References and Notes

(1) M. Allan, J. P. Maier, O. Marthaler, and J.-P. Stadelmann, *J. Chem. Phys.*, in press, and references therein.
(2) See J. P. Maier in "Kinetics of Ion-Molecule Reactions", P. Ausloos, Ed., Plenum Press, 1979, for a review of the field.
(3) M. Allan, E. Kloster-Jensen, and J. P. Maier, *J. Chem. Soc., Faraday Trans. 2*, **73**, 1406 (1977).
(4) T. B. Jones and J. P. Maier, *Int. J. Mass Spectrom. Ion Phys.*, in press.
(5) J. H. Callomon and F. Creutzberg, *Philos. Trans. R. Soc. London*, **277**, 157 (1974).
(6) R. N. Dixon, G. Duxbury, M. Horani, and J. Rostas, *J. Mol. Phys.*, **22**, 977 (1971); G. Duxbury, M. Horani, and J. Rostas, *Proc. R. Soc. London, Ser. A*, **331**, 109 (1972).
(7) H. Lew and I. Heiber, *J. Chem. Phys.*, **58**, 1246 (1973); H. Lew, *Can. J. Phys.*, **54**, 2028 (1976).
(8) K. T. Wu and A. J. Yencha, *Can. J. Phys.*, **55**, 767 (1977).
(9) H. Beyer, H. Jenne, J. B. Hynes, and K. Niedenzu, *Adv. Chem. Ser.*, No. **42**, 266 (1964).
(10) D. W. Turner, *Proc. R. Soc. London, Ser. A*, **307**, 15 (1968).
(11) D. R. Lloyd and N. Lynaugh, *Phil. Trans. R. Soc. London, Ser. A*, **268**, 97 (1970).
(12) J. Kroner, D. Proch, W. Fuss, and H. Bock, *Tetrahedron*, **28**, 1585 (1972).
(13) J. Vogt, personal communication.
(14) M. Allan and J. P. Maier, *Chem. Phys. Lett.*, **34**, 442 (1975); M. Allan, J. P. Maier, and O. Marthaler, *Chem. Phys.*, **26**, 131 (1977).
(15) J. P. Maier and O. Marthaler, *Chem. Phys.*, **32**, 419 (1978).
(16) B.-Ö. Jonsson and E. Lindholm, *Ark. Fys.*, **39**, 65 (1969); W. von Niessen, L. S. Cederbaum, and W. Kraemer, *J. Chem. Phys.*, **65**, 1378 (1976), and references therein.

Contribution from the Institut de Chimie Minérale et Analytique, University of Lausanne, CH-1005 Lausanne, Switzerland

High-Pressure Nuclear Magnetic Resonance Kinetics. 5. Proton Nuclear Magnetic Resonance Study of the Effect of Pressure on the Exchange of Nonaqueous Solvents on Nickel(II) and Cobalt(II)[1]

FELIX K. MEYER, KENNETH E. NEWMAN, and ANDRÉ E. MERBACH*

The effect of pressure (up to 200 MPa) on the solvent exchange of $MS_6(ClO_4)_2$ with M = Ni or Co and S = N,N-dimethylformamide (DMF), acetonitrile, or methanol has been studied by utilizing ^{1}H FT NMR T_2 measurements. The derived volumes of activation, ΔV^* ($cm^3\ mol^{-1}$), for the above solvent series with Ni(II) are 9.1 ± 0.3 (297 K), 9.6 ± 0.3 (294 K), and 11.4 ± 0.6 (307 K) and with Co(II) are 6.7 ± 0.3 (296 K), 9.9 ± 0.7 (260 K), and 8.9 ± 0.3 (279 K). These values are in accord with a dissociative interchange mechanism, although they suggest Co(II) exhibits less dissociative character than Ni(II). For both ions, the solvent variation of $\Delta V^*/V^\circ$ mirrors that of ΔG^*; these results may suggest that the faster the reaction, the less dissociative character it has.

1. Introduction

The effect of pressure on the rate of a chemical reaction is now a well-accepted approach in elucidating reaction mechanisms.[4] For the understanding of the mechanisms of complex formation and inner-sphere redox processes, the exchange of solvent molecules between the primary solvation shell of a metal ion and bulk solvent may be considered the fundamental reaction. It is precisely for solvent-exchange reactions, where conventional mechanistic tests such as variation of the nature and the concentration of reacting ligands are not possible, that pressure effects will prove most useful. The parameter derived from the pressure dependence of a reaction rate constant by using transition state theory is the volume of activation $\Delta V^* = -RT(\partial \ln k/\partial P)_T$. It expresses the change in volume during the activation process, i.e., the difference in volume between the transition state and the reactants. ΔV^* primarily consists of two contributions: the intrinsic part, ΔV^*_{int}, and the electrostrictive part ΔV^*_{el}. ΔV^*_{int} represents the intrinsic difference in molecular size between reactants and transition state, due to the effects of bond making, breaking, and stretching. ΔV^*_{el} represents the accompanying change of volume of the surrounding solvent resulting from changes in electrostriction. As discussed by Swaddle[5] and Stranks[6] the electrostriction changes between reactants and transition state must be negligibly small for solvent exchange reactions where no charge separation or cancellation is involved. Therefore ΔV^* is a good measure of ΔV^*_{int}, and it is possible to correlate directly a positive volume of activation with a dissociative activation mode or a negative value with an associative activation mode for the exchange process.

Until recently, the only high-pressure solvent exchange studies have been those of the nonlabile ions cobalt(III), chromium(III), rhodium(III), and iridium(III)[4-6] by means of isotopic labeling. ΔV^* values for the latter three ions are in accord with an associative interchange, I_a, mechanism, whereas a dissociative interchange, I_d, mechanism is indicated for cobalt(III). It has been suggested that I_a mechanisms are the rule for 3+ ions, Co^{3+} being an exception due to its small size.[5] It is widely believed that the 2+ ions exchange solvent via I_d mechanisms;[7] however, for these labile ions no activation volumes are available for solvent-exchange reactions. The experimental technique used to obtain kinetic information on these systems is NMR. We have recently reported the design of a high-pressure proton NMR probe-head,[8] as well as the results on the effect of pressure on the methanol[9] and acetonitrile[2] exchange on nickel(II). In this paper, we report the results of the first systematic study by ^{1}H NMR of the effect of pressure on the methanol, acetonitrile, and dimethylformamide exchange on nickel(II) and cobalt(II). The results show that the solvent exchange on nickel(II) and cobalt(II) are both clearly dissociative interchange, I_d, but suggest that the latter exchange systems have *less* dissociative character than the former.

2. Experimental Section

Solvents. Methanol (Fluka puriss p.a.) was shaken with anhydrous calcium sulfate for 24 h and distilled (water content by Karl-Fischer titration less than 50 ppm). Anhydrous dilute acidic methanol was obtained by adding 65% $HClO_4$ to methanol and removing the water by reaction with a slight excess of methyl orthoformate N,N-Dimethylformamide (Fluka puriss p.a.) was distilled from BaO under reduced pressure and stored over previously activated 4-Å molecular

sieves (Merck) (water content <30 ppm). Acetonitrile (Fluka puriss p.a.) was purified by distillation at least twice from P_2O_5 and stored similarly (water content <10 ppm).

Preparation of Complexes. Dry $[Ni(CH_3OH)_6](ClO_4)_2$ and $[Co(CH_3OH)_6](ClO_4)_2$ were prepared from the hydrated salt and methyl orthoformate by using van Leeuwen's procedure.[10] The amide complexes $[Ni(DMF)_6](ClO_4)_2$ and $[Co(DMF)_6](ClO_4)_2$ were prepared by the method of Drago et al.[11] $[Co(CH_3CN)_6](ClO_4)_2$ was prepared according to the method of Wickenden and Krause.[12] The metal content of the crystalline products was checked by EDTA titration. The water content of the complexes, as determined by Karl-Fischer titration, was always less than 0.05 mol of water/mol of salt.

Solutions for NMR Study. Solutions for NMR study were prepared by weight in a glovebox (water <6 ppm). Except for the solutions of $[Co(CH_3CN)_6](ClO_4)_2$ which contained 1% benzene, all solutions contained 1% by weight Me_4Si as internal shift and line width standard. For the prevention of base-catalyzed exchange in the methanol solutions, acidic methanol was added to produce an acid concentration of ~0.06 M.

Measurements. ^1H FT NMR spectra were obtained on a Bruker WP-60 spectrometer operating at 60 MHz with an external ^{19}F lock. T_2 measurements were obtained from the full width at half height of the NMR absorption resonance, $\Delta\nu_{1/2}$, in Hz, by means of the relationship $(T_2)^{-1} = \pi(\Delta\nu_{1/2})$. All line widths were corrected for magnet inhomogeneity and instability by substracting the width of the reference. Paramagnetic broadening of the internal reference (as determined by using a 5-mm coaxial cell) was negligible except for the acetonitrile solutions, and the width of the ambient pressure benzene resonance was added to take into account the overcorrection.[2] The high-pressure NMR probe used is similar to that described previously.[8] The temperature stability over periods of several hours was better than ± 0.1 K.[13]

3. Data Treatment and Results

3.1. Basic NMR Equations. The detailed expressions for the effect of solvent exchange on the transverse NMR relaxation time and the chemical shift for the free or coalesced signal taking into account a possible outer-sphere interaction have been discussed in a previous paper.[2] The basic equations needed in this paper will be given for easier reference. Defining

$$\frac{1}{T_{2r}} = \frac{1}{P_m}\left(\frac{1}{T_2} - \frac{1}{T^\circ_{2A}}\right) \quad (1)$$

we have the modified Swift and Connick equation:[14]

$$\frac{1}{T_{2r}} = \frac{1}{\tau_m}\left[\frac{T_{2m}^{-2} + (T_{2m}\tau_m)^{-1} + \Delta\omega_m^2}{(T_{2m}^{-1} + \tau_m^{-1})^2 + \Delta\omega_m^2}\right] + \frac{1}{T_{2os}} \quad (2)$$

where T_2 is the observed relaxation time, T°_{2A} is the relaxation time of the pure solvent, P_m is the mole fraction of bound solvent, T_{2m} is the relaxation time of the bound solvent in the absence of exchange, T_{2os} is the outer-sphere contribution, τ_m is the residence time of a bound solvent molecule, and $\Delta\omega_m$ is the shift between bound and free solvent in the absence of exchange. τ_m may be related to the pseudo-first-order reaction rate constant for solvent exchange k by the relationship $k = 1/\tau_m$ and its temperature dependence is given by Eyring's equation.

As has been clearly demonstrated,[2] the simplified eq 3 may

$$\frac{1}{T_{2r}} = \frac{1}{\tau_m} + \frac{1}{T_{2os}} \quad (3)$$

be used to obtain reliable ΔV^* values in the slow-exchange region. In the region of intermediate exchange, it is in general necessary to use the full eq 2.

3.2. Volumes of Activation. According to transition state theory, the volume of activation ΔV^* is related to the rate constant by

$$\Delta V^* = -RT(\partial \ln k/\partial P)_T \quad (4)$$

and if we assume a polynomial relationship between $\ln k$ and P, the pressure dependence of the rate constant can be expressed as

$$\ln k_p = \ln k_0 - \Delta V_0^* P/RT + \Delta\beta^* P^2/2RT \quad (5)$$

where k_0 is the zero pressure rate constant, ΔV_0^* is the zero pressure volume of activation, and $\Delta\beta^*$ is the pressure-independent compressibility of activation.

For all the systems discussed, the compressibility term is small. Thus in order to distinguish between values of activation volume at zero pressure derived by assuming zero and variable $\Delta\beta^*$, we will use ΔV^* to refer to the former and ΔV_0^* to the latter treatment.

All the experiments were performed at least twice at closely similar (but not identical) temperatures. The volume of activation shows only small variation with temperature whereas k_0 shows large variation. The data for each system were thus analyzed by using an equation of the form

$$\ln k_p^i = \ln k_0^i - \Delta V_0^* P/RT + \Delta\beta^* P^2/2RT \quad (6)$$

where i refers to the experiment number (N experiments) and k_0^i ($i = 1, N$), ΔV_0^*, and $\Delta\beta^*$ were treated as parameters to be optimized with a nonlinear least-squares fitting procedure.

This technique is of particular importance if one requires significant values of $\Delta\beta^*$ which are very sensitive to the dispersion of the data in a single experiment.

Full details of the experimental and calculated results for the six systems studied are given in the supplementary material.

3.3. $[Ni(CH_3OH)_6](ClO_4)_2$ in CH_3OH. The optimum choice of temperature for high-pressure line width studies in the slow-exchange regions requires the balancing of two opposed effects. First, one wishes to work at the highest possible temperature in order to reduce the relative importance of the outer-sphere contribution but, second, the simplified eq 3 becomes more accurate the lower the temperature.

Variable-temperature ^1H T_2 measurements on the CH_3 group by Luz and Meiboom[15] show that a convenient temperature to perform the variable-pressure experiments is ~300 K. This temperature is in the middle of the slow-exchange region where we have previously shown that the simplified eq 3 may be used with little error.[2] We have repeated the variable-temperature T_2 measurements between 334 and 216 K and our results appear closely similar to those of Luz and Meiboom. Since these authors do not give sufficient information to calculate the outer-sphere contribution, we shall use our values.

A preliminary account of this system has already been published[9] but we have recalculated the results by using the multiple fitting technique discussed above. Experimental and calculated values (assuming $\Delta\beta^* = 0$) of $\ln(k_p/k_0)$ are shown in Figure 1. Table I gives the volumes and compressibility of activation ΔV^*, ΔV_0^*, and $\Delta\beta^*$ together with their standard deviations. Also given are the variances σ^2 for the respective functional dependence (linear or quadratic) used in the data treatment.

Since, for this system, the outer-sphere contribution to $(T_{2r})^{-1}$ in eq 3 is significant (~13% at ambient pressure), its pressure dependence was studied at 243 K. At this temperature chemical exchange effects on $(T_{2r})^{-1}$ are negligible. The outer-sphere contribution appeared to increase by about 9% for 100 MPa. This is much less than what one expects from viscosity changes (~40%). However, such a change, as reported earlier, has a negligible effect on the derived value of the volume of activation.

3.4. $[Ni(DMF)_6](ClO_4)_2$ in DMF. Variable-temperature T_2 measurements have been made for this system by several authors (see Table III below). We shall use Matwiyoff's ^1H

Table I. Activation Volumes for Solvent Exchange on Nickel(II) and Cobalt(II) Perchlorates

cation	solvent	T, K	ΔV^*, $cm^3\ mol^{-1}$	$10^3 \sigma^2$ [a]	ΔV_0^*, $cm^3\ mol^{-1}$	$10^2 \Delta\beta^*$, $cm^3\ mol^{-1}\ MPa^{-1}$	$10^3 \sigma^2$ [a]
Ni^{2+}	CH_3OH	307	11.4 ± 0.6	4.27	13.0 ± 1.6	2.0 ± 2.0	4.28
	DMF	297	9.1 ± 0.3	1.03	10.1 ± 0.9	1.0 ± 1.0	1.02
	CH_3CN	294	9.6 ± 0.3	0.82	11.3 ± 1.0	1.8 ± 1.0	0.74
Co^{2+}	CH_3OH	279	8.9 ± 0.3	1.01	10.9 ± 0.7	2.0 ± 0.7	0.72
	DMF	296	6.7 ± 0.3	0.64	8.4 ± 0.8	1.4 ± 0.7	0.49
		253	9.2 ± 0.3	0.30	9.9 ± 0.8	0.8 ± 0.9	0.31
	CH_3CN	260	9.9 ± 0.7	3.28	8.2 ± 2.3	-1.7 ± 2.2	3.33

[a] σ^2 is the variance.

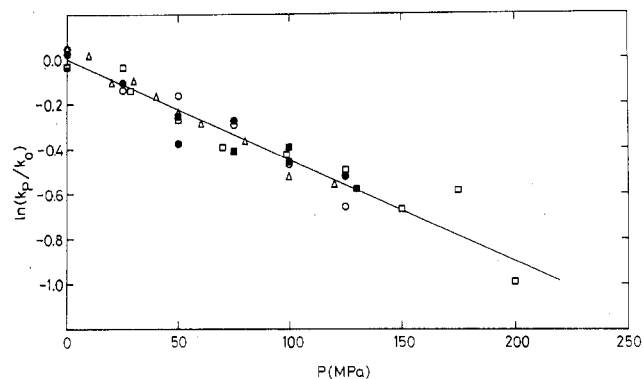**Figure 1.** Experimental and calculated values of ln (k_p/k_0) as a function of pressure for $[Ni(CH_3OH)_6](ClO_4)_2$ in CH_3OH, assuming ΔV^* independent of pressure: (O) $P_m = 0.0440$, $T = 310$ K; ($\bullet$) $P_m = 0.1032$, $T = 303$ K; ($\square$) $P_m = 0.0638$, $T = 303$ K; ($\blacksquare$) $P_m = 0.0638$, $T = 310$ K; ($\triangle$) $P_m = 0.0377$, $T = 308$ K.

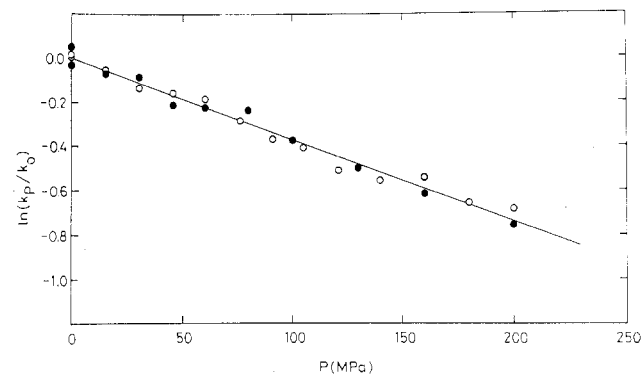**Figure 2.** Experimental and calculated values of ln (k_p/k_0) as a function of pressure for $[Ni(DMF)_6](ClO_4)_2$ in DMF, assuming ΔV^* independent of pressure: (O) $P_m = 0.0099$, $T = 297$ K; ($\bullet$) $P_m = 0.0099$, $T = 297$ K.

Figure 3. Experimental and calculated values of ln (k_p/k_0) as a function of pressure for $[Ni(CH_3CN)_6](ClO_4)_2$ in CH_3CN, assuming ΔV^* independent of pressure: (O) $P_m = 0.0315$, $T = 294$ K; ($\bullet$) $P_m = 0.0252$, $T = 294$ K.

Figure 4. Experimental and calculated values of ln (k_p/k_0) as a function of pressure for $[Co(CH_3OH)_6](ClO_4)_2$ in CH_3OH, assuming ΔV^* independent of pressure: (O) $P_m = 0.0343$, $T = 279$ K; ($\bullet$) $P_m = 0.0296$, $T = 278$ K.

study of the formyl group.[16] Using the same criteria as above, we chose an optimum temperature of 297 K for the variable pressure study. At this temperature the outer-sphere contribution is considerably less ($\sim$5%) than for the above system and an estimation for $(T_{2os})^{-1}$ from the graph of Matwiyoff's study was deemed accurate enough for our purpose. The results obtained by using eq 3 are shown in Figure 2 and Table I.

3.5. $[Ni(CH_3CN)_6](ClO_4)_2$ in CH_2CN. The temperature and pressure dependence of this exchange has already been discussed in an earlier paper.[2] For the sake of consistency, the variable-pressure data have been reanalyzed by using the multiple fitting procedure discussed above and the full Swift–Connick equation together with outer-sphere contribution (eq 2). The results are shown in Figure 3 and Table I.

3.6. $[Co(CH_3OH)_6](ClO_4)_2$ in CH_3OH. Variable-temperature ^1H T_2 measurements on the CH_3 resonance by Luz and Meiboom[15] suggest that the optimum temperature for the variable-pressure study is about 280 K and fortuitously at this
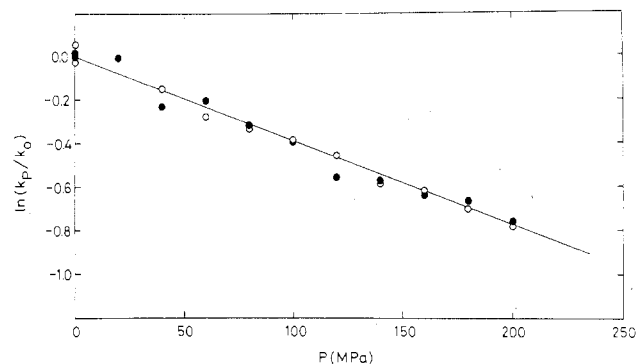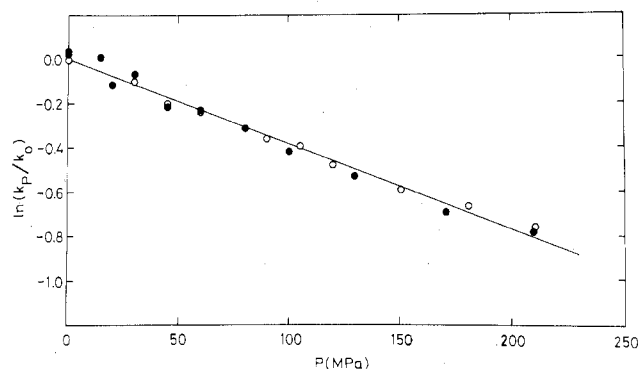
temperature the outer-sphere contribution is less than 2% and has thus been neglected in the data analysis. The results by use of the simplified eq 3 are shown in Figure 4 and Table I.

3.7. $[Co(DMF)_6](ClO_4)_2$ in DMF. For this system, the fast-, intermediate-, and slow-exchange regions are well defined and shift data are available.[16] This gave us the opportunity to measure the volume of activation at two widely different temperatures (43 K apart). Matwiyoff's variable-temperature ^1H study of the formyl resonance shows that at a temperature of 253 K we are at the high-temperature end of the slow-exchange region and at 298 K in the intermediate-exchange region. With reference to Figure 3 of the previous paper,[2] it is clear that the Swift–Connick approximation for this latter region $((T_{2r})^{-1} = \tau_m(\Delta\omega_m)^2)$ is very poor and their full equation must thus be used.

Utilizing values of $(T_{2m})^{-1}$ and $\Delta\omega_m$ obtained from the graphs of Matwiyoff at the respective temperatures and assuming $(T_{2os})^{-1}$ is negligible, we fitted ln $((T_{2r})^{-1})$ values to the full eq 2 with the pressure dependence of $\tau_m (=1/k)$ given by eq 5 and by optimizing k_0^i, ΔV_0^*, and $\Delta\beta^*$. The results
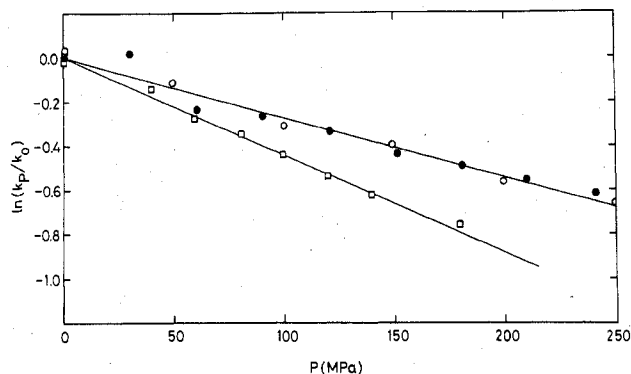
Figure 5. Experimental and calculated values of ln (k_p/k_0) as a function of pressure for $[Co(DMF)_6](ClO_4)_2$ in DMF, assuming ΔV^* independent of pressure: (O) $P_m = 0.00625$, $T = 298$ K; (●) $P_m = 0.00625$, $T = 294$ K; (□) $P_m = 0.00625$, $T = 253$ K.

Table II. Derived ^{14}N and ^1H Variable-Temperature NMR and Kinetic Parameters[a] (Together with Their Standard Deviations) for the System $[Co(CH_3CN)_6](ClO_4)_2$ in CH_3CN

$k_{298.1}$, s^{-1}	$(3.38 \pm 0.04) \times 10^5$
ΔH^*, kJ mol^{-1}	49.54 ± 0.7
ΔS^*, J K^{-1} mol^{-1}	27.09 ± 2.3

	^{14}N parameter	^1H parameter
B_0, rad s^{-1}	set to zero	$(-5.9 \pm 0.9) \times 10^3$
B_1, rad K s^{-1}	$(1.253 \pm 0.007) \times 10^8$	$(2.1 \pm 0.3) \times 10^6$
C_1, rad K s^{-1}	set to zero	$(1.1 \pm 0.4) \times 10^5$
E_m,[b] kJ mol^{-1}	set to zero	$(3.4 \pm 0.5) \times 10^3$
A_m, s^{-1}	set to zero	38 ± 12

[a] The data were fitted to eq 2 and $\Delta\omega_r = \Delta\omega_m/((\tau_m/T_{2m} + 1)^2 + \tau_m^2\Delta\omega_m^2) + \Delta\omega_{os}$ with $\Delta\omega_m = B_0 + B_1/T$, $\Delta\omega_{os} = C_1/T$ and $1/T_{2os} = 0$. [b] E_m, A_m defined by $1/T_{2m} = A_m \exp(E_m/RT)$.

obtained at 253 and 296 K are shown in Figure 5 and Table I.

3.8. $[Co(CH_3CN)_6](ClO_4)_2$ in CH_3CN. Variable-temperature proton line-broadening measurements by West and Lincoln[17] suggested that it was necessary to work in the intermediate exchange region where, as discussed above, the Swift–Connick approximation is very poor. It should be noted that in variable-pressure work one is precluded from working close to the solution freezing point since for nearly all solvents, except water, the freezing point increases markedly with pressure. Preliminary variable-temperature measurements gave line widths slightly lower than these of West and Lincoln and it was decided to repeat the variable-temperature analysis. It must be emphasized that the homogeneity corrected line widths varied from only 2 to 35 Hz over the entire range. It is not possible to increase the complex concentration significantly in order to give broader lines due to solubility problems. Thus it is extremely difficult to obtain reliable values of all the NMR and kinetic parameters simultaneously. However, the ^{14}N line widths and shifts for this system are extremely large, sufficiently so that one may ignore $1/T_{2m}$ and hence the data define ΔH^* and ΔS^* very well. It was thus decided to fit West and Lincoln's ^{14}N shifts and line widths and our ^1H shifts and line widths simultaneously by using a four-equation, nonlinear least-squares procedure similar to that used earlier.[2] Full details are given in the supplementary material. Table II gives the values obtained from this analysis.

The variable-pressure NMR line widths were analyzed by using the full Swift–Connick equation as described in section 3.7 with the NMR parameters derived from the variable-temperature analysis. The results for this system are shown in Table I and Figure 6.

3.9. Summary of the Results. Table I summarizes the volumes of activation obtained by assuming both finite and zero $\Delta\beta^*$. The fact that ΔV_0^* is always significantly different
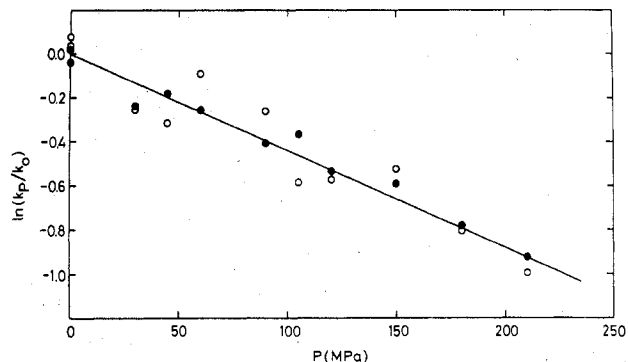

Figure 6. Experimental and calculated values of ln (k_p/k_0) as a function of pressure for $[Co(CH_3CN)_6](ClO_4)_2$ in CH_3CN, assuming ΔV^* independent of pressure: (O) $P_m = 0.0747$, $T = 260$ K; (●) $P_m = 0.0747$, $T = 260$ K.

from ΔV^* reflects the presence of some curvature in the pressure dependence of ln k_p but the inclusion of a $\Delta\beta^*$ term does not significantly improve the fit and derived values are barely above experimental uncertainty. In order to quantify this curvature more accurately, one would require more accurate rate constants. It is gratifying to note, however, that all the $\Delta\beta^*$ values except one are of the same sign, the sign predicted for an I_d mechanism which is operating for these systems (see below). Since, in future work, $\Delta\beta^*$ may be significantly nonzero, we shall always give both linear and quadratic fits but shall restrict our discussion at present to the linear results.

The random errors in ΔV^* should be approximately twice their standard deviations but should be increased to 1–2 cm^3 mol^{-1} to include possible effect of nonrandom errors. As discussed above, the system which posed most difficulties with regard to obtaining reliable NMR parameters was $Co(CH_3CN)_6^{2+}$ and is likely to be the least reliable value of ΔV^*. For such systems, it would be better to choose an NMR nucleus closer to the paramagnetic center (e.g., ^{13}C or ^{14}N). Since the line broadening and shifts would be so much larger, the temperature range over which the exchange-broadening contribution predominates is much larger. Furthermore, this extension to the "kinetic window" occurs to higher temperatures, enabling faster reactions to be studied than by ^1H NMR.

4. Discussion

For ligand-substitution reactions (7) it is conventional to

$$ML_5X + Y \rightleftharpoons ML_5Y + X \qquad (7)$$

discuss the mechanism in terms of the classification of Langford and Gray.[21] This classification is "operational" in nature; i.e., it is based on kinetic tests that may be applied. Thus, if a mechanistic test shows the presence of a seven- or five-coordinate intermediate, the mechanism is assigned associative, A, or dissociative, D, respectively. Otherwise it is assigned as an interchange, I, process. This last class is subdivided into two groups: associative interchange, I_a, when there are large entering group effects, and dissociative interchange, I_d, when there are not.

For solvent exchange reactions (8) this same classification

$$MS_6 + {}^*S \rightleftharpoons MS_5{}^*S + S \qquad (8)$$
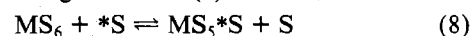
is also used although for such reactions there is a serious lack of kinetic tests that may be applied since the nature of the entering group cannot be altered and the concentration of reactant "ligand" cannot be changed without going to mixed solvents. Probably, the only true kinetic test is that embodied in the Eigen–Wilkins mechanism[22] which was applied to nickel(II) in water. They showed that the ratios of complex formation on $Ni(H_2O)_6^{2+}$, after correction for outer-sphere

Table III. Activation Parameters for Solvent Exchange on Nickel(II) and Cobalt(II) Perchlorates (Derived from NMR Studies)

cation	solvent	k_{298}, s^{-1}	ΔH^*, kJ mol^{-1}	ΔS^*, J K^{-1} mol^{-1}	$\Delta V^{*,a}$ cm^3 mol^{-1}	$\Delta V^*/V^{\circ}$ [b]	ref[c]
Ni^{2+}	DMF	3.8×10^3	62.8	33.5	9.1 (297 K)	0.12	16
		7.7×10^3	39.3	−37.7			18[d]
		6.9×10^3	58.6	25.1			19
	CH$_3$CN	2.8×10^3	64.3	37.0	9.6 (294 K)	0.18	2[e]
	CH$_3$OH	1.0×10^3	66.1	33.5	11.4 (307 K)	0.28	15
Co^{2+}	DMF	3.9×10^5	56.9	52.7	6.7 (296 K)	0.09	16
					9.2 (253 K)	0.12	
		2.3×10^5	29.7	−41.8			18[d]
	CH$_3$CN	1.4×10^5	33.9	−31.4			20
		3.2×10^5	47.7	20.9			17[f]
		3.5×10^5	47.7	20.9			17
		3.4×10^5	49.5	27.1	9.9 (260 K)	0.20	this work
	CH$_3$OH	1.8×10^4	57.7	30.1	8.9 (279 K)	0.22	15

^{a} Temperature given in parentheses. ^{b} V°, the solvent molar volumes, were obtained from density data at the temperature of the ΔV^* measurements. ^{c} References given refer to variable-temperature studies only. ^{d} ^{17}O NMR. ^{e} Activation parameters for this system from other studies are given and discussed in this reference. ^{f} ^{14}N NMR.

association, were closely similar, suggesting that the transition states were similar and involved little bonding to the leaving group, hence implicating an I_d mechanism.

For nonaqueous solutions there is still controversy concerning the applicability of the Eigen–Wilkins mechanism. The rate constants for ligand substitution of various bi- and tridentate ligands on nickel(II) in various nonaqueous solvents show large variations in rate even after the outer-sphere association correction.[23] Caldin and Bennetto[24] have noted that the differences in ΔH^* for solvent exchange and an arbitrarily chosen complex formation reaction in that solvent correlate well with the solvent enthalpy of vaporization and fluidity (density/viscosity). They discuss this correlation in terms of solvent structure by using a Frank and Wen[25] solvation model. This work has been criticized by Coetzee,[26] who points out that the differences are very much smaller for monodentate ligands and that the two extremes of solvent behavior noted for Me$_2$SO and acetonitrile solutions may be rationalized in terms of steric hindrance and enhanced outer-sphere association, respectively, with water behaving normally. Further, Frankel[27] has observed that the rate of exchange of Me$_2$SO from nickel(II) is independent of added cosolvent, nitromethane, and he concludes that this is strong evidence for a dissociative D mechanism.

A less direct way of obtaining mechanistic information is from a comparison of activation parameters. The entropy of activation in particular has long been used for this purpose but as discussed by McGlashan[28] there are severe difficulties in regarding the entropy as a measure of increased "disorder" or "randomness". However, it is more than likely that for a reaction involving an increase in the number of product molecules over reactant molecules, ΔS° should be positive and similarly, for a dynamic process, ΔS^* should be positive or negative for dissociative and associative processes, respectively. Therefore, a comparison of ΔS^* for closely related reactions in the same solvent can be used for mechanistic comparison. From a more practical viewpoint, the errors in ΔS^* values for solvent exchange on paramagnetic ions obtained by NMR are frequently so large to prevent any correlation.[2,29]

Volumes of activation should not be subject to such limitations since, in terms of transition-state theory, ΔV^* simply represents the difference in partial molar volume between reactants and transition state. ΔV^* is generally considered to be made up of two contributions: ΔV^*_{int}, a term due to bond making, breaking, and stretching, and ΔV^*_{el}, a term due to changes in electrostriction. As discussed in the Introduction to this paper, for solvent-exchange reactions, the second term is negligible with respect to the first. For a pure D mechanism, ΔV^* should equal the partial molar volume of the solvent by assuming that the partial molar volumes of the n-coordinate reactant and the $(n - 1)$-coordinate transition state are

identical.[6] Similarly for an A mechanism, ΔV^* should equal minus the solvent partial molar volume. For the latter case, the assumption of equal partial molar volumes of reactants and transition state is probably not very good particularly for octahedral complexes where steric crowding in the transition state would increase the partial molar volume, thus making the overall ΔV^* less negative. In the area of carbon chemistry, there is still discord concerning whether or not bond formation and cleavage involve similar ΔV^*_{int} contributions, but of opposite sign, to the measured ΔV^*. Thus Asano and LeNoble[4] give contributions of −10 and +10 cm^3 mol^{-1} to the two processes whereas Kohnstam[30] quotes −10 to −15 and +5 cm^3 mol^{-1}, respectively. Thus, in general, changeover between associative and dissociative mechanisms may not be exactly at zero ΔV^*. However, since the A and D limits for ΔV^* are minus and plus the solvent partial molar volume V°, comparisons between different solvents may be made simply by comparing the dimensionless parameter $\Delta V^*/V^{\circ}$. For solvent exchange on octahedral solvato complexes, this parameter should equal +1 for a dissociative reaction and tend to −1 for an associative A reaction. Interchange I processes should have values between these limits. As discussed by both Stranks[6] and Swaddle,[5] the compressibility of activation $\Delta \beta^*$ for solvent exchange is also a useful mechanistic parameter being predicted large positive for a D and large negative for an A solvent-exchange mechanism. For interchange mechanisms, the value should be small but slightly positive for an I_d mechanism and slightly negative for I_a.

The various activation parameters for the six solvent-exchange reactions studied are given in Table III. The small values of $\Delta V^*/V^{\circ}$ and the almost negligible values of $\Delta \beta^*$ (Table I) are strongly in accord with an interchange mechanism. Furthermore, the positive values for $\Delta V^*/V^{\circ}$ and the slightly positive values of $\Delta \beta^*$ (with the exception of the reaction subject to most uncertainty in the data, acetonitrile exchange on Co^{2+}) are in accord with a dissociative interchange I_d. For dimethylformamide exchange on Co^{2+}, where ΔV^* has been measured at two significantly different temperatures, ΔV^* decreases with increasing temperature although, due to possible nonrandom errors, not too much significance should be placed on the numerical value of $\partial \Delta V^*/\partial T$.

Also shown in Table III are the values of ΔS^*. For CH$_3$CN exchange on nickel(II), the data have been discussed in an earlier paper[2] and it was clear that early evaluations tended to grossly underestimate the entropy but more recent evaluations tended to converge on a value between 23 and 50 J K^{-1} mol^{-1}. For the other five reactions, no clear pattern emerges and it is extremely dubious that any reliable mechanistic information can be obtained from these values.

For a full discussion of the mechanism of solvent-exchange reactions, it is necessary to identify the properties of the solvent which affect the rate. Although there are still serious discrepancies in the ΔH^* and ΔS^* values (see above), the order of the rate of solvent exchange is well established and is the same for both Ni^{2+} and Co^{2+}: $NH_3 > H_2O \gg Me_2SO > DMF > CH_3CN > CH_3OH$.[31] Such an order is extremely difficult to rationalize and many different correlations and models have been proposed.

Gutmann and Schmid[32] have shown that the rate of reaction 9, where S is the solvent, is roughly inversely proportional to

$$Cl_5Sb-S + Ph_3CCl \rightleftharpoons Ph_3C^+ + SbCl_6^- + S \qquad (9)$$
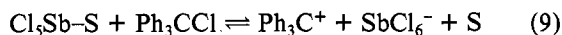
the donor number D_N of the solvent in accord with the idea that the Sb-S bond breaking is rate determining.

However, for reaction 10[33] the rate increases as the donor

$$S_5NiX^+ + S \rightleftharpoons NiS_6^{2+} + X^- \qquad (10)$$
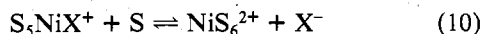
number of the solvent S is increased in accord with the idea that bonding between the metal ion and the leaving group is reduced by the large σ bonding to the remaining solvent molecules. For dissociatively activated solvent exchange, both the above opposing effects should occur simultaneously and any remaining correlation would depend on which of the two effects predominates.

Recently Funahashi and Jordan,[34] considering solvent-exchange reactions on 2+ ions, have used an approach originally developed by Hoffmann[33] which attempts to take into account both the above effects together in a quantitative way. They assume a D mechanism so that ΔH^* refers to the process

$$MS_6^{2+} \rightarrow \{MS_5^{2+}\} + S \qquad (11)$$
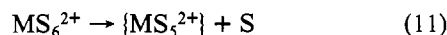
and it is further assumed the $\Delta H^* \propto$ (acidity of S_5M^{2+}) × (basicity of S) and that (acidity of S_5M^{2+}) $\propto$ (acidity of M^{2+}) − (basicity of S). If the basicity is assumed proportional to the donor number D_N, then

$$\Delta H^* = aD_N - bD_N^2 \qquad (12)$$

where a and b are constants depending on only the metal ion. This approach has been extremely successful in correlating the ΔH^* of solvent exchange on nickel(II), cobalt(II), iron(II), and manganese(II); of 23 exchange reactions only three fail to give agreement within 4 kJ mol^{-1}. More recently, Jordan and co-workers[35] studied reaction 13 where L_5 is a five-co-

$$L_5NiS^{2+} + {}^*S \rightleftharpoons L_5Ni^*S^{2+} + S \qquad (13)$$

ordinate Shiff base and S is either CH_3CN or DMF. Equation 12 simplifies then to

$$\Delta H^* \propto D_N \qquad (14)$$

since there is no solvent basicity effect on the acidity of L_5Ni^{2+}. The two values they obtained were identical whereas their theory predicts a ratio of 26.6/14.0, the ratio of the donor numbers. They thus conclude that the quantitative success of eq 12 is largely fortuitous.

A different approach to solvent exchange has been used by Tanaka,[36] who on the basis of a dissociative D mechanism has suggested that ΔG^* was made up of two contributions. The first is proportional to the free energy of discharge of a metal ion in the solvent and may be treated by a modified Born equation. The other, analogous to a condensation process, is proportional to the free energy of evaporation of the solvent. By conventional thermodynamic manipulation, he obtains an equation for ΔH^* involving, apart from the two proportionality constants, only known or calculable parameters. The correlations for solvent exchange on Ni^{2+}, Co^{2+}, Mn^{2+}, and VO_2^{2+} are good although the physical basis of the model fails for VO_2^{2+} and possibly Mn^{2+}. The pressure derivative of free

energy yields volume. It is thus possible to use Tanaka's approach to express ΔV^* as the sum of two terms. One term is simply proportional to the volume of evaporation of the solvent and is clearly the same for all solvents. The other term is the volume of discharge of the ion in the solvent for which the pressure dependence of solvent relative permittivity is a major term. It is unfortunate that, for most solvents, this dependence is unknown.

Experimentally, we have in fact found only small variation of ΔV^* with solvent. However, for Ni^{2+}, the observed values of $\Delta V^*/V^\circ$ vary in the order $CH_3OH > CH_3CN > DMF$. This order is precisely the order observed for ΔG^* and thus we are led to the possibility that, at least for these solvents, the slower the reaction the more dissociative character it has. If due account is also taken of the temperature effects on ΔV^* this selfsame order holds for the exchange on Co^{2+}.

For each of the solvents studied, if the effect of temperature on ΔV^* is taken into account, values for $\Delta V^*/V^\circ$ for Co^{2+} are always smaller than for Ni^{2+}. It is well established that solvent exchange on Co^{2+} is considerably faster than on Ni^{2+} and it is generally assumed that the predominant cause is the crystal field stabilization energy (CFSE).[37] Thus, assuming a D mechanism, we found that the CFSE difference between octahedral and square-pyramidal geometries for d^7 systems are such as to lead to a smaller energy of activation than for d^8 systems. However, the smaller values for $\Delta V^*/V^\circ$ of cobalt(II) over those of nickel(II) suggest that, while both ions exchange solvent via a dissociative interchange, I_d, mechanism, the cobalt(II) reaction exhibits less dissociative behavior. Such a proposal is in accord with the idea frequently expressed but never substantiated that, while the later members of the first transition series react by dissociative mechanisms, the earlier members may exhibit more associative character. Such behavior is rationalized by noting that the t_{2g} orbitals are essentially nonbonding whereas the e_g orbitals are antibonding. Hence for the later members, a seven-coordinate transition state is destabilized, whereas for the earlier members the presence of partially vacant nonbonding t_{2g} orbitals helps to stabilize it.

Further work is in progress to see whether the earlier members of the first-row d-block elements show even less positive $\Delta V^*/V^\circ$ values and also to measure ΔV^* for the faster exchanging solvents, e.g., H_2O by using ^{17}O NMR.

References and Notes

(1) For parts 3 and 4 of this series, see ref 2 and 3, respectively.
(2) Newman, K. E.; Meyer, F. K.; Merbach, A. E. *J. Am. Chem. Soc.* **1979**, *101*, 1470–6.
(3) Meyer, F. K.; Earl, W. L.; Merbach, A. E. *Inorg. Chem.* **1979**, *18*, 888–9.
(4) Asano, T.; LeNoble, W. J. *Chem. Rev.* **1978**, 407–89.
(5) Swaddle, T. W. *Coord. Chem. Rev.* **1974**, *14*, 217–68.
(6) Stranks, D. R. *J. Pure Appl. Chem.* **1974**, *3*, 303–23.
(7) (a) Tobe, M. L. "Inorganic Reaction Mechanisms"; Nelson: London, 1972; p 83. (b) Burgess, J. "Metal Ions in Solution"; Ellis Horwood: Chichester, England, 1978; pp 352–64.
(8) (a) Vanni, H.; Earl, W. L.; Merbach, A. E. *J. Magn. Reson.* **1978**, *29*, 11–9. (b) Earl, W. L.; Vanni, H.; Merbach, A. E. *Ibid.* **1978**, *30*, 571–76.
(9) Earl, W. L.; Meyer, F. K.; Merbach, A. E. *Inorg. Chim. Acta* **1977**, *25*, L91–2.
(10) van Leeuwen, P. W. N. M. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 247–53.
(11) Drago, R. S.; Meek, D. W.; Joesten, M. D.; LaRoche, L. *Inorg. Chem.* **1963**, *2*, 124–7.
(12) Wickenden, A. E.; Krause, R. A. *Inorg. Chem.* **1965**, *4*, 404–7.

(13) Meyer, F. K.; Merbach, A. E. *J. Phys. E* **1979**, *12*, 185–6.
(14) Swift, T. J.; Connick, R. E. *J. Chem. Phys.* **1962**, *37*, 307–20.
(15) Luz, Z.; Meiboom, S. *J. Chem. Phys.* **1964**, *40*, 2686–92.
(16) Matwiyoff, N. A. *Inorg. Chem.* **1966**, *5*, 788–95.
(17) West, R. J.; Lincoln, S. F. *Inorg. Chem.* **1972**, *11*, 1688–91.
(18) Babiec, J. S.; Langford, C. H.; Stengle, T. R. *Inorg. Chem.* **1966**, *5*, 1362–4.
(19) Frankel, L. S. *Inorg. Chem.* **1971**, *10*, 2360–1.
(20) Matwiyoff, N. A.; Hooker, S. V. *Inorg. Chem.* **1967**, *6*, 1127–33.
(21) Langford, C. H.; Gray, H. B. "Ligand Substitution Processes"; W. A. Benjamin: New York, 1966; Chapter 1.
(22) (a) Eigen, M.; Wilkins, R. G. *Adv. Chem. Ser.* **1965**, *No. 49*, 55. (b) Wilkins, R. G. *Acc. Chem. Res.* **1970**, *3*, 408–16.
(23) Bennetto, H. P.; Caldin, E. F. *J. Chem. Soc. A* **1971**, 2191–8.
(24) Caldin, E. F.; Bennetto, H. P. *J. Solution Chem.* **1973**, *2*, 217–38.
(25) Frank, H. S.; Wen, W-Y. *Discuss. Faraday Soc.* **1957**, *24*, 133.
(26) Coetzee, J. F. "Solute-Solvent Interactions"; Coetzee, J. F., Ritchie, C. D., Eds.; Marcel Dekker: New York, 1967; Vol. 2, Chapter 14.
(27) Frankel, L. S. *Inorg. Chem.* **1971**, *10*, 814–7.
(28) McGlashan, M. L. *J. Chem. Educ.* **1966**, *43*, 226–32.
(29) Reference 7b, p 313.
(30) Kohnstam, G. *Prog. React. Kinet.* **1970**, *5*, 335–408.
(31) Reference 7b, p 329.
(32) Gutmann, V. ; Schmid, R. *Monatsh. Chem.* **1971**, *102*, 1217–25.
(33) Hoffmann, H.; Janjic, T.; Sperati, R. *Ber. Bunsenges. Phys. Chem.* **1974**, *78*, 223–8.
(34) Funahashi, S.; Jordan, R. B. *Inorg. Chem.* **1977**, *16*, 1301–6.
(35) Rusnak, L. L.; Yang, E. S.; Jordan, R. B. *Inorg. Chem.* **1978**, *17*, 1810–3.
(36) Tanaka, M. *Inorg. Chem.* **1976**, *15*, 2325–7.
(37) (a) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967; Chapters 2 and 3. (b) Companion, A. L. *J. Phys. Chem.* **1969**, *73*, 739–41.

Systematic Variation of the Redox Potential of the Fe^{2+}/Fe^{3+} Couple in Iron(II) Complexes of 2,3,9,10-Tetrasubstituted-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene Ligands[1]

RAM G. GOEL,* PATRICK M. HENRY, and P. CALDEIRA POLYZOU

Fe(II) complexes of 2,3,9,10-tetrasubstituted-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene ligands have been synthesized and characterized by elemental analysis and by spectral (infrared, UV–visible, and ^{1}H NMR) measurements. The dependence of the half-wave oxidation potentials of the Fe^{2+}/Fe^{3+} couple upon the electronic properties of substituents on the macrocyclic ligand has been investigated. A linear relationship between the half-wave potentials for the Fe^{2+}/Fe^{3+} couple and the σ_P constants for the substituents on the macrocycle ring has been observed.

Recent work on iron complexes of synthetic macrocyclic ligands[2-4] has greatly increased our understanding of the mode of binding of molecular oxygen in naturally occurring oxygen carriers, hemoglobin and myoglobin. As an aid in understanding the catalytic role of heme proteins in various redox reactions, the redox properties of iron, cobalt, and nickel complexes of a variety of tetraaza tetradentate macrocycles have been investigated by Busch and co-workers.[5,6] In Ni(II) complexes the potential for the Ni^{2+}/Ni^{3+} couple has been found to be sensitive to the electron withdrawing or releasing ability of the substituents on the macrocyclic ring[5] but no such correlations have been reported for iron complexes. Iron complexes of the macrocyclic ligand 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene (TIM), complex V, Figure 1, have been studied recently[7] and crystallographic study[8] of the complex $[Fe^{II}TIM(CH_3CN)_2]^{2+}$ has shown that the Fe(II) and the four nitrogen donor atoms of the macrocyclic ligand in the complex are coplanar. Very recently it has been reported that the Fe^{II}–TIM complex catalyzes the oxidation of methanol in the presence of sunlight.[9] In order to study the effects of ring substituents on the potentials for the Fe^{2+}/Fe^{3+} couple in the iron complex of TIM type macrocycle framework, we have synthesized complexes in which the methyl groups of TIM have been replaced by C_6H_5, p-$CH_3C_6H_4$, and p-$CH_3OC_6H_4$ substituents.

Results and Discussion

Complexes I–IV were obtained in good yield from the reaction of 1,3-diaminopropane and the appropriate diketone in the presence of Fe(II) ions. Like Fe^{II}TIM,[7] these compounds are intensely colored, air-stable, diamagnetic solids. They are fairly soluble in donor solvents such as acetonitrile, pyridine, and dimethyl sulfoxide and sparingly soluble in dichloromethane. The ionic constitution of the complexes was established by conductance measurements in acetonitrile (data in Table I).

Infrared Spectra. The important infrared bands observed for the reported compounds are listed in Table II. The infrared spectra of all four compounds (I to IV) do not contain any bands that could be assigned to the C=O or NH_2 groups.[10] For each complex, an infrared band is observed in the 1245–1270-cm^{-1} region, which is similar to the 1210-cm^{-1} band observed for the Fe^{II}–TIM[7] complex V. Characteristic infrared bands due to the phenyl or substituted phenyl groups are present in the spectra of all the four compounds in the 700–770-cm^{-1} region. The infrared spectrum of Fe^{II}Ph–TIM (complex I) like that of Fe^{II}TIM does not show any band at 1600 cm^{-1}, which could be assigned to the C=N stretching vibrations.[7,11] However, a weak band at ca. 1620 cm^{-1} is present in the spectra for the complexes II, III, and IV. The infrared spectra for all the four compounds show two very weak bands in the 2340- and 2380-cm^{-1} region due to the C≡N stretching vibrations of the axial acetonitrile ligands[7,12] and strong bands at 845 and 560 cm^{-1} due to the PF_6^- anion.[13]

Proton Magnetic Resonance Spectra. The ^{1}H NMR data for the complexes are listed in Table III. The resonance signals due to the phenyl, methyl, and the α-CH_2 hydrogens as well as the hydrogens of the substituent groups on the phenyl rings can be assigned unambiguously although the resonance peaks due to the β-CH_2 groups for all the complexes are masked by the acetonitrile peak. In the case of complex IV, the broad resonance signal at 2.16 ppm (J = 2 Hz) could be in part due to the methyl protons of one isomer, which are coupled with the homoallylic protons, and in part due to the β-CH_2 protons. The neighboring acetonitrile peak prevents an exact integration of this part of the spectrum. The existence of two isomers of IV (cis and trans) is also supported by the observed broadness of the phenyl and α-CH_2 peaks. The lower