Contribution from the Chemical Institute of the University,
Centro Nazionale di Chimica delle Radiazioni e dei Radioelementi, Bologna, Italy,
and the Institute of General Chemistry of the University,
Centro Nazionale di Chimica dei Composti di Coordinazione ed
Elemento-organici del Consiglio Nazionale delle Ricerche, Ferrara, Italy

Kinetics of the Acid Hydrolysis of Dicyanobis(2,2′-bipyridine)iron(II) and Dicyanobis(1,10-phenanthroline) iron(II)

By VINCENZO BALZANI, VITTORIO CARASSITI, and LUCA MOGGI

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Detailed kinetic studies on the acid hydrolysis of the complexes $Fe(AA)_2(CN)_2$ (AA = 2,2′-bipyridine or 1,10-phenanthroline) are reported and discussed. The rate of hydrolysis was measured spectrophotometrically or by extraction of the neutral complex into isoamyl alcohol and then spectrophotometric analysis of the alcoholic solution. The first-order rate constants for acid hydrolysis are independent of ionic strength, but they decrease when the hydrogen ion concentration increases above 0.1 *N*. This acid dependence of the hydrolysis reaction is explained on the basis that protonated species react more slowly than do the neutral complexes. The activation energies (31 kcal.) and entropies (17 e.u. at 50°) are equal for both $Fe(bipy)_2(CN)_2$ and $Fe(phen)_2(CN)_2$ and are independent of hydrogen ion concentration. The observed results are discussed and a mechanism for the hydrolysis reaction is proposed. Photochemical reactions of $Fe(bipy)_2(CN)_2$ are also investigated.

Introduction

In a previous paper[1] the photochemical behavior of ferrocyanide solutions in the presence of 2,2′-bipyridine or 1,10-phenanthroline (generally bidentate ligands AA) was reported. It was demonstrated that light causes the formation of the complexes $Fe(AA)(CN)_4^{2-}$ and $Fe(AA)_2(CN)_2$, and the mechanisms of these reactions were investigated. These mixed ligand complexes have long been known,[2] and the behavior in photosubstitution reactions has been reported[3] for $Fe(bipy)(CN)_4^{2-}$ and $Fe(phen)(CN)_4^{2-}$.

The related compounds dicyanobis(2,2′-bipyridine)iron(II) and dicyanobis(1,10-phenanthroline)iron(II) have now been investigated. This paper reports kinetics of their thermal acid hydrolysis and also the photochemical reactions of $Fe(bipy)_2(CN)_2$.

Experimental

Preparation of Complexes.—$Fe(bipy)_2(CN)_2$ and $Fe(phen)_2(CN)_2$ were prepared following Barbieri's method[2] as modified by Schilt.[4]

Thermal Acid Hydrolysis.—All kinetic studies were carried out in water solutions at regulated temperatures (±0.1°). Initial complex concentrations were approximately 1×10^{-4} *M*, as this concentration afforded the most convenient absorbancy readings (see below). The acid hydrolysis was carried out at 20, 30, 40, 50, and 60°, in various acid solutions and also in buffer solutions (Sørensen's citrate–HCl mixtures); pH values are related to 20°. The temperature coefficients of pH for these buffer solutions are very low,[5] negligible for our purposes.

The experimental conditions are given in Tables I and II. In addition, the kinetic salt effect was investigated by adding NaCl, NaBr, $NaNO_3$, KCl, and Na_2SO_4 to the reaction mixture (maximum value of ionic strength: $^1/_2\Sigma c_i z_i^2 = 3.10$; $[H^+] = 0.1$ *M*).

For solutions containing a sufficient concentration of hydrogen ion ($[H^+] > 0.1$ *M*), the acid hydrolysis of $Fe(AA)_2(CN)_2$ is complete, and the final reaction products are $Fe(H_2O)_6^{+2}$, HCN, and AAH^+ ($Fe(H_2O)_6^{2+}$ detected by analytical tests and AAH^+ by its ultraviolet spectrum[6,7]).

Therefore the visible absorption band of $Fe(AA)_2(CN)_2$ disappears as it reacts, and the rate of reaction may be followed spectrophotometrically. The changes in optical density with time were measured at the maximum of the visible absorption band, the wave length position of which varies considerably with increasing acid concentration.[8] At low $[H^+]$, it is not possible to measure directly the rate of the hydrolysis reaction by a spectrophotometric method. In fact at low H^- concentration, $Fe(bipy)_3^{2+}$ and $Fe(phen)_3^{2+}$ are also produced[9]; these species strongly absorb in the visible region of the spectrum. In such cases the changes in the concentration of $Fe(AA)_2(CN)_2$ with time were measured by extracting the neutral complex in isoamyl alcohol and then making a spectrophotometric analysis of the alcoholic solution. The procedure used for this extraction was as follows: 5 ml. of isoamyl alcohol was added to 5 ml. of the sample solution, cooled to quench the reaction, and the mixture was stirred for a fixed time. Then the optical density of the alcoholic solution, containing only the neutral complex $Fe(AA)_2(CN)_2$, was measured. At high H^+ concentration this method gives, within experimental errors, the same results as does the direct spectrophotometric method.

Spectrophotometric measurements were made on a Beckman DU spectrophotometer using 1-cm. quartz cells.

Photochemical Reactions.—Photochemical studies were made only on $Fe(bipy)_2(CN)_2$. The ϵ_{365} and the solubility of the analogous phenanthroline complex are too low for sufficient light absorption to permit its investigation. The same general irradiation equipment was used as previously described.[1] A 25-ml. sample of a 1.4×10^{-4} *M* solution of the reagent was placed in the reaction cell (thickness 3.0 cm.) and exposed to light of wave length 365 mμ (intensity *ca.* 1×10^{-6} einstein/min.), isolated from a Hanau mercury vapor lamp by means of a suitable filter combination.[10] The ϵ_{365} of $Fe(bipy)_2(CN)_2$ (dependent upon the acid concentration) is about 4.5×10^3.

Since the temperature coefficient is presumably lower for the

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(1) V. Balzani, V. Carassiti, and R. S. Loos, *Ann. chim.* (Rome), **54**, 103 (1964).

(2) G. A. Barbieri, *Rend. accad. nazl. Lincei*, [6] **20**, 273 (1934).

(3) V. Balzani, V. Carassiti, and L. Moggi, *Ann. chim.* (Rome), **54**, 251 (1964).

(4) A. A. Schilt, *J. Am. Chem. Soc.*, **82**, 3000 (1960).

(5) L. E. Walbum, *Biochem. Z.*, **107**, 219 (1920).

(6) P. Krumholz, *J. Am. Chem. Soc.*, **73**, 3487 (1951).

(7) V. Balzani, A. Bertoluzza, V. Carassiti, and A. Malaguti, *Ann. chim.* (Rome), **52**, 1052 (1962).

(8) A. A. Schilt, *J. Am. Chem. Soc.*, **82**, 5779 (1960).

(9) The production of $Fe(AA)_3^{2+}$ in the acid hydrolysis of $Fe(AA)_2(CN)_2$ at low acidity was demonstrated spectrophotometrically: the visible spectrum of the solution, after total extraction of the reagent by means of isoamyl alcohol, is consistent with the spectrum[1] of $Fe(AA)_3^{2+}$.

(10) E. J. Bowen, "The Chemical Aspects of Light," Clarendon Press, Oxford, 1946, p. 279.

photochemical than for the thermal reaction, the photochemical experiments were done at 20 ± 0.2° in order to reduce the effect of the simultaneous thermal reaction. The photoreactions were followed spectrophotometrically as were the thermal reactions, and the changes in H^+ concentration were measured by a Leeds and Northrup glass electrode pH meter. Side by side with the photoreaction, the thermal reaction was followed also on a batch of the same preparation.

TABLE I
FIRST-ORDER RATE CONSTANTS FOR THE ACID HYDROLYSIS OF $Fe(bipy)_2(CN)_2$

	$k \times 10^5$, sec.$^{-1}$				
Solvent	20°	30°	40°	50°	60°
5 *N* HCl	...	...	0.185	0.840	3.85
2 *N* HCl	...	...	0.565	2.60	11.5
1 *N* HCl	0.026	0.140	0.695	3.25	14.0
0.5 *N* HCl	0.032	...	0.755	3.45	15.0
0.1 *N* HCl	0.033	0.155	0.810	3.70	16.0
0.05 *N* HCl	0.033	0.165	0.805	3.55	15.5
10^{-2} *N* HCl	0.033	...	0.810	3.40	16.5
10^{-3} *N* HCl	...	...	0.845	3.45	15.5
10^{-4} *N* HCl	...	...	0.805	...	...
Buffer pH 2	...	...	0.825	3.50	16.0
Buffer pH 3	...	...	0.830	3.70	16.5
Buffer pH 4	...	...	0.835	3.60	15.0
1 *N* H_2SO_4	0.031	0.170	0.775	3.60	...
0.1 *N* H_2SO_4	0.035	0.170	0.865	3.80	...
0.05 *N* H_2SO_4	0.036	0.180	0.825	...	...
1 *N* $HClO_4$	...	0.130	0.660	...	...
0.1 *N* $HClO_4$	0.035	0.160	...	3.70	...
0.05 *N* $HClO_4$	0.034	0.170	0.830	...	...

TABLE II
FIRST-ORDER RATE CONSTANTS FOR THE ACID HYDROLYSIS OF $Fe(phen)_2(CN)_2$

	$k \times 10^5$, sec.$^{-1}$				
Solvent	20°	30°	40°	50°	60°
5 *N* HCl	...	...	0.170	0.785	3.70
2 *N* HCl	...	...	0.660	3.05	14.5
1 *N* HCl	0.039	0.185	0.960	4.20	20.5
0.5 *N* HCl	...	...	1.10	5.35	23.0
0.1 *N* HCl	0.047	0.230	1.25	5.80	27.5
0.05 *N* HCl	0.049	0.245	1.25	5.75	27.0
10^{-2} *N* HCl	...	...	1.20	6.10	27.0
10^{-3} *N* HCl	...	...	1.30	6.00	26.0
10^{-4} *N* HCl	...	...	1.25	...	...
Buffer pH 2	...	...	1.20	6.00	27.5
Buffer pH 3	...	...	1.30	6.05	25.5
Buffer pH 4	...	...	1.35	5.90	25.5
1 *N* H_2SO_4	...	0.225	1.10	5.30	...
0.1 *N* H_2SO_4	...	0.255	1.35	6.15	...
0.05 *N* H_2SO_4	...	0.240	1.30	...	...
0.5 *N* $HClO_4$	0.048	...	1.10	5.40	...
0.1 *N* $HClO_4$	0.048	0.240	1.25	...	...
0.05 *N* $HClO_4$	0.052	0.260	1.25	...	...

Results

Thermal Acid Hydrolysis.—Excellent first-order behavior was obtained in all cases (see Fig. 1). First-order rate constants, summarizing the experimental data, are given in Tables I and II; the accuracy of these values is better than 5%.

The activation energy for the acid hydrolysis reaction for both $Fe(bipy)_2(CN)_2$ and $Fe(phen)_2(CN)_2$, calculated between 30 and 60°, is 31 ± 1 kcal. at all experimental conditions.

The activation entropy is positive and high (*ca.* 17 e.u. at 50°) for both complexes and for the different experimental conditions.

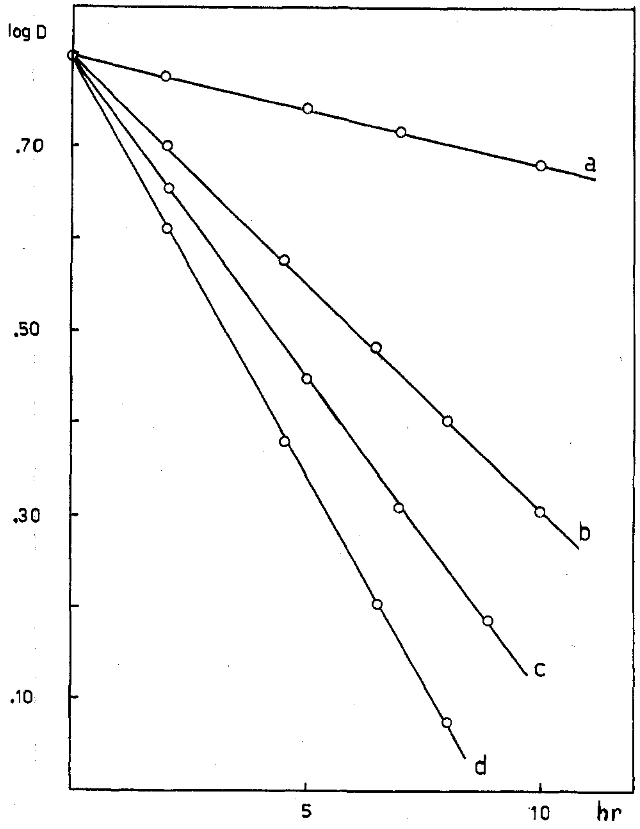


Fig. 1.—Plots of log *D* *vs.* time for the acid hydrolysis of $Fe(phen)_2(CN)_2$ at 50° with various concentrations of hydrochloric acid present: a, 5 *N*; b, 2 *N*; c, 1 *N*; d, 0.1 *N* (arbitrary displacement along the ordinate axis).

Values of kinetic constants for experiments made in the presence of added salts are constant and independent of the ionic strength.

Photochemical Acid Hydrolysis of $Fe(bipy)_2(CN)_2$.—Light of 365 mμ on an aqueous solution of $Fe(bipy)_2(CN)_2$ initially causes a slow increase in pH (~0.5 unit/5 hr.) and a small decrease in complex concentration (~3%/5 hr.). At longer times the pH and the complex concentration tend to assume a stationary value; the system appears to reach a photostationary equilibrium. Experiments in buffer solutions of low acidity (pH 5.0 and 6.6) show that the system attains a photostationary state more and more rapidly as the acidity of the solution decreases.

On the other hand, at higher H^+ concentration the photodecomposition of $Fe(bipy)_2(CN)_2$ goes to completion, giving rise to linear plots of the optical density *vs.* time, after corrections are made for the simultaneous thermal reaction and the small change in the light absorption (<2%). Therefore, in these conditions, the concentration of the reagent decreases linearly with time (zero-order reaction); values of the quantum yield obtained are given in Table III.

Discussion

Thermal Acid Hydrolysis.—Spectrophotometric data and analytical tests show that the acid hydrolyses of

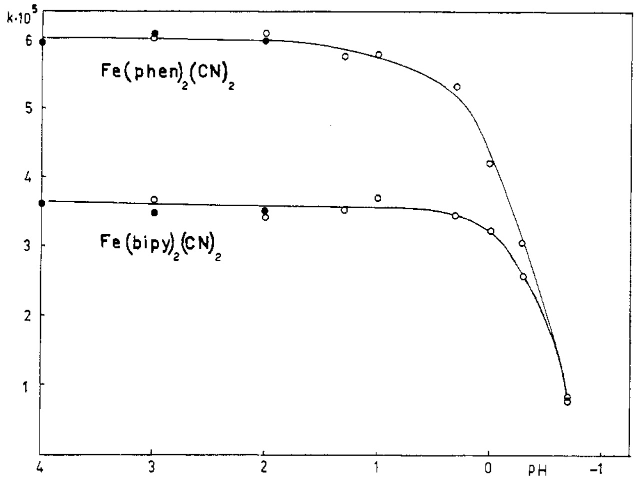
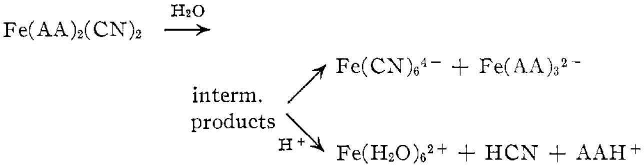


Fig. 2.—Effect of acid on the rate of hydrolysis of $Fe(bipy)_2(CN)_2$ and $Fe(phen)_2(CN)_2$ at 50°: ●, experiments in buffer solutions; ○, experiments in solutions of hydrochloric acid (considered completely dissociated).

TABLE III
QUANTUM YIELD FOR THE PHOTODECOMPOSITION OF $Fe(bipy)_2(CN)_2$

Solvent	$Nh\nu$/min. × 10^6	Φ × 10^3	Solvent	$Nh\nu$/min. × 10^6	Φ × 10^3
5 *N* HCl	0.85	1.3	1 *N* H_2SO_4	1.43	1.2
1 *N* HCl	1.38	1.2	0.1 *N* H_2SO_4	1.44	1.1
0.1 *N* HCl	1.41	1.2	0.05 *N* H_2SO_4	1.60	1.2
0.05 *N* HCl	1.54	1.3	0.1 *N* $HClO_4$	1.37	1.4
Buffer pH 3	0.90	1.3	0.05 *N* $HClO_4$	1.35	1.4

$Fe(bipy)_2(CN)_2$ and $Fe(phen)_2(CN)_2$ follow the scheme



$$Fe(AA)_2(CN)_2 \xrightarrow{H_2O}$$

$$\text{interm. products} \nearrow Fe(CN)_6^{4-} + Fe(AA)_3^{2-}$$

$$\text{interm. products} \xrightarrow[H^+]{} Fe(H_2O)_6^{2+} + HCN + AAH^+$$

Final products, however, are not the object of this discussion; it is more interesting in fact to observe the change of the pseudo-first-order rate constant with $[H^+]$.

The rates of most acid hydrolysis reactions are usually independent of hydrogen ion concentration below a pH of about 4. It has also been observed[11] that when ligands (1) are strongly basic, (2) have a large tendency to hydrogen bond, or (3) are flexible basic bi- or multidentate, acid hydrolysis reactions are acid catalyzed.

The values given in Tables I and II and plotted in Fig. 2 clearly show that the first-order rate constants of acid hydrolysis for $Fe(bipy)_2(CN)_2$ and $Fe(phen)_2(CN)_2$ do not increase but rather decrease with increasing $[H^+]$. This observed acid dependence, at first sight surprising, is explained providing that the protonated species react more slowly than do the neutral complexes.

Schilt[4,8] first observed that $Fe(bipy)_2(CN)_2$ and $Fe(phen)_2(CN)_2$ react reversibly with strong acid to give mono- and diprotonated ions. He initially suggested that hydrogen is attached directly to the metal in the protonated species. Later Wilkinson, finding no clear evidence for hydrogen to metal bonding by high-resolution n.m.r. or infrared techniques, proposed[12] that protonation involves the bound cyanide groups rather than the central metal atom. In addition, Hamer and Orgel found[13] that $Fe(phen)_2(CN)_2$, on treatment with methyl sulfate, is converted to the methyl isocyanide derivative $Fe(phen)_2(C{\equiv}NCH_3)_2^{2+}$; its absorption spectrum characteristics are not changed by treatment with sulfuric acid and closely resemble those of the diprotonated dicyano species present in 12 *M* H_2SO_4. Thus it appears that protonation occurs at the cyanide groups to give rise to the isocyanide derivative

$$Fe(AA)_2(CN)_2 + 2H^+ \rightleftarrows Fe(AA)_2(C{\equiv}NH)_2^{2+}$$

A strong displacement to the ultraviolet of the visible spectrum of $Fe(AA)_2(CN)_2$ in acid solution is in agreement with this hypothesis.[14] Therefore it follows that the reactions involved in these systems may be schematically written as

$$Fe(AA)_2(CN)_2 + nH^+ \rightleftarrows Fe(AA)_2(CN)_2H_n^{n+}$$

$$Fe(AA)_2(CN)_2 \xrightarrow{k_0} \text{products}$$

$$Fe(AA)_2(CN)_2H^+ \xrightarrow{k_1} \text{products}$$

$$Fe(AA)_2(CN)_2H_2^{2+} \xrightarrow{k_2} \text{products}$$

and the over-all rate equation results

$$-\frac{d[C]}{dt} = \frac{k_0 + k_1K'[H^+] + k_2K''[H^+]^2}{1 + K'[H^+] + K''[H^+]^2}[C] \quad (1)$$

where [C] is the total concentration of the reagent, including protonated forms,[15] k_0, k_1, and k_2 are, respectively, the pseudo-first-order rate constants for the acid hydrolysis of the non-, mono-, and diprotonated complexes, and K' and K'' are the stability constants of mono- and diprotonated complexes.

$$K' = \frac{[Fe(AA)_2(CN)_2H^+]}{[Fe(AA)_2(CN)_2][H^+]} \quad (2)$$

$$K'' = \frac{[Fe(AA)_2(CN)_2H_2^{2+}]}{[Fe(AA)_2(CN)_2][H^+]^2} \quad (3)$$

According to the experimental linear plot of log *D* *vs.* time (Fig. 1), integration of eq. 1 gives

$$\ln [C] = -kt + \text{constant}$$

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[11] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1960, p. 152.

[12] G. Wilkinson in "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 56.

[13] N. H. Hamer and L. E. Orgel, *Nature*, **190**, 439 (1961).

[14] A. A. Schilt, *J. Am. Chem. Soc.*, **85**, 94 (1963).

[15] In this interpretation eq. 1 explains the experimental results obtained by the direct spectrophotometric method, since this method cannot distinguish between the protonated and nonprotonated species. If [C] = $[Fe(AA)_2(CN)_2]$, eq. 1 represents the rate of disappearance of the nonprotonated form alone; therefore in this last interpretation eq. 1 explains results obtained by the extraction method, which measures only the concentration of the neutral complex.

where

$$k = \frac{k_0 + k_1K'[H^+] + k_2K''[H^+]^2}{1 + K'[H^+] + K''[H^+]^2} \quad (4)$$

is the over-all pseudo-first-order rate constant.

Experimental data (Tables I and II and Fig. 2) also show that k is not acid dependent at $[H^+] < 0.1$, whereas k decreases at higher hydrogen ion concentration. The proposed reaction scheme is also in agreement with this result. Considering eq. 4, it is apparent that at low $[H^+]$ the values of $K'[H^+]$ and $K''[H^+]^2$ are very low. From eq. 2 and 3 it follows that these values represent the ratios $[Fe(AA)_2(CN)_2H^+]/[Fe(AA)_2(CN)_2]$ and $[Fe(AA)_2(CN)_2H_2^{2+}]/[Fe(AA)_2(CN)_2]$, respectively. Furthermore the visible spectrum of acid solutions of $Fe(AA)_2(CN)_2$ differs from the visible spectrum of a neutral solution only at high acidity ($[H^+] > 0.1$). This shows that in solutions of low acidity the nonprotonated species are the most prevalent.

Consequentially, at low acidity the terms in eq. 4 containing $[H^+]$ and $[H^+]^2$ are negligible, k_1 and k_2 being also smaller than k_0. This can explain the initial behavior of the plot of k *vs.* $-\log [H^+]$ (Fig. 2). At higher acidity it is not possible to make these approximations. The effect of the terms containing $[H^+]$ and $[H^+]^2$ is greater in the denominator than in the numerator of eq. 4, since k_1 and k_2 are smaller than k_0 (in fact the derivative of k against $[H^+]$ is negative for $k_2 < k_1 < k_0$). It then follows that k decreases when the acid concentration increases above 0.1 N, in accord with the experimental results.

The independence of the rate constants on ionic strength proves that a nonionic species is involved in the rate-determining step; according to our hypothesis the most reactive form is the nonprotonated complex.

The experimental data show that the complexes $Fe(bipy)_2(CN)_2$ and $Fe(phen)_2(CN)_2$ behave very much the same in their acid hydrolysis reaction. On the other hand, large differences were observed[16-19] for the acid hydrolysis of $Fe(bipy)_3^{2+}$ and $Fe(phen)_3^{2+}$ and were explained on the basis of the different flexibility of the ligands. This suggests that the rate-determining step for the acid hydrolysis of $Fe(bipy)_2(CN)_2$ and $Fe(phen)_2(CN)_2$ involves a CN^- group rather than the different bidentate groups.

In this case, granting that protonation occurs at the nitrogen atom of cyanide groups, and on the supposition that an SN1-type mechanism is involved in the reaction, the experimental data require that CNH is replaced more slowly than CN^-[20]; the reactions of cyanide exchange with the protonated $Mn(CN)_6^{n-}$ complexes show the opposite effect.[21] However, if the rate-determining step involves the different bidentate ligands, then they behave very much the same in this reaction; moreover it is more difficult to remove the bidentate ligands from the CNH species relative to the nonprotonated.

Photochemical Acid Hydrolysis of $Fe(bipy)_2(CN)_2$.—The quantum yield is found to be approximately constant and always very small. Therefore this complex is very "inert," both in thermal and in photochemical reactions. A comparison of these results with those reported in previous papers[1,3,22] shows that the replacement of CN^- groups in $Fe(CN)_6^{4-}$ with bipyridine stabilizes the complex against photodecomposition.

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(16) J. H. Baxendale and P. George, *Trans. Faraday Soc.*, **46**, 736 (1950).

(17) P. Krumholz, *J. Phys. Chem.*, **60**, 87 (1956).

(18) T. S. Lee, I. M. Kolthoff, and D. L. Leussing, *J. Am. Chem. Soc.*, **70**, 3596 (1948).

(19) J. E. Dickens, F. Basolo, and H. M. Neumann, *ibid.*, **79**, 1286 (1957).

(20) This hypothesis is in agreement with the results of experiments, close to publication, on the acid hydrolysis of $Fe(phen)_2(CNCH_3)_2^{2+}$.

(21) A. Adamson, J. P. Welker, and M. Volpe, *J. Am. Chem. Soc.*, **72**, 4030 (1950).

(22) V. Carassiti and V. Balzani, *Ann. chim.* (Rome), **50**, 782 (1960).