Optical Inversion Reaction between Tris(1,10-phenanthroline)iron(II) and Cyanide[1]

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Abstract: The reaction of cyanide ion with aqueous Δ-$Fe(ophen)_3^{2+}$ involves an optical inversion. The concentration dependence of the inversion is not directly attributable to the observed overall cyanide-dependent rate constant, but appears related to competitive reactions. The circular dichroism of the $Fe(ophen)_2(CN)_2$ product compared with the circular dichroism of the reacting complex shows inversion for the long-axis $\pi^* \leftarrow \pi$ electronic transition, which is considered as nonempirical evidence of absolute configuration. The reaction appears to be the first example of an iron complex undergoing an octahedral or Bailar inversion.

An inverse correlation appears to exist between the ligand-field splitting of octahedral d^6 ions and the occurrence of stereochemical changes during substitution reactions.[3] Only low-spin complexes near the low to high spin crossover point exhibit stereochemical changes during substitution. To illustrate, cobalt(III) complexes with four amine donors and two weaker oxygen or halogen donors undergo substitution reactions with some stereochemical changes,[3,4] but corresponding rhodium(III)[5] and iridium(III)[6] complexes react with complete retention of configuration. Cobalt(III)–diimine complexes, which exhibit greater ligand-field splitting than the corresponding amine complexes, show no nucleophilic dependence and appear to substitute with stereochemical retention.[7]

In order to stay near the spin crossover point and learn whether the inverse correlation is fairly general, we decided to consider the reaction stereochemistry of some iron(II) chelates containing diimine ligands such as 1,10-phenanthroline and 2,2′-bipyridine. Iron(II) complexes containing diimine ligands possess spin-paired ground states if three diimine ligands are coordinated to the iron(II) or if two of the diimine ligands plus two relatively strong-field anions such as nitrite or cyanide compose the coordination sphere.[8] Weaker ligand combinations give labile, high-spin complexes with iron(II).

Another reason for considering the iron(II) diimine complexes is based on nucleophilicity considerations. Whereas most octahedral substitution reactions can be accommodated by dissociative type mechanisms,[9] good nucleophiles appear to exhibit some associative, or at least second-order, behavior toward racemic $Fe(ophen)_3^{2+}$.[10] The $Fe(ophen)_3^{2+}$ reactions are complicated by solvolysis reactions, which lead to spin-free products, as well as by intramolecular racemization.[11] Although the reaction stereochemistry of $Fe(ophen)_3^{2+}$ with strong-field ligands had not been investigated, previous studies[10,11] have suggested a composite rate law for the loss of the reactant in the presence of cyanide ion as follows

$$\frac{-d[\Delta\text{-Fe(ophen)}_3{}^{2+}]}{dt} = (k_d + k_i + k_1[CN^-])[\Delta\text{-Fe(ophen)}_3{}^{2+}] \quad (1)$$

where k_d is the dissociative rate constant which produces spin-free diaqua complex

$$\Delta\text{-Fe(ophen)}_3{}^{2+} \xrightarrow[k_d]{H_2O} Fe(ophen)_2(H_2O)_2 + ophen \quad (2)$$

and k_i is the intramolecular racemization rate constant which gives racemic tris complex

$$\Delta\text{-Fe(ophen)}_3{}^{2+} \xrightarrow[k_i]{} rac\text{-Fe(ophen)}_3{}^{2+} \quad (3)$$

The sum of these constants ($k_d + k_i$) is k_0, the total nucleophile-independent specific rate constant. The k_1 rate constant is for the nucleophile-dependent path, which gives neutral $Fe(ophen)_2(CN)_2$[10c]

$$\Delta\text{-Fe(ophen)}_3{}^{2+} \xrightarrow[k_1]{CN^-} Fe(ophen)_2(CN)_2 + ophen \quad (4)$$

No aquacyano intermediate has been observed,[10c] so the reaction has been assumed to be basically a rate-determining step

$$Fe(ophen)_3{}^{2+} + CN^- \xrightarrow{k_1} Fe(ophen)_2(CN)(H_2O)^+ + ophen \quad (5)$$

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[1] Presented in part at the 3rd Symposium on Coordination Chemistry, Debrecen, Hungary, Sept 1970; *cf.* R. D. Archer, L. J. Kluss, and V. M. Marganian, *Proc. Symp. Coord. Chem., 3rd*, 1, 291 (1970).

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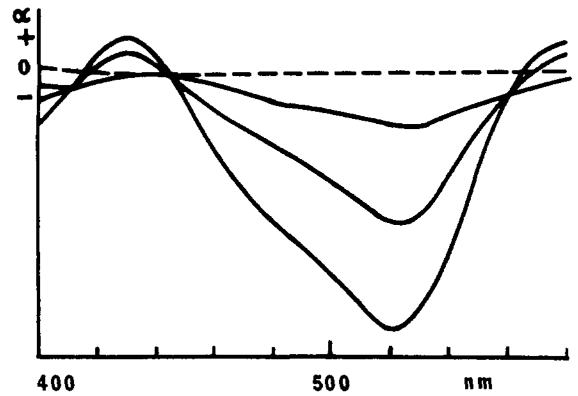

Figure 1. Nonzero isorotatory points indicating an optically active product in the reaction between Δ-Fe(ophen)$_3{}^{2+}$ and cyanide ion.

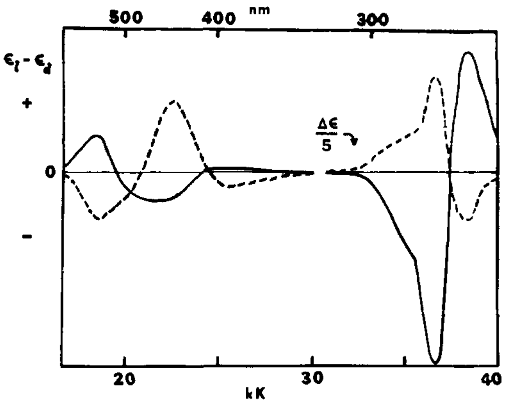

Figure 2. The circular dichroism of Δ-Fe(ophen)$_3{}^{2+}$ (——) and the Fe(ophen)$_2$(CN)$_2$ product (- - - -).

followed by a rapid reaction with another cyanide ion

$$\mathrm{Fe(ophen)_2(CN)(H_2O)^+ + CN^- \xrightarrow{k_{di}} Fe(ophen)_2(CN)_2} \quad (6)$$

The specific rate constants may be composites of ion multiplet equilibria and true rate constants,[10c] but no stereochemical detail has been available. Product stereochemical information cannot be obtained from the solvolysis reaction because subsequent rearrangement of the labile solvent-containing species to the thermodynamically stable racemate is certain to occur. Therefore, direct substitution by strong-field ligands such as cyanide is necessary in order to ascertain the reaction stereochemistry. This paper reports the results of our study between Δ-Fe(ophen)$_3{}^{2+}$ and cyanide near 0°.

Results

Kinetic optical rotatory dispersion and circular dichroism racemization (and mutarotation) studies at 0.5° have allowed the calculation of rate constants for racemization and cyanide nucleophilicity of Δ-Fe(ophen)$_3{}^{2+}$. The results are consistent with extrapolations of the spectrophotometric results of Margerum and Morgenthaler[10c] and with the racemization studies of Basolo and coworkers.[11c] See Table I.

The existence of nonzero isorotatory points during the course of the reaction of Δ-Fe(ophen)$_3{}^{2+}$ with cyanide ion (Figure 1) caused us to look deeper into the reaction. The circular dichroism of the product relative to the reactant (Figure 2) is indicative of an optical inversion, particularly in the $\pi^* \leftarrow \pi$ long-axis electronic transition spectral region. This band is considered as nonempirical evidence of absolute configuration by several spectroscopists,[12] and if so, the reaction is the first example of an iron complex undergoing an octahedral or Bailar inversion.[13]

Positive identification of the inverted product as the neutral Fe(ophen)$_2$(CN)$_2$ inner complex was made by extraction of the active species into chloroform. The extracted complex exhibits spectral characteristics noted previously for Fe(ophen)$_2$(CN)$_2$[10c] and slowly racemizes in chloroform at room temperature ($t_{1/2} \sim$ 4 days).

Table I. Specific Rate Constants for the Reaction of Δ Fe(ophen)$_3{}^{2+}$ with Aqueous Cyanide at 0.5 ± 0.1°

[CN$^-$], M^a	k_{obsd},^{b} sec^{-1}	k_{obsd},^{c} sec^{-1}	Comments
0.300	6.5×10^{-5}	6.3×10^{-5}	
0.400		9.0×10^{-5}	
0.500	9.1×10^{-5}	9.2×10^{-5}	
0.600	1.17×10^{-4}	1.21×10^{-4}	
0.700	1.34×10^{-4}	1.33×10^{-4}	
0.800	1.50×10^{-4}	1.51×10^{-4}	
0.900	1.79×10^{-4}	1.76×10^{-4}	
1.000	1.89×10^{-4}	1.85×10^{-4}	
2.000	$[3.7 \times 10^{-4}]^d$		3.36×10^{-4} at 0.0°; corrected with temperature effect observed for lower concentration
0.000	$[9.1 \times 10^{-6} = k_0]^d$		8.64×10^{-6} at 0.0°; plot of ref 11b, c data allows adjustment to 0.5°
	$k_1{}^e = 1.80 \pm 0.04 \times 10^{-4}$ sec^{-1} M^{-1}		

[a] Ionic strength = 2.00 M throughout. [b] Based on 391- and 435-nm data. [c] Based on 435- and 525-nm data corrected for inversion. [d] Based on 272- and 285-nm CD measurements at 0.0° corrected to 0.5° as noted. [e] Based on least-squares analysis of the data.

An even slower product racemization rate was observed in water ($t_{1/2} \sim$ 2 months). As a final proof of the neutral nature of the product, electrophoresis experiments were performed and compared with known electrolytes, but the product did not move under conditions where charged species move appreciably.

A reaction which is dominated by a second-order term (first order in substrate and first order in nucleophile) should exhibit only a small product isomer de-

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pendence as the nucleophile concentration is changed (Table II). That is, if the optical inversion were due to a simple k_1 cyanide-dependent path, the per cent inversion should change from 8.6 to about 9.4% as the cyanide concentration is increased from 0.4 to 2.0 *M*. Instead, as is shown in Table II, the per cent inversion more than doubles under these conditions. The per cent inversion is based on an assumed rotatory strength for the $\pi^* \leftarrow \pi$ transition of the bis complex of 50% the rotatory strength of the corresponding tris complex. Related complexes for which data are available range from less than 10 to about 70% of the corresponding tris species even though simple theory predicts 50%.[12]

Table II. A Comparison of the k_0 and k_1 Paths with Per Cent Inversion for the Reaction of Δ-Fe(ophen)$_3{}^{2+}$ with Cyanide at 0.5°

[CN⁻], M^a	$k_0 + k_1[\mathrm{CN}^-]^b$	% by $k_0{}^c$	% by $k_1{}^d$	% Inversion Calcd for k_1	% Inversion Exptl^f
0.000	9.1×10^{-6}	100.0	0.0	0	0
0.400	8.1×10^{-5}	11.2	88.8	8.6^e	8.6
0.600	1.17×10^{-4}	7.8	92.2	8.9	10.6
0.800	1.53×10^{-4}	5.9	94.1	9.1	12.4
1.000	1.89×10^{-4}	4.8	95.2	9.2	14.4
2.000	3.7×10^{-4}	2.5	97.5	9.4	17.5

^{a} Total ionic strength = 2 *M*. ^{b} Calculated from k_0 and k_1 as determined in Table I; in sec^{-1}. ^{c} $k_0/(k_0 + k_1[\mathrm{CN}^-])$. ^{d} $k_1/(k_0 + k_1[\mathrm{CN}^-])$. ^{e} Standard point, not calculated. ^{f} Based on assumption that $\pi^* \leftarrow \pi$ rotatory strength of bis complex is 50% rotatory strength of tris complex.

The per cent inversion *vs.* concentration indicates a greater dependence on cyanide ion for the infinite time reactions than expected for the k_1 path. An additional $k_2[\mathrm{CN}^-]^2[\Delta\text{-Fe(ophen}_3)^{2+}]$ term could be used to explain such an increase.[1] A calculation of a hypothetical k_2 specific rate constant based on the measured rates for k_0 and k_1 and the per cent inversion for infinite time reactions showed that the k_2 term should be observed at high cyanide concentrations. However, the experimental error in determining the specific rate constants up to 1 *M* CN⁻ is such that the k_2 term could have been missed by Margerum and Morgenthaler[10c] or by the data to 1 *M* noted in Table I. Extension to 2 *M* CN⁻ gave a continued straight line with no evidence for a k_2 term, however. Instead, the infinite-time percentages for the rate data and the inverted product can be fit to the expression

$$\%\ \text{by}\ k_1/\%\ \text{inverted} = A + B/[\mathrm{CN}^-] \qquad (7)$$

where $A = 4.39$ and $B = 2.44$ at 0.5°, as indicated in Table III.

An attempt to study the inversion reaction at an even higher cyanide ion concentration was unsuccessful. The iron complex reactant proved to be insoluble in saturated aqueous potassium cyanide. The dicyano product obstructs optical measurements as it coagulates at higher iron complex concentrations, so the studies had to be made at concentrations where the inversion data error is about ±1% of the initial optically active species. The per cent inversion decreases at lower cyanide concentrations and becomes zero without cyanide ion under conditions of comparable ionic strength.

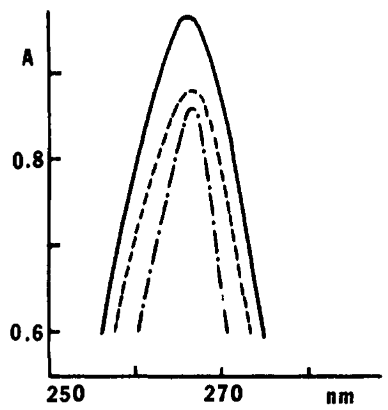

Figure 3. The absorption peak of the $\pi^* \leftarrow \pi$ transitions of Fe(ophen)$_3{}^{2+}$ (——), Fe(ophen)$_2$(CN)$_2$ (– – – –), and Fe(ophen) (CN)$_4{}^{2-}$ (–·–·); at different concentrations to show consistency of transition—see text for ϵ values.

A spectrophotometric check of the reaction rate indicated that the k_1 measured by ORD and CD is the same as that measured by spectrophotometry. Furthermore, changes in iron concentration did not influence the rate except at high concentrations when colloidal Fe(ophen)$_2$(CN)$_2$ precluded meaningful results.

Table III. Least-Squares Fit of % by k_1/% Inverted *vs.* 1/[CN⁻]

[CN⁻]	1/[CN⁻]	% by k_1/% inverted	Calcd ratio^a
0.40	2.50	10.33	10.49
0.60	1.67	8.71	8.46
0.80	1.25	7.58	7.43
1.00	1.00	6.61	6.82
2.00	0.50	5.57	5.61

^{a} Least-squares fit which gives an intercept of 4.39 and a slope of 2.44; calculated values are all less than 3.3% from observed values.

The aqueous $\pi^* \leftarrow \pi$ absorption spectra of the reactant and product are shown in Figure 3. For a comparison of the $\pi^* \leftarrow \pi$ transitions the Fe(ophen)(CN)$_4{}^{2-}$ ion was also prepared and its absorption spectrum recorded (Figure 3). A comparison of the spectral properties of the tris, bis, and mono complexes shows slight, if at all significant, energy shifts in the long-axis $\pi^* \leftarrow \pi$ transition. The shift, if significant, is in the same direction from the mono to the bis and tris complexes. The optical rotatory dispersion and circular dichroism spectra have components far enough from each other that a significant reversal should be noted if the components were reversed from the normal energy ordering.[12] Whether the use of a vibronic coupling model could reverse the order of the levels is at present uncertain.[12e]

Discussion

Consideration of the optical inversion as a true chemical inversion is based on a so-called nonemperical analysis of the $\pi^* \leftarrow \pi$ electronic transitions of the bis and tris complexes.[12] The order of the long axis $\pi^* \leftarrow \pi$ components of tris unsaturated-chelate octahedral complexes as deduced from exciton theory is

$$\text{energy } (\psi_{A_2} \leftarrow \psi_0) > \text{energy } (\psi_E \leftarrow \psi_0) \qquad (8)$$

and in the corresponding bis complexes[14]

$$\text{energy } (\psi_B \leftarrow \psi_0) > \text{energy } (\psi_A \leftarrow \psi_0) \qquad (9)$$

The intensities of the A_2 and B components are predicted to be greater than those of the E and A ones. Therefore, the overall transition should shift in the same direction for the bis and tris complexes, consistent with our observations. Also a consideration of the chirality of these transitions allows the conclusion that the higher energy component has the same sign in both cases.[12]

The possibility of incorrect assignment by this model cannot be excluded,[12d,e] but the consistency of the $\pi^* \leftarrow \pi$ transition makes this possibility unlikely. Small shifts are possible from a number of things including overlap with other transitions and solvation effects due to ionic charge changes in this sequence. Such changes also make some of the conclusions of Ferguson and coworkers[12d] questionable.

A simple mechanism consistent with all observations is a breakdown of the cyanide dependent path into the reactions

$$\Delta\text{-Fe(ophen)}_3{}^{2+} + \text{CN}^- \xrightarrow{k_{1i}} \Lambda\text{-Fe(ophen)}_2(\text{H}_2\text{O})(\text{CN})^+ + \text{ophen} \qquad (10)$$

$$\Delta\text{-Fe(ophen)}_3{}^{2+} + \text{CN}^- \xrightarrow{k_{1r}} rac\text{-Fe(ophen)}_2(\text{H}_2\text{O})(\text{CN})^+ + \text{ophen} \qquad (11)$$

where

$$k_{1i} + k_{1r} = k_1(\text{obsd}) \qquad (12)$$

Owing to the relatively weak field of the aquacyano complex, partial racemization of the excess Λ isomer can occur before the relatively rapid addition of the second cyanide ligand.

$$\Lambda\text{-Fe(ophen)}_2(\text{H}_2\text{O})(\text{CN})^+ \xrightarrow{k_{ar}} rac\text{-Fe(ophen)}_2(\text{H}_2\text{O})(\text{CN})^+ \qquad (13)$$

Most simple octahedral substitution anations occur with retention of configuration.[3] Using this assumption

$$\frac{d[\Lambda\text{-Fe(ophen)}_2(\text{CN})_2]}{dt} = k_{di}[\text{CN}^-][\Lambda\text{-Fe(ophen)}_2(\text{H}_2\text{O})(\text{CN})^+] \qquad (14)$$

But since the aquacyano species is an unobservable intermediate, the steady-state assumption for the excess Λ isomer gives

$$0 = \frac{d[\Lambda\text{-Fe(ophen)}_2(\text{H}_2\text{O})(\text{CN})^+]}{dt} = k_{1i}[\Delta\text{-Fe(ophen)}_3{}^{2+}][\text{CN}^-] - k_{ar}[\Lambda\text{-Fe(ophen)}_2(\text{H}_2\text{O})(\text{CN})^+] - k_{di}[\Lambda\text{-Fe(ophen)}_2(\text{H}_2\text{O})(\text{CN})^+][\text{CN}^-]$$

$$[\Lambda\text{-Fe(ophen)}_2(\text{H}_2\text{O})(\text{CN})^+] = \frac{k_{1i}[\Delta\text{-Fe(ophen)}_3{}^{2+}][\text{CN}^-]}{k_{ar} + k_{di}[\text{CN}^-]} \qquad (15)$$

Since $k_{di} \gg k_1$ and our observation of a 2-month $t_{1/2}$ for the active dicyano complex implies a negligible reverse reaction in the second step, the total dicyano product arising from the k_1 path is

$$\frac{d\{[\text{Fe(ophen)}_2(\text{CN})_2] \text{ by } k_1\}}{dt} = (k_{1i} + k_{1r})[\Delta\text{-Fe(ophen)}_3{}^{2+}][\text{CN}^-] \qquad (16)$$

and the inverted dicyano product is

$$\frac{d[\Lambda\text{-Fe(ophen)}_2(\text{CN})_2]}{dt} = \frac{k_{1i}k_{di}[\Delta\text{-Fe(ophen)}_3{}^{2+}][\text{CN}^-]^2}{k_{ar} + k_{di}[\text{CN}^-]} \qquad (17)$$

The only variable with time in eq 16 and 17 is the Δ-Fe(ophen)$_3{}^{2+}$ species, because all reactions have cyanide present in excess by several orders of magnitude. Therefore, dividing eq 16 by eq 17 and integrating from $t = 0$ to ∞ gives

$$\frac{\%\text{ by } k_1}{\%\text{ inverted}} = \frac{(k_{1i} + k_{1r})(k_{ar} + k_{di}[\text{CN}^-])}{k_{1i}k_{di}[\text{CN}^-]} = 1 + \frac{k_{1r}}{k_{1i}} + \frac{(k_{1i} + k_{1r})k_{ar}}{k_{1i}k_{di}[\text{CN}^-]} \qquad (18)$$

From the plot of % by k_1/% inverted against $1/[\text{CN}^-]$

$$1 + k_{1r}/k_{1i} = 4.39 \qquad (19)$$

$$(k_{1i} + k_{1r})k_{ar}/k_{1i}k_{di} = 2.44 \qquad (20)$$

and

$$k_{1i} + k_{1r} = k_1 = 1.80 \times 10^{-4} \text{ sec}^{-1}\, M^{-1} \qquad (21)$$

from Table I, so

$$k_{1i} = 4.1 \times 10^{-5} \text{ sec}^{-1}\, M^{-1} \qquad (22)$$

$$k_{1r} = 1.4 \times 10^{-4} \text{ sec}^{-1}\, M^{-1} \qquad (23)$$

and a ratio is obtained for the other two constants

$$k_{di} = 1.8k_{ar} \qquad (24)$$

A plausible rationalization for the inversion is based on perturbation of the $t_{2g}{}^6$ electronic configuration of

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[14] The energy ordering in Table I of Bosnich's review[12a] should be disregarded for the bis complexes. His own statements therein and elsewhere[12b] indicate the energy of the B representation lies at higher energy than the A one as noted in eq 6; *cf.* ref 12c.

the pseudooctahedral $Fe(ophen)_3^{2+}$ ion by cyanide. The perturbation enhances loss of the ophen ligand "trans" to the nucleophilic cyanide ion. Rotation of either end of either retained ophen ligand plus entry of a second cyanide ion into the remaining coordination site completes the inversion. The original cyanide nucleophile replaces the ophen nitrogen, which rotates into a vacated site. In the absence of a second cyanide ion, an inverted aquacyano ion is formed which can either react with cyanide to give the inverted dicyano species or racemize prior to or during reaction with the second cyanide ion. The inversion is shown diagrammatically in Figure 4.

Details and justification of this scheme follow. Using pseudooctahedral d-orbital orientation, nucleophilic attack between N_a and N_f causes the equivalent nitrogen donors of the D_3 ion to lose their identical nature in the C_2 transition state; however, $N_c = N_d$, $N_a = N_f$, and $N_b = N_e$. Using an angular-overlap model,[15] the relative energy of the d-like orbitals becomes $d_{xz} \sim d_{yz} < d_{xy} < d_{x^2-y^2} < d_{z^2}$, with a concurrent possibility of a change in electron spin and orbital population.[16] Only a small perturbation would be necessary because $Fe(ophen)_2L_2$ complexes in which L = NCS (or weaker field ligand) result in a detectable or predominant spin-free species.[8] Entry of an electron into the $d_{x^2-y^2}$ orbital loosens N_a, N_c, N_d, and N_f. Because both nitrogens of ophen cd are loosened, it is the labilized ligand. The next logical step is the movement of N_a (or the equivalent N_f) to vacated position c (or d) with the concurrent occupancy of position a (or f) by the cyanide nucleophile. But two ophen ligands in the same plane is sterically improbable;[17] therefore, the preceding steps will reverse themselves or else ligand N_a (or N_f) will continue on to position d (or c), producing the inverted configuration. Entry of water or cyanide into the remaining position gives an inverted octahedral complex. Alternatively, as cd is loosened, N_a and N_f may become more tightly bonded. Hence, N_b and N_c may be equally likely to move and allow fixation of the cyanide into the coordination sphere. If N_b (or N_e) moves to vacated site c (or d), an inverted configuration is produced, too. Again, entry of water or cyanide into the remaining position produces an inverted octahedral complex.

The fate of the inverted complex produced by the above ligand movements depends on the ligand-field strength of the sixth ligand. If a second cyanide enters the sixth position, either directly or subsequently (but prior to racemization), an inert complex with a half-life of about 2 months at room temperature in water is produced. The starting material has a much shorter half-life (about 1 hr at room temperature), and ligand-field considerations along with isolated bis(ophenanthroline) complexes of iron(II) suggest that the aquacyano complex would not be very inert either. Hence, any dicyano product formed slowly from the aquacyano complex would be racemic.

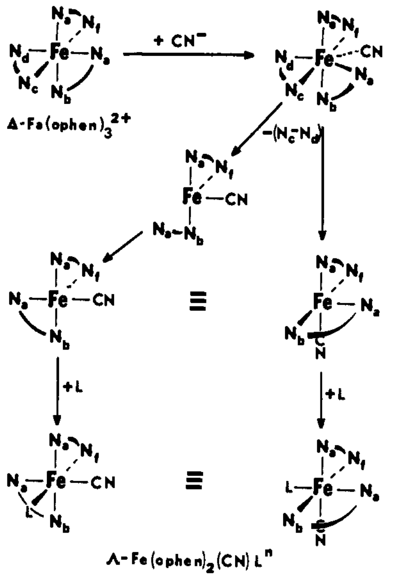

Figure 4. Possible inversion mechanism for the reaction between $Fe(ophen)_3^{2+}$ and cyanide ion. When cyanide is available in the outer coordination sphere (L = CN), an inert and inverted dicyano product results. Otherwise, a labile aquacyano complex results.

Alternatively, a more involved look at the details might include some type of ion multiplets.[10c] Consistency with our observations can be obtained by the inclusion of the equilibria

$$\Delta\text{-Fe(ophen)}_3^{2+} + CN^- \underset{K_{IP}}{\rightleftharpoons} \underset{\Delta\text{-IP}}{\Delta\text{-Fe(ophen)}_3^{2+}\cdot CN^-} \tag{25}$$

and

$$\Delta\text{-IP} + CN^- \underset{K_{IT}}{\rightleftharpoons} \underset{\Delta\text{-IT}}{CN^-\cdot\Delta\text{-Fe(ophen)}_3^{2+}\cdot CN^-} \tag{26}$$

and the reaction

$$\Delta\text{-IP} \xrightarrow{k_1'} \Lambda\text{-Fe(ophen)}_2(H_2O)(CN)^+ + \textit{rac}\text{-Fe(ophen)}_2(H_2O)(CN)^+ \tag{27}$$

followed by reactions 13 and/or 6 to give *rac*-$Fe(ophen)_2(CN)_2$ product, and reactions

$$\Delta\text{-IT} \xrightarrow{k_1''} \Lambda\text{-Fe(ophen)}_2(CN)_2 \tag{28}$$

and

$$\Delta\text{-IT} \xrightarrow{k_1'''} \textit{rac}\text{-Fe(ophen)}_2(CN)_2 \tag{29}$$

An analogous steady-state treatment to that given above yields the expression

$$\frac{\%\text{ by }k_1}{\%\text{ inverted}} = 1 + \frac{k_1'''}{k_1''} + \frac{k_1'}{k_1''K_{IT}[CN^-]} \tag{30}$$

From the results of eq 7

$$k_1'''/k_1'' = 3.39 \tag{31}$$

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(15) (a) C. K. Jørgensen, R. Pappalardo, and H. H. Schmidtke, *J. Chem. Phys.*, **39**, 1422 (1963); (b) C. E. Schäffer, *Struct. Bonding (Berlin)*, **5**, 68 (1968); (c) K. B. Yatsimirskii, *Teor. Eksp. Khim.*, **2**, 451 (1966); *Theor. Exp. Chem.*, **2**, 342 (1966).

(16) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 236.

(17) A trans product is not expected from steric considerations. Although "trans" bis(ophen) complexes have been reported in the scientific literature, definitive support for such species is lacking. The preportedly trans complexes can usually be shown to be other complexes: (a) J. G. Gibson, R. Laird, and E. D. McKenzie, *J. Chem. Soc. A*, 2089 (1969); (b) J. G. Gibson and E. D. McKenzie, *ibid.*, *A*, 2637 (1969).

and

$$k_1'/k_1''K_{\mathrm{IT}} = 2.44 \qquad (32)$$

The first ratio suggests that the production of inverted dicyano results in only about 23% of the activation processes in which a second cyanide is near. This is consistent with a partially nonrigid intermediate, such as often occurs with five-coordinate intermediates near the spin-free–spin-paired crossover point.[3]

The ion triplet has twice the opportunity to have a cyanide ion activate the tris reactant as the ion pair so

$$k_1'' + k_1''' \sim 2k_1' \qquad (33)$$

Combined with eq 31

$$k_1'/k_1'' \sim 2.20 \qquad (34)$$

From eq 32 and 34, $K_{\mathrm{IT}} = 0.9\ M^{-1}$, and K_{IP} would be at least that large, and probably larger. The term ion triplet is used to include a solvent cage containing two cyanide ions in appropriate proximity to give dicyano product during the reaction sequence as distinguished from an ion-pair solvent cage which produces an aquacyano intermediate which routinely racemizes. The K_{IT} of $0.9\ M^{-1}$ appears large for a 2:1 species in water. In fact, an earlier attempt to observe even ion pairs of this type using the $\mathrm{Fe(ophen)_3}^{2+}$ ion with uninegative ions[11c] was unsuccessful; however, the methods used would detect only intimate ion pairs as distinguished from the larger solvent cage being considered above.

If the ion-multiplet concept is combined with cyanide attack from the bulk solvent the constants could be lowered accordingly. Further refinement is not feasible at this time.

Although Bailar and Auten[13a] noted the first octahedral Δ to Λ inversion in 1934 with $\mathrm{Co(en)_2Cl_2}^+$, attempts to extend such inversions to other octahedral systems have been largely unsuccessful.[13b,c] Polydentate ligands sometimes show inversion when the movement of one end of a ligand gives the opposite chirality if the rest of the ligand stays intact as in the Δ-α to Λ-β reactions of quadridentate ligands. But for octahedral complexes containing only bidentate and unidentate ligands, only dihalobis(aliphatic diamine)-cobalt(III) ions have been found to undergo such inversions during octahedral substitution reactions. Ligand-field considerations suggest that the tris(ophen)-iron(II) system has a similar d-electron separation to the cobalt(III)–amine complexes without the conjugate base complications of the latter.

Attempts to use nitrite as a nucleophile in water were less than successful. Although the rate of racemization of $\mathrm{Fe(ophen)_3}^{2+}$ is slightly greater in the presence of nitrite ion, no dinitro product could be obtained. On the other hand, solutions of $\mathrm{[Fe(ophen)_3](NO_2)_2}$ in nitromethane are rapidly converted to $\mathrm{Fe(ophen)_2(NO_2)_2}$ upon the addition of ether. These observations suggest that the solvation of nitrite prevents an ion-pair or interchange reaction from occurring.[1] The rapidity of the nitrite reaction in the nitromethane–ether solutions suggests that a number of inversions might be found in nonaqueous media of low dielectric constants.

Related experiments with unsymmetrical chelating ligands should allow stereochemical information on which end of the ligand is moving during the inversion process. Temperature-dependent studies with activation parameters are also anticipated.

Experimental Section

Preparation of Δ-$\mathbf{[Fe(ophen)_3](ClO_4)_2 \cdot 3H_2O}$. This complex was prepared according to the procedure of Dwyer and Gyarfas.[18] *Anal.*[19] Calcd for $\mathrm{Fe(C_{12}H_8N_2)_3(ClO_4)_2 \cdot 3H_2O}$: C, 50.90; H, 3.56; N, 9.89. Found: C, 51.18; H, 3.48; N, 9.90.

Preparation of $\mathbf{Fe(ophen)_2(CN)_2}$ and $\mathbf{K_2Fe(ophen)(CN)_4 \cdot 4H_2O}$. These species were prepared according to the procedures given by Schilt.[20] Purity was ascertained from spectral characteristics given by Margerum and Morganthaler[10c] and Schilt.[20]

Kinetic Studies. As far as possible, conditions were the same as those used by Margerum and Morganthaler[10c] in their study of $\mathrm{CN^-}$-catalyzed dissociation of $\mathrm{Fe(ophen)_3}^{2+}$.

Stock solutions of 2.50 *M* KCl (186.6 g/l.) and 1.25 *M* KCN (88.0 g/l. of KCN) in 1.25 *M* KCl were used. Final solutions for the kinetic runs were 50 ml in total volume: 10 ml of an aqueous solution of Δ-$\mathrm{Fe(ophen)_3(ClO_4)_2}$, enough KCN–KCl solution to obtain the required $[\mathrm{CN^-}]$, and the remainder KCl solution to keep the final ionic strength at 2.00 *M*. The KCN and KCl solutions (40 ml in total volume) were added to a 50-ml volumetric flask and thermostated at 0.5°. The 2.00 *M* KCN kinetic study was prepared similarly using 40 ml of 2.50 *M* KCN. A solution of Δ-$\mathrm{Fe(ophen)_3(ClO_4)_2}$ was made by dissolving a small amount of the solid in ~5 ml of $\mathrm{H_2O}$ at room temperature, immediately adding this to ~100 ml of ice-cold $\mathrm{H_2O}$, mixing, and filtering to remove undissolved complex. A 10.0-ml portion of this solution was pipetted into the KCl–KCN solution, the solutions were mixed, and the time recorded as t_0. The solution was kept thermostated at 0.5° and samples were transferred (with a syringe) to a thermostated cell for the ORD scans. The concentration of $\mathrm{Fe(ophen)_3(ClO_4)_2}$ was determined from the visible absorption spectrum of the initial solution. The half-life was determined from a plot of log Δ *vs.* time, where Δ is the difference in rotation at two wavelengths where the rotations of the product have a negligible effect on the calculations, and large enough differences for reproducible results. The most convenient wavelengths were 391 and 435 nm. A second set of calculations was obtained from 435- and 525-nm data, with the 525-nm data corrected for the slight inversion observed at infinite time at this wavelength. The specific rate constant k_1 was obtained from a pair of least-squares plots of the pseudo-first-order rate constants *vs.* cyanide ion for the two sets of data. The 0 and 2 *M* KCN data were determined in the ultraviolet at 272 and 385 nm with corrections for inversion made for the 2 *M* values.

Infinite-time spectra were obtained by allowing equivalent solutions to proceed to completion ($>10t_{1/2}$). The solutions then were allowed to come to room temperature for *ca.* 90 min in order that traces of the reactant were completely racemized. The initial reactant spectra were obtained by extrapolation of racemization data to zero time in 2 *M* HCl. The per cent inversion was determined from the relative values at 272 nm using 310-nm data as a check on base-line stablity

Spectra. The optical rotatory dispersion and circular dichroism spectra were obtained in 1- and 5-cm thermostated cells in a Cary Model 60 instrument The absorption spectra were obtained with a Hitachi Model EPS-3T double-beam recording spectrophotometer

A spectral comparison of iron(II)–ophen complexes in the $\pi^* \leftarrow \pi$ region was made. The coordination entity, $\bar{\nu}_{\max}$ ($\mathrm{cm^{-1}}$), $\bar{\nu}_{\mathrm{av}}$ at two-thirds peak height,[21] and ϵ were observed as follows: $\mathrm{Fe(ophen)_3}^{2+}$ 37,540 ± 30, 37,640 ± 40, 9.4×10^4; $\mathrm{Fe(ophen)_2(CN)_2}$ 37,510 ± 30, 37,640 ± 40, 5.1×10^4; $\mathrm{Fe(ophen)(CN)_4}^{2-}$ 37,470 ± 30, 37,670 ± 40, 4×10^4.

Electrophoresis. Electrophoresis of saturated Δ-$\mathrm{[Fe(ophen)_3](ClO_4)_2 \cdot 3H_2O}$ and the above reaction product filtrate on cellulose

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(18) F. P. Dwyer and E. C. Gyarfas, *J. Proc. Roy. Soc. N. S. W.*, **83**, 263 (1949).

(19) Chemical analyses by Mr. C. Meade, University of Massachusetts Microanalytical Laboratory.

(20) A. A. Schilt, *J. Amer. Chem. Soc.*, **82**, 3000 (1960).

(21) Peak overlap with other transitions precludes meaningful analysis at lower values.

polyacetate (Sepraphore, Gelman) at 190 V and pH 10.8 in a Gelman Model 51100 chamber indicated a neutral product and a cationic reactant. A boric acid–NaOH buffer solution was used.

Acknowledgment. The authors wish to express their appreciation for the support of this research through National Science Foundation Grants No. GP-8304 and GP-20275. A matching fund grant by the National Science Foundation to the Department of Chemistry for the spectropolarimeter used in this study is also gratefully acknowledged. Discussions with O. E. Weigang, W. 'A. Baker, P. Krumholz, V. M. Marganian, J. O. Edwards, and J. C. Bailar, Jr., concerning this work have also been extremely helpful. Constructive cirticism by the referees is also acknowledged.

Chemistry and Kinetics of the Thermal Decomposition of Zinc and Magnesium Oxalates

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Abstract: The thermal decompositions of magnesium and zinc oxalates have been studied by a technique which allows the independent and quantitative measurements of carbon monoxide and carbon dioxide formed during 2-min intervals throughout a decomposition. From these measurements, the average rate of decomposition during any interval and the fraction decomposed at any time can be calculated. An equation was found to represent the kinetic data for the decomposition of both oxalates. This equation, $d\alpha/dt = k_1(1 - \alpha) + k_2\alpha(1 - \alpha)$, has relevant interpretations in terms of the kinetics of the decompositions. Thus, the term $k_1(1 - \alpha)$ can be considered to represent a thermal decomposition path (negligible for zinc oxalate), while the term $k_2\alpha(1 - \alpha)$ may be considered as representing a path that is accelerated by the oxide formed during the decomposition. This equation can be used to correctly predict the values of the fraction decomposed at which the maximum rate will be observed. A single activation energy was obtained from Arrhenius plots of rate constants. A reasonable decomposition mechanism has been suggested on the basis of the common activation energy and the kinetic behavior.

In this paper we report the results of experiments on the kinetics and stoichiometry of the thermal decompositions of zinc and magnesium oxalates. Rates of formation of carbon dioxide and carbon monoxide were independently and quantitatively determined. Yankwich and Zavitsanos[1] reported kinetic data for these decompositions that were based on the observed pressures of the gaseous products during the decomposition. Giovanoli and Wiedemann[2] have shown that water is present in zinc oxalate even after drying, and that this water caused the conversion of carbon monoxide to carbon dioxide and hydrogen. This reaction was especially significant during the early phases of the decomposition. When gas pressures were used to obtain values of the fraction decomposed, rates of decomposition would appear to be higher, initially, and the maximum rate would be attained at lower values of the fraction decomposed. In our studies, the independent and quantitative measurements of carbon dioxide and carbon monoxide made it possible to obtain values of the fraction decomposed and the value of the fraction decomposed at which the rate was a maximum that were not in error due to the reaction with water.

The equation $d\alpha/dt = k_1(1 - \alpha) + k_2\alpha(1 - \alpha)$ represented our data over larger ranges of decomposition than did any of the equations used by Yankwich and Zavitsanos in the correlation of their data for the same decompositions.[1]

Experimental Section

Materials. Zinc oxalate and magnesium oxalate dihydrate were prepared by the methods of Yankwich and Zavitsanos.[1]

Apparatus and Techniques. The apparatus and some of the techniques have been previously described.[3-5] A 25-mg sample of the oxalate dihydrate was charged to the sample chamber and was dehydrated at 180–200° for 1.5–2 hr in flowing helium. The amount of water removed was approximately the theoretical quantity, although for each substance residual small amounts of water remained. The residual water was not removed by longer dehydration times or by evacuation for 24 hr at 200°.

After dehydration, the temperature of the chamber was raised to the temperature of the run. Volatile decomposition products were trapped in the sample chamber while helium carrier gas flowed through the by-pass chamber. In these studies the carrier gas was routed to the sample chamber for 30 sec to pick up volatile products and sweep them into a chromatographic column. Gas flow was then diverted to the by-pass chamber for 90 sec, then back to the sample chamber for 30 sec, and so on for the duration of the run. The chromatographic column was one that separated the carbon monoxide and carbon dioxide into distinct peaks.

From the peak areas of carbon monoxide and carbon dioxide which were measured by an integrator, the fraction decomposed, α, at each sample time was calculated by conventional procedures. The rate, $\Delta\alpha/\Delta t$, was calculated for each sample interval. At the beginning of a run the mole ratio of carbon dioxide to carbon monoxide was as high as three because of the conversion of carbon monoxide to carbon dioxide by reaction with water. This ratio decreased during a run but never attained the theoretical ratio of one. Hydrogen formed by the reaction of carbon monoxide with

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(1) (a) P. E. Yankwich and P. D. Zavitsanos, *J. Phys. Chem.*, **68**, 457 (1964); (b) *ibid.*, **68**, 1275 (1964); (c) *ibid.*, **69**, 442 (1965); (d) *ibid.*, **69**, 918 (1965).

(2) R. Giovanoli and H. G. Wiedemann, *Helv. Chim. Acta*, **51**, 1134 (1968).

(3) J. D. Danforth and J. H. Roberts, *J. Catal.*, **10**, 252 (1968).

(4) J. D. Danforth, U. S. Patent 3,431,077 (March 4, 1969).

(5) J. D. Danforth and J. Dix, *Inorg. Chem.*, **10**, 1623 (1971).