. Meyer, *Z. anorg. allgem. Chem.*, **81**, 385 (1913).

(20) O. T. Christensen, *J. prakt. Chem.*, **31**, 163 (1885).

appears that Adamson, Welker and Wright have extrapolated the former workers results to changes in cold solutions on standing; however, the experimental conditions differ greatly in these two cases.

This investigation should be regarded as only a preliminary study on photodissociation in complex cyanide systems but it is of interest in that it gives further examples of slow dissociation in inorganic compounds.

As a preliminary empirical classification, it may be stated that those complex cyanides which are relatively unreactive toward acids, (*e.g.*, potassium hexacyanoferrate(II), potassium hexacyanoferrate(III), potassium hexacyanocobaltate(III) and potassium octacyanomolybdate(IV)), show a photodissociation effect, while those that are fairly easily decomposed by acids (*e.g.*, potassium hexacyanochromate(III) and potassium hexacyanomanganate(III)), show no such effect.

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Absorption Spectra of Some Metallic Chelate Compounds

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This paper points out that the absorption bands of about twenty chelate compounds of Co, Ni, Cu, Pd, Fe and other metals can be generally classified into (A) weak bands of the central metallic cations, and (B) strong bands due to the ligands. In some cases other band types appear. The formation of some of these anomalous bands may be due to the formation of a certain chromophore containing the metals, such as the band of covalent Ni chelates (Mellor, *et al.*) or some of the ferrous chelates indicated by the author. In some cases it is possible to indicate a connection between the extent of the shift of the ligand band caused by chelate formation and the stability of the chelate complex.

Introduction

Little is known about the absorption spectra of metallic chelate compounds. Smith, *et al.*,[2] report that a number of such compounds show intense visible bands differing considerably from their organic ligands, and central metallic cations. Mellor, *et al.*,[3] found that the Ni chelates of square-planar dsp^2 covalent structure show a characteristic band near 400 mμ which is lacking in the Ni chelates of sp^3 ionic structure.

In earlier studies on the metallic complex salts of 2,2′-dipyridyl and 1,10-phenanthroline, K. Yamasaki and his collaborators[4] reported that the visible and ultraviolet absorption spectra of the aqueous solutions were generally composed of: (A) weak absorption bands ($\log \epsilon$ 0–2) in the visible and near ultraviolet regions, characteristic of the central metallic cations, and similar to those bands observed in the hydrated and amine cations of the same metals; (B) very strong absorption bands ($\log \epsilon$ 4–5) in the ultraviolet region which were due to the organic ligand molecules and which were shifted somewhat toward longer wave lengths than the original positions found for the free ligand molecules.

They also reported that both bands were present in such chelates as those of Co(II), Co(III), Ni and Cu, while in the case of Zn and Mn chelates only the latter (B) was observed. In the case of Fe(II) and Fe(III) chelates, a completely new type of absorption band, considerably stronger and quite different from those of Fe(II) and Fe(III) ions, appeared in the visible and near ultraviolet regions.

The author[5] found that a number of other Fe(II) chelates also showed the same type of bands, and it was assumed that the formation of some sort of an unsaturated five-membered intramolecular ring containing ferrous ion acts as a chromophore to produce such absorption bands.

Studies on the absorption spectra of the metallic acetylacetonates carried out by the author and his collaborators,[6] showed that the above-mentioned classification of absorption bands A and B was applicable, and that the Fe(III) chelate also showed a very anomalous absorption curve. Moreover, it was found that the shift of the band of acetylacetone at 273 mμ produced by chelate formation was larger for the more stable trivalent chelates than for the divalent ones which are mainly of ionic character, and that for the divalent chelates, the magnitudes of these shifts were found to be in the order[7]:

$$\mathrm{Cu} > \mathrm{Ni} > \mathrm{Co} > \mathrm{Zn}$$

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(2) G. M. Smith, *et al.*, THIS JOURNAL, **62**, 1669 (1940); **63**, 3071 (1941); **64**, 1650 (1942); however, many of their observed bands might presumably be attributed to the deformed ligand bands discussed in this article.

(3) J. B. Willis and D. P. Mellor, *ibid.*, **64**, 181 (1942); **69**, 1237 (1947); H. A. MacKenzie, D. P. Mellor, J. E. Mills and L. N. Short, *J. Proc. Roy. Soc. New South Wales*, **78**, 70 (1944).

(4) K. Yamasaki, *Bull. Chem. Soc. Japan*, **12**, 390 (1937); **14**, 538 (1939); **15**, 130, 461 (1940); K. Yamasaki, H. Yokoi and K. Sone, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **69**, 137 (1948); *C. A.*, **44**, 9295 (1950).

(5) K. Sone, *Bull. Chem. Soc. Japan.*, **25**, 1 (1952).

(6) K. Sone, I. Miyake, H. Kuroya and K. Yamasaki, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **69**, 70 (1948); K. Yamasaki and K. Sone, *Nature*, **166**, 998 (1950).

(7) The ultraviolet spectra of the divalent chelates can be considered as the deformed ligand band, although in the Cu chelate a new band appears at *ca.* 245 mμ. The Cu chelate does not obey Beer's law in the near ultraviolet region, and also shows a weak band at 640 mμ which is due to the Cu ion. Similar but weaker bands were observed also for Ni and Co(II) chelates. The ultraviolet spectra of trivalent chelates are very different from those of the divalent ones, and generally two bands appear at *ca.* 270 and 300–330 mμ, both of which might be considered to be the ligand band extremely deformed from its original position. The visible and near-ultraviolet weak bands of Co(III) and Cr are those of the central cations; the band of the Fe(III) chelate in this region is quite anomalous as described in the text.