Table III. Classification of Energy Types for the Calculated Structure Models[a]

model	α	repulsion	dispersion	Coulombic	Morse
B	2.50	55.4	−88.3	0.0	0.0
	3.51	28.8	−63.1	0.0	0.0
B + D	2.50	38.1	−49.9	−21.4	0.0
	3.51	15.9	−23.3	−26.8	0.0
B + M	2.50	55.7	−82.6	0.0	−5.3
	3.51	28.7	−47.8	0.0	−13.1
B + Q + M	2.50	56.1	−82.6	0.1	−5.6
	3.51	28.7	−47.7	0.1	−13.2
B + D + M	2.50	54.8	−80.4	−1.1	−5.2
	3.51	28.1	−46.3	−0.9	−12.9

[a] The total observed energy is −31.92 kJ mol^{-1}.

of the isolated chlorine molecule. If this description is used, each partial-bond energy ranges from 1.1 to 2.7% of the dissociation energy of chlorine, for the various models considered. The best B + D + M model has a partial-bond energy of 1.1%. The net charge of 0.0914 e on chlorine might be related to the partial bond formation.

We have explored the vicinity of the minimum energy of the B + D + M model. We took grid points at ±0.1 and ±0.2 Å in the lattice constants and ±1 and ±2° in the molecular tilt from the values at the minimum-energy position. The resulting 625 energy values were plotted. Table IV (supplementary material) gives the energy values for the six sections passing through the minimum: *ab*, *ac*, *aθ*, *bc*, *bθ*, and *cθ*. The energy shows the expected positive definite curvature in all sections. The contours are fairly circular and the minimum-energy position is well defined.

If a Cl–Cl dipole exists in the crystal, the infrared spectrum should show a nonzero intensity for the stretching frequency. Walmsley and Anderson[15] observed such infrared stretching frequencies in solid bromine and iodine. Wong and Whalley[16] state that the Cl_2 stretching frequency is absent from the infrared spectrum of solid Cl_2. But they mention experimental problems of high background in the expected frequency region. They also noticed differences in the spectrum which depended on the temperature of deposition of the sample. We think that careful remeasurement of the infrared spectrum of the solid is needed. It is known from the Raman spectrum that the stretching frequency is shifted from 557 cm^{-1} in the gas to 538 cm^{-1} in the crystal at 77 K. While this shift is not as large as those shown by Br_2 or I_2, it indicates a significant interaction which could be accompanied by charge transfer, in agreement with our model. A solution of Cl_2 in benzene,[17] for instance, shows a Cl–Cl infrared stretching absorption at 526 cm^{-1}. Gaseous chlorine dimer, $(Cl_2)_2$, has a detectable observed dipole moment[18] of at least 0.2 D.

Acknowledgment. We thank Dr. Thomas L. Starr for helpful suggestions with regard to the infrared spectra.

Registry No. chlorine, 7782-50-5.

Supplementary Material Available: Table IV, giving the energy values for the six sections passing through the minimum (1 page). Ordering information is given on any current masthead page.

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Contribution from the Department of Inorganic Chemistry,
University of Melbourne, Parkville 3052, Victoria, Australia

Volumes of Activation for Substitution Reactions of Tris(1,10-phenanthroline)- and Tris(2,2′-bipyridyl)iron(II) Complexes with Hydroxide and Cyanide Ions from High-Pressure Solution Kinetics

GEOFFREY A. LAWRANCE,* DONALD R. STRANKS, and SURAPONG SUVACHITTANONT

Received April 18, 1978

The effect of high pressure on the rates of substitution of $Fe(phen)_3^{2+}$ and $Fe(bpy)_3^{2+}$ (phen = 1,10-phenanthroline; bpy = 2,2′-bipyridyl) with hydroxide and cyanide ion has been evaluated. All reaction rates are significantly retarded upon the application of pressure. The hydroxide-dependent component of the rate expression exhibits volumes of activation ($\Delta V^{\ddagger}$) of +19.7 ± 0.3 and +21.5 ± 0.4 cm^3 mol^{-1} for substitution of $Fe(phen)_3^{2+}$ and $Fe(bpy)_3^{2+}$, respectively. The cyanide-dependent term exhibits $\Delta V^{\ddagger}$ of +19.8 ± 1.0 and +20.9 ± 1.6 cm^3 mol^{-1} for substitution of $Fe(phen)_3^{2+}$ and $Fe(bpy)_3^{2+}$, respectively. A rate-determining dissociative interchange mechanism is most consistent with the observation that $\Delta V^{\ddagger}$ for substitution of each complex is positive, pressure-independent, and independent of nucleophile.

Introduction

Substitution reactions of diimine metal complexes of the type $M(aa)_3^{n+}$ (aa = phen = 1,10-phenanthroline or aa = bpy = 2,2′-bipyridyl) have been the subject of many investigations which have been reviewed on several occasions previously.[1-4] For the extensively studied $Fe(aa)_3^{2+}$ complexes, the rate of ligand substitution has been observed to be enhanced in the presence of hydroxide, cyanide, and azide ions. A general rate expression of the type

$$k_{obsd} = k_a + k_X[X^-] \qquad (1)$$

has been reported for $X^- = CN^-$ or N_3^- when $[X^-] < 1.0$ M. This expression is also adequate for $X^- = OH^-$ at $[OH^-] \leq 0.1$ M at least, although a further term in $[OH^-]^2$ is necessary to account for experimental behavior at high hydroxide ion concentrations.

These complexes are of particular interest because of the lack of readily ionizable protons on the ligands, which makes a conjugate base mechanism of the type proposed for many reactions of complexes of the isoelectronic cobalt(III) ion implausible. A variety of different mechanisms have been proposed for substitution reactions of these iron(II) complexes. For $Fe(bpy)_3^{2+}$, a dissociative mechanism involving nucleophilic attack on a five-coordinate intermediate formed by one-ended dissociation of a bpy ligand via twisting about the C(2)–C(2′) bond joining the two pyridine rings in the chelate has been proposed.[3] While such a twisting process cannot occur in the fused phen ring system of $Fe(phen)_3^{2+}$, dissociation via simultaneous stretching of both Fe–N bonds of a phen chelate in the transition state may occur. An effectively associative mechanism involving direct attack at the iron center by the nucleophile has been considered for the nucleophile-dependent term for substitution of both $Fe(phen)_3^{2+}$ and $Fe(bpy)_3^{2+}$.[5-7] Further, a mechanism for hydrolysis involving nucleophilic attack at a chelate ring carbon adjacent to a nitrogen atom and subsequent deprotonation of the quaternary nitrogen formed, followed by an intermolecular shift of the hydroxyl group to the metal ion, has been proposed.[4,8,9] Finally, an ion-pairing mechanism similar to that considered for hydrolysis of $Fe(phen)_3^{2+}$ [2] and $Cr(bpy)_3^{2+}$ [10] may be a general mechanism.

The elucidation of inorganic reaction mechanisms from volumes of activation ($\Delta V^{\ddagger}$) determined from the effect of high pressure on reaction rates in solution has been reviewed.[11] Previously in these laboratories, volumes of activation for acid aquation of $Fe(phen)_3^{2+}$ ($\Delta V^{\ddagger} = +15.4$ cm^3 mol^{-1} [12]) and $Fe(bpy)_3^{2+}$ ($\Delta V^{\ddagger} = +11.7$ cm^3 mol^{-1} [13]) have been measured and have been interpreted in terms of a rate-determining dissociative mechanism. A similar mechanism has also been proposed for nucleophilic attack on $Fe(CN)_5(3,5\text{-}Me_2py)^{3-}$ by cyanide, pyridine, or imidazole (Me_2py = dimethylpyridine), since a nucleophile-independent $\Delta V^{\ddagger}$ of approximately +21 cm^3 mol^{-1} was observed for each reaction.[14]

The uncertainty regarding the mechanism operating in nucleophilic substitution reactions of $Fe(phen)_3^{2+}$ and $Fe(bpy)_3^{2+}$ has prompted us to measure $\Delta V^{\ddagger}$ for reactions of these complexes with cyanide and hydroxide ions. Comparison of experimental $\Delta V^{\ddagger}$ values with those expected for different proposed mechanisms, deferred to the Discussion, allows mechanistic differentiation.

Experimental Section

Preparative Methods. Both $Fe(phen)_3^{2+}$ and $Fe(bpy)_3^{2+}$ were prepared using previously published methods and were isolated analytically pure as the perchlorate salts.[15]

Standard solutions of 0.1 M sodium cyanide and 0.1 M sodium hydroxide were prepared directly from analytical reagent grade materials in distilled water.

Kinetic Methods. The rates of substitution at high pressures were determined by monitoring absorbance changes at 526 nm using a Varian 635D spectrophotometer incorporating a high-pressure cell in which the reaction solution was pressurized at pressures up to 1380 bar while monitoring absorbance change directly. The temperature within the cell block was maintained to within ±0.1 °C by thermostated water circulation.

Complex concentrations of 4×10^{-4} M were employed throughout, thus maintaining a 250-fold excess of nucleophile.

Rate constants (k_{obsd}) were evaluated using least-squares analysis via the Guggenheim method. The nucleophile-dependent second-order rate constant (k_X) was obtained by first subtracting the previously determined nucleophile-independent aquation rate at each pressure from k_{obsd} at that pressure. Volumes of activation can be determined using expression 2[11] obtained from graphs of ln k_X vs. pressure (P).

$$-RT(\partial \ln (k_X)/\partial P)_T = \Delta V^{\ddagger} \qquad (2)$$

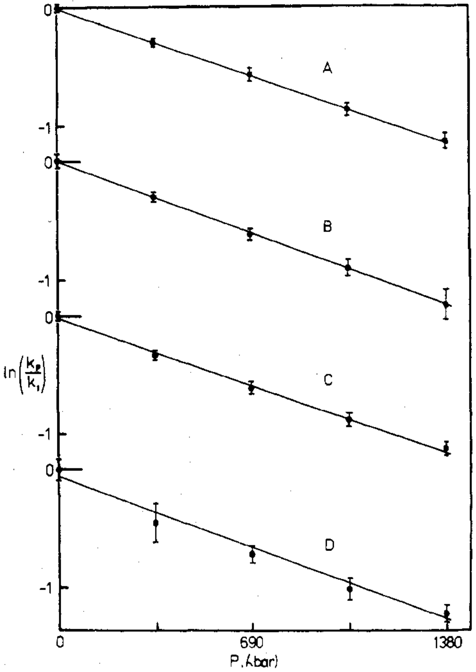


Figure 1. Pressure dependence of nucleophile-dependent rates of substitution of (A) $Fe(phen)_3^{2+}$ and (B) $Fe(bpy)_3^{2+}$ with hydroxide ion and of (C) $Fe(phen)_3^{2+}$ and (D) $Fe(bpy)_3^{2+}$ with cyanide ion.

Table I. Pressure-Dependent Rates of Reaction of Iron(II) Complexes in 0.1 M Hydroxide Ion Solution

$Fe(phen)_3^{2+}$			$Fe(bpy)_3^{2+}$		
P, bar	$10^4 k_{obsd}$,[a] s^{-1}	$10^3 \times k_{OH}$,[b] dm^3 mol^{-1} s^{-1}	P, bar	$10^4 k_{obsd}$,[a] s^{-1}	$10^4 \times k_{OH}$,[b] dm^3 mol^{-1} s^{-1}
1	7.41 ± 0.07 (3)[c]	7.10	1	5.13 ± 0.08 (3)[c]	15.5
345	5.49 ± 0.03 (2)	5.24	345	4.19 ± 0.03 (3)	11.4
690	4.23 ± 0.16 (3)	4.02	690	3.43 ± 0.03 (3)	8.3
1034	3.26 ± 0.12 (4)	3.09	1034	2.83 ± 0.04 (2)	6.2
1380	2.43 ± 0.12 (3)	2.30	1380	2.34 ± 0.07 (4)	4.6

[a] Temperature = 20.0 ± 0.1 °C. [b] Calculated from $k_{obsd} = k_a + k_{OH}[OH^-]$ using data for the pressure dependence of the nucleophile-independent aquation reaction from ref 12 and 13. [c] Standard deviations and number of independent runs (in parentheses) included.

In certain cases the volume of activation itself can exhibit a pressure dependence. By means of first-, second-, and third-order polynomial regressions on the data, it was found that the simple first-order dependence on pressure (eq 2) provides the best fit for all reactions studied. Graphs of ln k_X vs. pressure for each complex are illustrated in Figure 1, where the similar slope of the graph for each reaction indicates similar $\Delta V^{\ddagger}$ values in each case.

Results

Hydroxide-Dependent Substitution Reactions. The rates of reaction of both $Fe(phen)_3^{2+}$ and $Fe(bpy)_3^{2+}$ in 0.1 M sodium hydroxide solution are significantly retarded by the application of pressure. Observed reaction rates and the second-order hydroxide-dependent rate determined at five different pressures for each complex are presented in Table I. The $Fe(phen)_3^{2+}$ complex exhibits a $\Delta V^{\ddagger} = +19.7 \pm 0.3$ cm^3 mol^{-1}, while for $Fe(bpy)_3^{2+}$ $\Delta V^{\ddagger} = +21.5 \pm 0.4$ cm^3 mol^{-1}.

Cyanide-Dependent Substitution Reactions. The rates of reaction of both $Fe(phen)_3^{2+}$ and $Fe(bpy)_3^{2+}$ in 0.1 M sodium cyanide are also significantly retarded by the application of pressure. Observed reaction rates and second-order cyanide-dependent rates determined at five different pressures for each complex are presented in Table II. The $Fe(phen)_3^{2+}$

Table II. Pressure-Dependent Rates of Reaction of Iron(II) Complexes in 0.1 M Cyanide Ion Solution

$Fe(phen)_3^{2+}$			$Fe(bpy)_3^{2+}$		
P, bar	$10^4 k_{obsd}$,[a] s^{-1}	$10^4 \times k_{CN}$,[b] $dm^3\ mol^{-1}\ s^{-1}$	P, bar	$10^4 k_{obsd}$,[d] s^{-1}	$10^4 \times k_{CN}$,[b] $dm^3\ mol^{-1}\ s^{-1}$
1	1.98 ± 0.05 (3)[c]	12.5	1	4.66 ± 0.10 (4)[c]	10.8
345	1.48 ± 0.05 (3)	8.7_5	345	3.71 ± 0.13 (3)	6.6
690	1.16 ± 0.03 (3)	6.7	690	3.01 ± 0.02 (3)	5.1
1034	0.91 ± 0.02 (4)	5.1_5	1034	2.60 ± 0.04 (2)	3.9
1380	0.73 ± 0.02 (2)	4.1	1380	2.20 ± 0.04 (4)	3.2

[a] Temperature = 25.0 ± 0.1 °C. [b] Calculated from $k_{obsd} = k_a + k_{CN}[CN^-]$ using data for the pressure dependence of the nucleophile-independent aquation reaction from ref 12 and 13. [c] Standard deviations and number of independent runs (in parentheses) included. [d] Temperature = 20.0 ± 0.1 °C.

Table III. Activation Parameters for Substitution Reactions of Iron(II) Complexes in Aqueous Solution

complex	nucleophile	$\Delta H^‡$, kJ mol^{-1}	$\Delta S^‡$, J K^{-1} mol^{-1}	$\Delta V^‡$, cm^3 mol^{-1}	ref
$Fe(phen)_3^{2+}$	*a*	122.4 (±0.8)	+88 (±3)	+15.4 (±0.4)	12
	OH^-	96.3 (±0.5)	+18 (±3)	+19.7 (±0.3)	*b*, 6
	CN^-	86.2 (±7)[c]	+4 (±20)[c]	+19.8 (±1.0)	*b*, 2
$Fe(bpy)_3^{2+}$	*a*	114.5 (±2)	+71 (±4)	+11.7 (±0.7)	13
	OH^-			+21.5 (±0.4)	*b*
	CN^-	96.4 (±2.5)	+37 (±9)	+20.9 (±1.6)	*b*, 7

[a] Aquation in 1.0 M aqueous HCl. [b] This work. [c] Recomputed from original data.

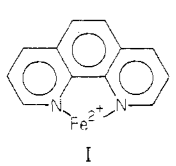
complex exhibits a $\Delta V^‡ = +19.8 \pm 1.0$ cm^3 mol^{-1}, while for $Fe(bpy)_3^{2+}$ $\Delta V^‡ = +20.9 \pm 1.6$ cm^3 mol^{-1}.

Volumes of activation for all four reactions studied are collected in Table III. Enthalpies and entropies of activation previously determined for these reactions are also included in Table III, together with activation parameters for acid aquation of the complexes, for comparative purposes.

Discussion

Volumes of activation for both the hydroxide-dependent and cyanide-dependent substitution reactions of $Fe(phen)_3^{2+}$ are identical within experimental error. A similar relationship holds for reactions of $Fe(bpy)_3^{2+}$ with these nucleophiles. These observations indicate that a mechanism in which the rate-determining step is independent of nucleophile may be operating. Further, $\Delta V^‡$ for substitution of $Fe(phen)_3^{2+}$ and $Fe(bpy)_3^{2+}$ with nucleophiles are similar.

Chelated phen (structure I) is a rigid flat ligand which can best be visualized as dissociating via simultaneous stretching of both Fe–N bonds in order to avoid severe steric interactions with other coordinated phen chelates. The protons in the 2 and 9 positions of phen are almost in van der Waals contact with adjacent phen rings and preclude one-ended dissociation with pivoting about the intact Fe–N bond.[12] Chelated bpy (structure II) can dissociate in an analogous manner to that proposed for phen or, alternatively, in a one-ended manner by rotation of one donor group about the C(2)–C(2′) bond joining the two pyridine rings.[3,13] If a dissociative mechanism were assumed, the similar $\Delta V^‡$ values for the phen and bpy complexes could reflect a common mode of dissociative ligand release for the two complexes.



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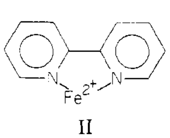

II

An associative mechanism has been proposed previously for these nucleophile-dependent substitution processes.[5-7] Reactivity trends for substitution reactions of $Fe(bpy)_3^{2+}$ with CN^- in mixed aqueous solvents[16] can be rationalized in terms of associative character for the reaction. However, variation of the degree of solvation of the initial or transition state of a dissociative mechanism could equally well account for these observations.

Each ion in solution is surrounded by layers of severely electrostricted water molecules which experience electrostatic compression and exhibit distinctly lower intrinsic volumes and compressibilities than water in the bulk solvent.[11,17] An associative mechanism involving direct attack by the nucleophile at the metal center would require appreciable desolvation of the attacking nucleophile as it approaches to within bonding distance of the metal ion from both steric and charge neutralization contributions. Desolvation and subsequent release of electrostricted solvent to the bulk solvent would involve a substantial positive contribution to both the volume and compressibility of activation. From available data for the volume change for ionization of weak acids in aqueous solution,[18] the hydroxide ion exhibits an unusually large volume of electrostriction (V^0_{el}) of +22 cm^3 mol^{-1}, while the cyanide ion exhibits a smaller V^0_{el} of +8 cm^3 mol^{-1}. Since the intrinsic volumes of OH^- and CN^- can be assumed to be similar,[14,19] direct nucleophilic attack at the metal center should produce positive *but distinctly different* overall $\Delta V^‡$ values for the different nucleophiles. Further, appreciable changes in compressibility of released water molecules expected on desolvation should lead to a pressure dependence of $\Delta V^‡$ itself.[11] The observation of identical positive pressure-independent values of $\Delta V^‡$ for OH^- and CN^- substitution reactions of both substrates (Table III) do not support such an associative mechanism.

The mechanism proposed by Gillard specifically for the hydrolysis reaction involves direct nucleophilic attack on the unsaturated diimine ligand as the initial step,[4,8,9] rather than attack directly at the metal center. As for the associative mechanism discussed above, this would involve desolvation of the nucleophile and a pressure-dependent value of $\Delta V^‡$. The same mechanism applied in the case of cyanide attack would lead to a distinctly different $\Delta V^‡$ value, as argued earlier for an associative mechanism. On the other hand, if the mechanism of cyanide substitution differed from that proposed by Gillard for hydroxide substitution, then different values of $\Delta V^‡$ would be expected. Recently, infrared evidence for partial formation of a pseudo-base intermediate from a solution of $Fe(phen)_3^{2+}$ with concentrated cyanide ion has been presented, although in dilute cyanide solutions the concentration of the species $[Fe(phen)_2(phenCN)]^+$ will be very small.[20] The mechanistic significance of such preequilibria at low nucleophile concentrations is not clearly established, and support for this type of mechanism is not forthcoming from our experimental $\Delta V^‡$ data. Previously, it has been indicated that Gillard's mechanism is not appropriate at least for hydrolysis of bpy–Pt^{II} complexes.[21]

An ion-pairing interchange mechanism formally satisfies the observed reaction kinetics for substitution of both $Fe(phen)_3^{2+}$ and $Fe(bpy)_3^{2+}$ but already such a mechanism has been discounted by previous authors for the hydroxide substitution of $Cr(bpy)_3^{3+}$ [10] and $Fe(phen)_3^{2+}$.[2] The ion-pairing mechanism also seems unlikely from the volumes of activation determined in this study. The values of $\Delta V^‡$ for nucleophilic substitution of $Fe(phen)_3^{2+}$ and $Fe(bpy)_3^{2+}$ by OH^- and CN^- reported in this study are very similar to $\Delta V^‡$ for substitution of $Fe(CN)_5(3,5\text{-}Me_2py)^{3-}$; all $\Delta V^‡$ values are pressure-independent. In the case of nucleophilic substitution of the anionic substrate $Fe(CN)_5(3,5\text{-}Me_2py)^{3-}$ by the nucleophiles CN^-, pyridine, and imidazole, an average activation volume of $\pm 20.7 \pm 1.0$ cm^3 mol^{-1} was observed irrespective of the nucleophile.[14] In this reaction there is no likelihood of an ion-pairing mechanism, and the common $\Delta V^{\ddagger}$ values constitute strong evidence of a dissociative D mechanism for which there is also other kinetic evidence. The similarity in $\Delta V^{\ddagger}$ values for nucleophilic substitution of $Fe(phen)_3^{2+}$ and $Fe(bpy)_3^{2+}$ suggests related dissociated mechanisms for these two substrates, although a fortuitous coincidence of $\Delta V^{\ddagger}$ values for an ion-pair interchange mechanism might be possible. Furthermore, pressure-independent $\Delta V^{\ddagger}$ values for nucleophilic substitution of $Fe(phen)_3^{2+}$ and $Fe(bpy)_3^{2+}$ are not consistent with an ion-pair mechanism involving desolvation of the anions in reversible formation of an ion-pair precursor.

The nucleophilic substitution reactions of $Fe(phen)_3^{2+}$ and $Fe(bpy)_3^{2+}$ are best interpreted in terms of a dissociative mechanism. It has been suggested that acid aquation of $Fe(bpy)_3^{2+}$ and $Fe(phen)_3^{2+}$ involves a low-spin to high-spin excitation in forming the transition state.[22,23] Experimental $\Delta V^{\ddagger}$ for aquation should subsequently involve positive contributions from spin excitation leading to an expanded transition state and from release of the dissociating chelate wedge into the solvent.[22] Assuming that such a spin transition is generally involved in dissociation reactions of these complexes, the estimated[22] contribution of approximately +9 cm^3 mol^{-1} from this component for $Fe(phen)_3^{2+}$ indicates a substantially positive component of +11 to +13 cm^3 mol^{-1} remains, assigned to release of a diimine ligand into the solvent. As has been argued previously[12,13] for acid aquation of $Fe(phen)_3^{2+}$ and $Fe(bpy)_3^{2+}$, the positive $\Delta V^{\ddagger}$ observed are most consistent with a dissociative interchange (I_d) description of the mechanism. Similar $\Delta V^{\ddagger}$ for nucleophilic substitution of both phen and bpy complexes may indicate a common mode of dissociative release of diimine ligand. Cyanide and hydroxide ion, which are much better nucleophiles than the solvent water, can subsequently compete effectively even at low concentrations for the dissociated sites of the transition state in the complexes. The nucleophile-independent nature of $\Delta V^{\ddagger}$ for each complex is consistent with such a primarily dissociative (I_d or D) mechanism. The I_d mechanism would allow minor participations of the incoming OH^- and CN^- nucleophiles; this is reflected in different values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ accounting for detectable differences in the reactivities of the two nucleophiles.

Recently, evidence for a direct relationship between $\Delta V^{\ddagger}$ and $\Delta S^{\ddagger}$ has been presented by Twigg.[24] For the systems studied in the paper, it can be seen (Table III) that, while $\Delta V^{\ddagger}$ remains relatively constant, significant variation of $\Delta S^{\ddagger}$ from near zero to positive has been observed. While the relationship of $\Delta V^{\ddagger}$ and $\Delta S^{\ddagger}$ appears to hold for a number of aquation and isomerization reactions,[24] it is apparent that there is no effective relationship for the systems reported here. It is likely that contributions to $\Delta S^{\ddagger}$ arising from disorder of the solvent in the vicinity of the complex ion need not also contribute to $\Delta V^{\ddagger}$ if movement to areas of significantly different electrostriction does not occur. These entropy contributions, perhaps arising simplistically from rotational or circular displacement motion in regions where the compressibility and intrinsic volume of electrostricted solvent remains relatively constant, could be of significance for certain reactions where no relationship of $\Delta V^{\ddagger}$ and $\Delta S^{\ddagger}$ is observed. It would seem that the use of $\Delta S^{\ddagger}$ alone as a mechanistic guide should be approached with more caution than interpretations based on $\Delta V^{\ddagger}$ data. This would seem exemplified by results presented in this paper, since consideration of $\Delta V^{\ddagger}$ data alone allows a mechanistic interpretation to be drawn, whereas $\Delta S^{\ddagger}$ data are less consistent.

Acknowledgment. We thank the Australian Research Grants Committee for financial support. S.S. thanks the Prince of Songkla University, Thailand, for leave of absence.

Registry No. $Fe(phen)_3^{2+}$, 14708-99-7; $Fe(bpy)_3^{2+}$, 15025-74-8; OH^-, 14280-30-9; CN^-, 57-12-5.

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