appreciable below 300 mμ. The quantum yield of photoreduction of thiobenzophenone is 4.74 × 10^{-3}, only about half as large as that for benzophenone.

The far ultraviolet is sufficiently energetic to affect thiobenzophenone even in a relatively inert solvent such as cyclohexane. Products could not be isolated since they absorb light and are subsequently photolyzed bylig ht of this wave length region. All one observes as irradiation proceeds is a decrease in absorption in the K band and an increase in end absorption below 210 mμ.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY, LAFAYETTE, INDIANA]

Kinetics of 1,10-Phenanthroline Chelation. III. Effect of Cyanide and Azide Ions on the Dissociation Rate of Tris-(1,10-phenanthroline)-iron(II)

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Cyanide and azide ions as well as hydroxide ion greatly increase the rate of displacement of 1,10-phenanthroline from the tris-(1,10-phenanthroline)-iron(II) complex. A mechanism is proposed based on the interaction of the nucleophile with the Fe(II) at its octahedral face within the pockets formed between the 1,10-phenanthroline molecules in the tris complex.

Introduction

A pronounced hydroxide ion effect on the rate of dissociation of tris-(1,10-phenanthroline)-iron(II) was reported previously.[3] This effect is of particular interest because an SN1CB mechanism is not feasible with 1,10-phenanthroline as a ligand. In view of the efforts to prove the SN1CB mechanism[4,5] or the SN2 mechanism[6] for Co(III) reactions, it is worthwhile to examine other nucleophiles with this Fe(II) system which is isoelectronic with Co(III). The present work shows that the hydroxide ion behavior was not a specific effect and that cyanide ion and azide ion also greatly accelerate the dissociation of FePh_3^{+2}. As a subsequent paper[7] shows, this is in striking contrast to the behavior of NiPh_3^{+2} substitution reactions.

Experimental

$\text{FePh}_3(\text{ClO}_4)_2$ was prepared by the reaction of stoichiometric quantities of ferrous ammonium sulfate and 1,10-phenanthroline monohydrate in water and precipitation of the perchlorate salt with sodium perchlorate. The solid was twice recrystallized from aqueous sodium perchlorate solutions.

$\text{FePh}_2(\text{CN})_2 \cdot 2\text{H}_2\text{O} \cdot \text{CHCl}_3$ was prepared by the method proposed by Schilt[8,9] for the preparation of $\text{FePh}_2(\text{CN})_2$. After recrystallization from chloroform in a Soxhlet extractor, shiny dark purple crystals were obtained which were washed with a small quantity of chloroform and dried over magnesium perchlorate.

Anal. Calcd. for $\text{FePh}_2(\text{CN})_2 \cdot 2\text{H}_2\text{O} \cdot \text{CHCl}_3$: C, 51.89; H, 3.39; N, 13.45; Cl, 17.02; Fe, 8.94. Found: C, 52.15; H, 3.48; N, 13.37; Cl, 17.50; Fe, 9.06.

Part of the chloroform containing product was recrystallized from sulfuric acid. The solid was dried *in vacuo* over sulfuric acid and stored over magnesium perchlorate.

Anal. Calcd. for $\text{FePh}_2(\text{CN})_2 \cdot \text{H}_2\text{O}$: C, 64.21; H, 3.73; N, 17.28. Found: C, 62.98; H, 3.75; N, 17.61.

Sodium azide was recrystallized from hot water and standardized by oxidation with permanganate ion.[10]

Spectra were measured on a Cary 14 spectrophotometer and kinetic studies were followed with a thermostated Beckman DU spectrophotometer. All *p*H measurements were made on a Beckman Model G *p*H meter. All kinetic studies were made at constant ionic strength maintained with Na_2SO_4 or KCl. The precision of rates was 5% or better.

Results and Conclusions

Cyanide System.—In his original paper describing the properties of the $\text{FePh}_2(\text{CN})_2$ and FePh(CN)_4^{-2} complexes,[8] Schilt proposed the rapid and complete disproportionation of the neutral complex in water

$$2\text{FePh}_2(\text{CN})_2 \rightleftharpoons \text{FePh}_3^{+2} + \text{FePh(CN)}_4^{-2} \quad (1)$$

This was based on spectrophotometric analyses of aqueous solutions of $\text{FePh}_2(\text{CN})_2$. However, he reported the concentration of the tetracyano complex as twice the concentration of FePh_3^{+2}, which is impossible in the disproportionation reaction.

In this Laboratory it was found that aqueous mixtures of FePh_3^{+2} and FePh(CN)_4^{-2} would not form sufficient quantities of $\text{FePh}_2(\text{CN})_2$ to be extracted by chloroform for several days. On the other hand all the 1,10-phenanthroline containing species could be extracted into chloroform from solutions of $\text{FePh}_2(\text{CN})_2$ which were one week old. Neither of these facts is consistent with the disproportionation reaction. If an equilibrium such as (1) occurs, it must be very slow in both directions.

The aqueous spectrum of $\text{FePh}_2(\text{CN})_2$ has an ϵ_{max} at 510 mμ, about 2/3 that for FePh_3^{+2}, but the former spectrum is broader and is distinguishable from the latter. If the ratio of FePh(CN)_4^{-2} to FePh_3^{+2} is calculated from the spectrum assuming the disproportionation in equation 1, the inconsistent value of 2.0 is found. Furthermore, the total iron content is 17% too high when calculated in this manner.

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[1] Abstracted from a thesis submitted by L. P. Morgenthaler to the Graduate School of Purdue University, June 1961, in partial fulfillment of the requirements of the degree of Doctor of Philosophy.

[2] Western Electric Engineering Research Center, Princeton, New Jersey.

[3] D. W. Margerum, *J. Am. Chem. Soc.*, **79**, 2728 (1957).

[4] F. Basolo, H. H. Schmidtke and R. G. Pearson, *ibid.*, **82**, 4434 (1960).

[5] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y.

[6] C. K. Ingold, R. S. Nyholm and M. L. Tobe, *Nature*, **187**, 477 (1960); D. D. Brown, C. K. Ingold and R. S. Nyholm, *J. Chem. Soc.*, 2678 (1953); C. K. Ingold, Fifth Weizmann Memorial Lecture Series, the Weizmann Science Press of Israel, 1959.

[7] L. P. Morgenthaler and D. W. Margerum, *J. Am. Chem. Soc.*, **84**, 710 (1962).

[8] A. A. Schilt, *ibid.*, **79**, 5421 (1957).

[9] A. A. Schilt, *ibid.*, **82**, 3000 (1960).

[10] J. H. van der Meulen, *Rec. trav. chim.*, **67**, 600 (1948).

The $FePh_2(CN)_2$ complex appears to be stable in aqueous solution. The sharp color change from orange-red to purple on extraction of this compound into chloroform apparently is due to a solvent interaction.[8,9,11]

The rate of dissociation of $FePh_3^{+2}$ in the presence of CN^-, measured spectrophotometrically assuming $FePh_2(CN)_2$ as the product of the reaction, was found to be identical with the rate of formation of $FePh_2(CN)_2$ measured by extraction of the neutral complex into chloroform and then spectrophotometric analysis of the chloroform solutions at 575 mμ.

The dissociation rates of $FePh_3^{+2}$ in excess CN^- were obtained from plots of log $[FePh_3^{+2}]$ against time. The plots were linear for 85% of the reaction. The concentration of $FePh_3^{+2}$ was calculated by the relation

$$[FePh_3^{+2}] = \frac{A - \epsilon_{FePh_2(CN)_2}[FePh_3^{+2}]_0}{\epsilon_{FePh_3} - \epsilon_{FePh_2(CN)_2}}$$

where A is the absorbance in 1 cm. cells, $\epsilon_{FePh_2(CN)_2}$ is the molar absorptivity of $FePh_2(CN)_2$ at 510 mμ which is 7,400, ϵ_{FePh_3} is the molar absorptivity of $FePh_3^{+2}$ at 510 mμ which is 10,700 and $[FePh_3^{+2}]_0$ is the initial concentration of the complex which was 3.13×10^{-5} M for most solutions. The cyanide ion concentration was calculated from the pH and the acid dissociation constant for HCN of 4.5×10^{-10} [12,13] at 25.0°. This constant changes little with ionic strength but appropriate temperature corrections were made.[14] The corrections for cyanide hydrolysis were small in most cases. With excess cyanide the values for $k_1 = k_0/[CN^-]$ were the same at different pH since the hydroxide rate was negligible compared to the cyanide rate. The kinetic data are summarized in Table I, where k_0 is a pseudo first-order rate constant. The plot of k_0 against $[CN^-]$ is linear with the intercept at zero $[CN^-]$, in agreement with the previously measured dissociation rate constant, k_d. The second order rate constants (k_1) for various conditions of temperature and ionic strength are given in Table II. Between 10° and 35° E_a was 20 ± 3 kcal. in 2 M KCl, ΔH^* was 20 kcal. and ΔS^* was -3 e. u. The data in Table II indicate that sulfate ion is much more effective at repressing the reaction rate than is chloride ion.

The reaction of cyanide ion with $FePh_3^{+2}$ must follow two paths, the first being the well established first order dissociation of 1,10-phenanthroline from the complex. This is followed by the rapid addition of two cyanide ions. The second path is a second order reaction with direct cyanide attack followed by the rapid addition of another cyanide.

$$FePh_3 \xrightarrow{k_d} FePh_2^{+2} + Ph$$

$$FePh_2^{+2} + 2CN^- \xrightarrow{\text{fast}} FePh_2(CN)_2$$

$$FePh_3^{+2} + CN^- \xrightarrow{k_1} FePh_2CN^+ + Ph$$

$$FePh_2CN^+ + CN^- \xrightarrow{\text{fast}} FePh_2(CN)_2$$

TABLE I

DISSOCIATION OF $FePh_3^{+2}$ IN THE PRESENCE OF CYANIDE ION

Temp., °C.	μ	pH	Corrected $[CN^-]$	$k_0 \times 10^3$, min.$^{-1}$
25.0	0.01	10.30	0.00620	13.7[a]
25.0	0.10	10.20	.00605	6.61[a]
25.0	1.00	10.05	.00571	5.51[a]
25.0	0.10	10.38	.00970	9.17[a]
25.0	.10	10.11	.00393	6.19[a]
25.0	.10	9.87	.00177	4.78[a]
25.0	.10	9.68	.00690	4.26[a]
25.0	2.0	10.49	.0087	10.9
25.0	2.0	10.89	.0260	20.9
25.0	2.0	11.04	.0533	38.4
25.0	2.0	11.18	.0791	55.9
25.0	2.0	11.20	.105	76.6
25.0	2.0	11.32	.133	98.9
25.0	2.0	11.58	.186	108
25.0	2.0	11.67	.239	190
25.0	2.0	11.86	.294	175[b]
25.0	2.0	11.99	.347	200[b]
25.0	2.0	12.00	.401	215[b]
25.0	2.0	12–13	.80	480
25.0	2.0	12–13	.90	490
25.0	2.0	12–13	1.00	600
10.0	2.0	11.21	0.105	6.52
10.0	2.0	11.65	.239	18.4
10.0	2.0	12.05	.534	35.5
35.0	2.0	11.20	.105	168
35.0	2.0	11.68	.239	398
35.0	2.0	12.04	.534	696

[a] Ionic strength controlled with Na_2SO_4. Ionic strength for all other solutions was adjusted with KCl. [b] $FePh_3^{+2} = 6.26 \times 10^{-6}$; for all others $= 3.13 \times 10^{-5}$

TABLE II

SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF $FePh_3^{+2}$ WITH CYANIDE AND AZIDE IONS

Nucleophile	Maximum nucleophile concn., M	Temp., °C.	μ	Added salt	k_1, min.$^{-1}$ l. mole^{-1}
CN^-	6.2×10^{-3}	25.00 ± 0.05	0.01	Na_2SO_4	1.6
CN^-	9×10^{-3}	25.00 ± .05	0.10	Na_2SO_4	0.48
CN^-	5.7×10^{-3}	25.00 ± .05	1.00	Na_2SO_4	.28
CN^-	0.53	10.0 ± .1	2.00	KCl	.073
CN^-	1.00	25.00 ± .05	2.00	KCl	.60
CN^-	0.53	35.00 ± .05	2.00	KCl	1.5
N_3^-	1.00	10.0 ± .1	2.00	KCl	9.1×10^{-4}
N_3^-	1.00	25.00 ± .05	2.00	KCl	9.9×10^{-3}
N_3^-	1.00	35.00 ± .05	2.00	KCl	2.4×10^{-2}

Then the observed dissociation rate constant k_0 up to a $[CN^-]$ of 1.00 M is expressed as

$$k_0 = k_d + k_1[CN^-]$$

Azide System.—The dissociation of $FePh_3^{+2}$ in the presence of azide ion was followed spectrophotometrically at 510 mμ but unlike the cyanide system the products of the reaction were essentially colorless. The rate constants obtained from the first 15% loss of $FePh_3^{+2}$ are given in Table III. These reactions were pH 9.1 to 9.5 where OH^- attack and the hydrolysis of azide ion are negligible. After 15% of the $FePh_3^{+2}$ absorbance had disappeared, the apparent rate slowed considerably. This change in rate could be caused by either the formation of an absorbing product or by back reaction of the products. If the product of the reaction absorbs appreciably, a plot of the pseudo first-order rate constant k_0 against $[N_3^-]$ will de-

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

(12) H. T. Britton and R. A. Robinson, *J. Chem. Soc.*, 458 (1931).

(13) H. T. Britton and E. N. Dodd, *ibid.*, 2332 (1931).

(14) R. W. Harman and F. P. Worley, *Trans. Faraday Soc.*, **20**, 502 (1924).

TABLE III

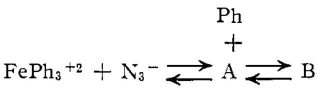
DISSOCIATION OF $\mathrm{FePh_3^{+2}}$ IN THE PRESENCE OF AZIDE ION

$[\mathrm{FePh_3^{+2}}]_0 = 3.13 \times 10^{-5}$; constant μ of 2.0 using KCl

Temp., °C.	$[\mathrm{N_3^-}]$	$k_0 \times 10^3$, min.$^{-1}$
25.0	0.40	7.9
25.0	.50	9.2
25.0	.60	8.8
25.0	.70	10.9
25.0	.80	11.7
25.0	.90	13.0
25.0	1.00	13.9
35.0	0.70	27 ± 3
35.0	.80	27 ± 3
35.0	.90	35 ± 3
35.0	1.00	34 ± 3
10.0	0.60	0.55
10.0	0.80	0.76

viate from the known value of k_d at $[\mathrm{N_3^-}] = 0$. Experimentally, assuming no absorbing product, azide ion was 3.9×10^{-3} min.$^{-1}$ which is the expected value at this ionic strength.[3] Even with a value of ϵ_x as high as 6000 the first order rate plots still deviated after 15% reaction and the new values calculated for k_0 gave an extrapolated k_d value of 7.5×10^{-3} min.$^{-1}$, which is not correct. Therefore, the product of the azide reaction does not have a strong absorbance relative to that of $\mathrm{FePh_3^{+2}}$. However, the product of the reaction could have a molar absorptivity of 1000 without a serious displacement of the k_d value and the values reported for k_0 could be slightly larger.

Correcting for the back reaction by means of the equilibrium absorbance values, assuming that the product of the reaction did not absorb, did not straighten the rate plots. Thus the final equilibrium predicts inappreciable back reaction under conditions when, in fact, the rate slows greatly. The observed kinetics may be explained by the reaction



$$\mathrm{FePh_3^{+2}} + \mathrm{N_3^-} \rightleftharpoons \overset{\mathrm{Ph}}{\overset{+}{\mathrm{A}}} \rightleftharpoons \mathrm{B}$$

where A is the first product of the reaction and B forms slowly. Both A and B must have low molar absorptivities at 510 mμ. Attempts to prepare or detect the mixed complexes $\mathrm{FePh_2(N_3)_2}$ and $\mathrm{FePh(N_3)_4^{-2}}$, analogous to the cyanide complexes, were fruitless. The equilibrium solutions corresponded to the complex $\mathrm{FePh_2N_3^+}$, but this has not been established definitely. This should not detract from the kinetic conclusions concerning the disappearance of the characteristic red $\mathrm{FePh_3^{+2}}$ complex.

The reaction of azide ion with $\mathrm{FePh_3^{+2}}$ appeared to follow two paths similar to the cyanide reaction even though the products formed were not analogous.

From the data in Table III, E_a was calculated to be 22 ± 3 kcal., ΔH^* was 21 kcal. and ΔS^* was −10 e.u.

Hydroxide System.—Because of the formation of mixed complexes of $\mathrm{Fe^{+2}}$, Ph and $\mathrm{CN^-}$ and the formation of a relatively stable intermediate in the azide ion system, the reaction of $\mathrm{FePh_3^{+2}}$ with hydroxide ion was re-examined for mixed hydroxide ion–1,10-phenanthroline-iron(II) complexes. Spectrophotometric measurements of the dissociation of $\mathrm{FePh_3^{+2}}$ in basic solution gave parallel plots of log absorbance against time for 85% of the reaction from 410 to 540 mμ, indicating that no absorbing species was being formed. Extraction of the phenanthroline into dichloromethane and its subsequent analysis[7] were used to measure the dissociation rate of $\mathrm{FePh_3^{+2}}$, in basic solution. Assuming that three 1,10-phenanthroline molecules were released per molecule reacting, the dissociation rate by the release of 1,10-phenanthroline was identical with the dissociation rate measured spectrophotometrically for 75% of the reaction. Therefore, there is no evidence of a stable intermediate in the hydroxide reaction. An additional check was made for any neutral mixed complex such as $\mathrm{FePh_x(OH)_2}$ which might precipitate along with the hydrated ferric oxide which is one of the products of the reaction. A solution of $\mathrm{FePh_3^{+2}}$ in the presence of a 200 fold excess of 1,10-phenanthroline was decomposed by base and the precipitate was found to contain no 1,10-phenanthroline.

Qualitative observations of the reactions of hydroxide and cyanide ions with $\mathrm{FePh_3^{+2}}$ in methanol indicated that the reaction rates are greatly enhanced. In the presence of 0.3 *M* $\mathrm{NaOCH_3}$, $\mathrm{FePh_3^{+2}}$ became completely colorless in 30 seconds, and in 0.1 *M* KCN there was no further change in hue after 15 seconds.

Discussion

Hydroxide, cyanide and azide ions all interact with $\mathrm{FePh_3^{+2}}$ in a similar manner causing an acceleration in the dissociation of $\mathrm{FePh_3^{+2}}$. The reactions are first order in $\mathrm{FePh_3^{+2}}$ and first order in the nucleophile. At higher hydroxide ion concentrations $[\mathrm{OH^-}]^2$ and $[\mathrm{OH^-}]^3$ terms also appear, but the cubed term is observed in such concentrated electrolyte that it is difficult to assess its significance. Unlike the hydroxide ion reaction, neither the cyanide nor the azide ions have greater than a first order dependence up to one molar concentrations.

Several mechanisms were discussed previously[3] for the hydroxide ion effect. One of these was based on a singly bonded 1,10-phenanthroline dissociative intermediate, similar to that postulated for the acid dissociation of mono-(1,10-phenanthroline)-nickel(II).[15] Another system showing the importance of the stepwise rupture of chelates is the dissociation of the mono-(ethylenediamine)-nickel(II) complex.[16] Here, as with $\mathrm{NiPh^{+2}}$, proton addition to one dentate group blocks the reformation of the chelate and increases the over-all dissociation rate by a factor of 20 to 25. The reformation of a chelate also can be blocked by metal coördination as shown in the reaction of triethylenetetramine-nickel(II) with EDTA.[17] Nevertheless, this explanation of the hydroxide ion effect is not satisfactory in view of the fact that the $\mathrm{NiPh_3^{+2}}$ dissociation rate is not affected by the

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[15] D. W. Margerum, R. I. Bystroff and C. V. Banks, *J. Am. Chem. Soc.*, **78**, 4211 (1956).

[16] K. S. Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 3700 (1959).

[17] D. W. Margerum and J. F. G. Clarke, Jr., unpublished work.

presence of hydroxide ion or the other nucleophiles.[7] Furthermore, neither $\mathrm{NiPh_3^{+2}}$ nor $\mathrm{FePh_3^{+2}}$ have increased dissociation rates in acid, but their rates are some 20 to 30% lower.[18,19] The work of Wilkins and Williams on the dissociation and racemization rates of the nickel(II)–1,10-phenanthroline complexes indicates that singly bonded 1,10-phenanthroline intermediates are not possible for an SN1 mechanism, otherwise racemization rates would exceed dissociation rates.

The SN1 IP type mechanism[20] is not satisfactory for this system either. If ion pairs formed with the iron(II) complex they also would form with the nickel(II) complex as they have the same size and charge. In general, increased ionic strength represses the dissociation rates, and the nucleophiles which do accelerate the $\mathrm{FePh_3^{+2}}$ dissociation do not affect the $\mathrm{NiPh_3^{+2}}$ dissociation.

The other mechanism previously discussed for the hydroxide ion effect necessitated the formation of some unique species between $\mathrm{FePh_3^{+2}}$ and $\mathrm{OH^-}$ which was not a mere ion pair. This would be possible if interaction occurred between the nucleophile and the antibonding d-orbitals of the iron on the octahedral face. This interaction could weaken the metal-ligand bonds and result in increased dissociation rates.[21]

Close approach of the metal and the nucleophile would be necessary for such interaction and this is possible in the 1,10-phenanthroline complexes due to the formation of inner ion-pairs where anions replace the water molecules held in the pockets between the planar 1,10-phenanthroline molecules.[22] The kinetics of dissociation for the three systems can be explained by equations 2, 3 and 4. The initial step is the replacement of a water molecule by a nucleophilic ion to form an ion-pair. Interaction then may occur between the π orbitals of the nucleophile and the antibonding d orbital of the metal with resultant destabilization of the metal–ligand bonds and subsequent dissociation of the complex. The nucleophilic ion then may move rapidly into the vacated coördination site.

$$\begin{tikzcd}
\mathrm{FePh_3^{+2}} + \mathrm{OH^-} \arrow[r, shift left, "K_1^{\mathrm{OH}}"] \arrow[d, "k_d"] & {[\mathrm{FePh_3\cdot OH}]^+} \arrow[l, shift left] \arrow[r, shift left, "K_2^{\mathrm{OH}}"] \arrow[d, "k_1'"] & {[\mathrm{FePh_3(OH)_2}]} \arrow[l, shift left] \arrow[d, "k_2'"] & (2) \\
\text{Products} & \text{Products} & \text{Products} &
\end{tikzcd}$$

$$\begin{tikzcd}
\mathrm{FePh_3^{+2}} + \mathrm{CN^-} \arrow[r, shift left, "K_1^{\mathrm{CN}}"] \arrow[d, "k_d"] & {[\mathrm{FePh_3\cdot CN}]^+} \arrow[l, shift left] \arrow[d, "k_1'"] & (3) \\
\text{Products} & \text{Products} &
\end{tikzcd}$$

$$\begin{tikzcd}
\mathrm{FePh_3^{+2}} + \mathrm{N_3^-} \arrow[r, shift left, "K_1^{\mathrm{N_3}}"] \arrow[d, "k_d"] & {[\mathrm{FePh_3\cdot N_3}]^+} \arrow[l, shift left] \arrow[d, "k_1'"] & (4) \\
\text{Products} & \text{Products} &
\end{tikzcd}$$

This type of reaction does not occur for the Ni-$\mathrm{Ph_3^{+2}}$ [7] because of its electronic configuration.[21]

Using the mechanism proposed in equations 2, 3 and 4 the value of k_1 in Table II thus becomes K_1-k_1' and can be seen to be dependent on both the stability of the ion pair and the extent of interaction with the antibonding orbitals. Steric effects would be expected to have considerable effect on K_1 because of the restricted size of the anion pockets in the complex. The values of K_1^{OH} and K_2^{OH} thus would be expected to be greater than the corresponding values for $\mathrm{CN^-}$ and $\mathrm{N_3^-}$ and this can account for the appearance of a $[\mathrm{OH^-}]^2$ term at relatively low hydroxide ion concentrations. On this basis $k_1'_{(\mathrm{CN})}$ is greater than $k_1'_{(\mathrm{OH})}$. The relative magnitude of $k_1'_{(\mathrm{N_3})}$ is difficult to estimate since the steric factor for the $\mathrm{N_3^-}$ ion pair may be quite important.

If this mechanism is correct, any change that stabilizes these weak ion pairs should further enhance the dissociation rate. The reaction of Fe-$\mathrm{Ph_3(ClO_4)_2}$ with NaCN in methanol is approximately 400 times faster than the reaction with similar $[\mathrm{CN^-}]$ in water. Similarly $\mathrm{NaOCH_3}$ in methanol reacts with $\mathrm{FePh_3(ClO_4)_2}$ much faster than the corresponding $[\mathrm{OH^-}]$ in water.

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