

Table IV. Enthalpies of Adduct Formation for HFIP Adducts

	$-\Delta H_{\text{exptl}}^a$	$-\Delta H_{\text{calcd}}^b$		$-\Delta H_{\text{exptl}}^a$	$-\Delta H_{\text{calcd}}^b$
Ethyl acetate	7.5 ± 0.8	6.9 ± 0.1	Pyridine	11.0 ± 0.3	10.9 ± 0.1
Acetonitrile	7.0 ± 0.12	6.1 ± 0.1	Diethyl ether	8.2 ± 0.3	7.8 ± 0.1
Acetone	7.8 ± 0.1	7.3 ± 0.1	Hexamethylphosphoramide	10.9 ± 0.1	11.3 ± 0.2
<i>N,N</i> -Dimethylacetamide	9.5 ± 0.4	9.5 ± 0.1	Triethylamine	13.1 ± 2.6	12.8 ± 0.2
Dimethyl sulfoxide	9.8 ± 0.1	9.8 ± 0.1	Tetrahydrofuran	8.0 ± 0.1	8.5 ± 0.1

^a Experimental values corrected for $-1.1 \text{ kcal mol}^{-1}$ of intramolecular hydrogen bonding. ^b Calculated using E_A and C_A of 5.93 and 0.623¹ respectively, and E_B and C_B values from ref 3b, except for HMPA for which better E and C values of 1.52 and 3.55, respectively, are now available.

the calculated negative value (*i.e.*, it should be made less negative by $1.1 \text{ kcal mol}^{-1}$). Furthermore, it is found that $1.0 \text{ kcal mol}^{-1}$ should be subtracted from all experimental enthalpies of PFTB before employing them in eq 1 while for TFE no corrections are necessary. The E and C parameters for PFTB are 7.34 and 0.731, respectively, while those for TFE are 3.88 and 0.451. These E and C parameters should only be used with the E_B and C_B parameters reported in ref 3b. In a recent article, Wiley and Miller¹⁵ failed to realize that since different parameters were fixed to determine the solution to eq 1 in earlier reports,^{3a} the parameters from different references cannot be used interchangeably. One must be consistent using only those in ref 3a or 3b with others in the same article. To avoid confusion

(15) G. R. Wiley and S. I. Miller, *J. Amer. Chem. Soc.*, **94**, 3287 (1972).

we recommend disregarding all of the parameters except those in ref 3b.

With these new parameters, it was of interest to check our experimental results and our predicted enthalpies with those reported by Purcell, *et al.*^{1,2} We calculated the ratio of marginal to conditional standard deviations from his reported data and found that a wide range of slopes in the K^{-1} vs. ΔH plots were generally obtained. However, several of the marginal standard deviations were such as to require large error limits on the data. The results are summarized in Table IV. Two of the systems that miss badly (CH_3CN and THF) are difficult to handle experimentally and could contain systematic errors.

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Solvent Exchange Rates from Iron(III) and Iron(III)–Porphyrin Systems

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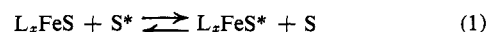
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Abstract: Solvent exchange rates have been measured by studying the temperature dependence of pmr line widths and chemical shifts for three high-spin iron(III) systems. In *N,N*-dimethylformamide (DMF) the $\text{Fe}(\text{DMF})_6^{3+}$ –DMF exchange has $\Delta H^\ddagger = 10.1 \pm 1 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = -16.5 \pm 3 \text{ cal mol}^{-1} \text{ deg}^{-1}$, and the reciprocal of the lifetime of one solvent molecule in the first coordination sphere of iron(III) (τ_M^{-1}) is 61 sec^{-1} at 25° . For $\alpha,\beta,\gamma,\delta$ -tetraphenylporphineiron(III) in DMF $\Delta H^\ddagger = 9.4 \pm 0.4 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = 3.8 \pm 0.7 \text{ cal mol}^{-1} \text{ deg}^{-1}$, and $\tau_M^{-1}(25^\circ) = 5.4 \times 10^6 \text{ sec}^{-1}$. The FeTPP^+ ion in methanol gave $\Delta H^\ddagger = 11.3 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = 9.0 \text{ cal mol}^{-1} \text{ deg}^{-1}$, and $\tau_M^{-1}(25^\circ) = 3.0 \times 10^6 \text{ sec}^{-1}$; however, the interpretation is subject to some uncertainty and realistic error limits cannot be placed on the parameters. Bulk solvent proton chemical shifts were observed in both FeTPP^+ systems and yield values of the hyperfine coupling constants of $3.7 \times 10^6 \text{ sec}^{-1}$ for the CH proton in DMF, and $1.4 \times 10^6 \text{ sec}^{-1}$ and $1.3 \times 10^6 \text{ sec}^{-1}$ for the OH and CH_3 protons, respectively, in methanol.

In previous work it has been noted^{1–3} that substitution reactions on a metal ion are considerably faster in the metalloporphyrin complex than in the hexa-solvated metal ion. In order to study this rate enhancement further the solvent exchange rates have been measured for iron(III) in *N,N*-dimethylformamide (DMF) and for $\alpha,\beta,\gamma,\delta$ -tetraphenylporphineiron(III) (FeTPP^+) in DMF and methanol.

- (1) L. Rusnak and R. B. Jordan, *Inorg. Chem.*, **11**, 196 (1972).
 (2) N. S. Angerman, B. B. Hasinoff, H. B. Dunford, and R. B. Jordan, *Can. J. Chem.*, **47**, 3217 (1969).
 (3) E. B. Fleischer, S. Jacobs, and L. Mestichelli, *J. Amer. Chem. Soc.*, **90**, 2527 (1968).

The general reaction being studied is



where S and S* are initially coordinated and free solvent molecules and L_x represents any nonexchanging ligand(s). The reaction rate has been followed by studying the temperature dependence of the line widths in the bulk solvent proton nmr spectrum.

Experimental Section

The hexa(*N,N*-dimethylformamido)iron(III) perchlorate was prepared by distilling *N,N*-dimethylformamide (DMF), under vacuum, into a flask containing hydrated iron(III) perchlorate (Alfa Inor-

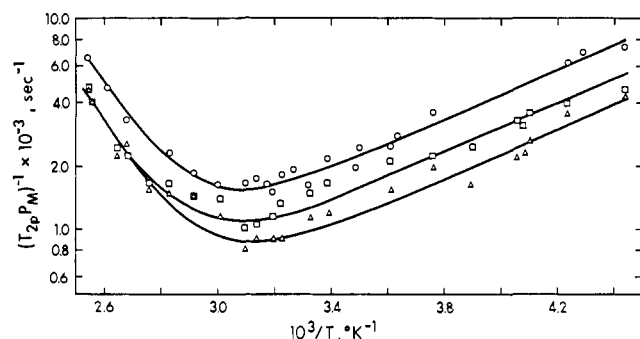


Figure 1. Temperature dependence of $(T_{2p}P_M)^{-1}$ for solutions of $\text{Fe}(\text{ClO}_4)_3$ in *N,N*-dimethylformamide. Smooth curves are calculated from fits with $\Delta H^\ddagger = 9.98 \text{ kcal mol}^{-1}$ (Table I) for CH (○), higher field CH_3 (□), and lower field CH_3 (△) protons.

ganics) and molecular sieves. The mixture was stirred for 24 hr while under vacuum. Then the molecular sieves were removed by filtration and the solvent was removed, by vacuum distillation, until a volume suitable for crystallization was obtained. The solution was cooled in the freezing compartment of a refrigerator overnight. The yellow crystals were collected in a dry nitrogen atmosphere. The product was stored under vacuum and only handled in a dry nitrogen atmosphere.

Anal. Calcd for $\text{FeC}_{15}\text{H}_{12}\text{Cl}_3\text{N}_6\text{O}_{18}$: C, 27.1; H, 5.26; N, 10.5. Found: C, 27.2; H, 5.71; N, 10.7.

The crystal structure of this material has been determined in a separate study.⁴

The $\alpha,\beta,\gamma,\delta$ -tetraphenylporphineiron(III) chloride (FeTPPCL) was prepared by the reaction of TPP^5 with iron(II) chloride in refluxing DMF. The product was isolated and purified by chromatography on neutral alumina following the method of Adler, *et al.*⁶ The chloroform eluate from the chromatography column was treated with gaseous hydrogen chloride and methanol to induce crystallization.

Anal. Calcd for $\text{FeTPPCL} \cdot \text{H}_2\text{O}$, $\text{FeC}_{44}\text{H}_{50}\text{N}_4\text{ClO}$: C, 73.18; H, 4.16; N, 7.76. Found: C, 72.09; H, 4.27; N, 7.24.

The compound was characterized further by its visible absorption spectrum in benzene. The absorption maxima with molar extinction coefficients in parentheses were observed at 422 nm ($9 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and 510 nm ($1.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) with weaker broad peaks at 590 and 700 nm. These results agree with values given in ref 7 and 8. The presence of water in the compound was indicated by bands at 3200–3500 and 1570–1600 cm^{-1} in the infrared spectrum in a KBr disk.

The solvents used in the nmr study were doubly distilled under vacuum from molecular sieves, retaining the middle fraction from each distillation. The solvents were stored over molecular sieves and handled only under vacuum.

All nmr samples were prepared on a vacuum line using standard techniques. The concentration of paramagnetic ion was calculated from the weights of the iron(III) complex and the solvent. The $\text{FeTPPCL} \cdot \text{H}_2\text{O}$ samples were treated with a slight molar excess of silver perchlorate and molecular sieves in order to remove chloride ion and water, respectively.¹ Blank experiments showed that at the concentration levels used the excess AgClO_4 had no effect on the solvent line widths. Anhydrous 2,4-dinitrobenzenesulfonic acid was added to the methanol solutions in order to collapse the proton spin-spin coupling. Cyclopentane was used as an internal standard in all cases.

The nmr spectra were run on a Varian A56/60 spectrometer equipped with a V-4343 temperature controller. The temperatures were determined from the peak separation in methanol or ethylene glycol calibrated standard samples. The line widths of the pure solvent samples were determined immediately after the paramagnetic sample with the same temperature and instrument settings.

(4) R. Sumner, Ph.D. Thesis, University of Alberta, 1971.

(5) D. Dolphin, *J. Heterocycl. Chem.*, **7**, 275 (1970).

(6) A. D. Adler, F. R. Longo, F. Kampas, and J. Kim, *J. Inorg. Nucl. Chem.*, **3**, 2443 (1970).

(7) G. D. Dorough, J. R. Miller, and F. M. Huennekens, *J. Amer. Chem. Soc.*, **73**, 4315 (1951).

(8) E. B. Fleischer, J. M. Palmer, T. S. Srivastava, and A. Chatterjee, *ibid.*, **93**, 3162 (1971).

Results

The solvent proton line broadening caused by the paramagnetic ion can be expressed as

$$(T_{2p}P_M)^{-1} = \frac{\pi(\Delta\nu_{\text{obsd}} - \Delta\nu_{\text{sol}})}{P_M} \quad (2)$$

where $\Delta\nu_{\text{obsd}}$ and $\Delta\nu_{\text{sol}}$ are the full widths at half-height (in Hz) of the nmr line in the presence and absence of the paramagnetic ion, respectively, and $P_M = n[\text{Fe complex}]/([\text{solvent}]_0 - n[\text{Fe complex}])$, where n is the number of solvent molecules in the first coordination sphere of the metal ion and $[\text{solvent}]_0$ is the concentration of solvent in the pure solvent.

$\text{Fe}(\text{DMF})_6(\text{ClO}_4)_3$ in *N,N*-Dimethylformamide. The temperature dependence of the line broadening was studied for six samples in the concentration range 3.49×10^{-3} – $2.11 \times 10^{-2} \text{ m}$. At a given temperature the line broadening was directly dependent on the $\text{Fe}(\text{DMF})_6^{3+}$ concentration. Line broadenings in the range of 10–70 Hz were observed depending on the temperature and the iron(III) concentration.

The line broadening of the two methyl resonances was determined by digitizing the spectra and fitting the two overlapping resonances by a least-squares method to the sum of two equally intense Lorentzian curves. The resolved best-fit line widths were used to calculate T_{2p}^{-1} for the methyl protons.

The temperature dependence of $(T_{2p}P_M)^{-1}$ for this system is shown in Figure 1.⁹ These results indicate that $(T_{2p}P_M)^{-1}$ is controlled by the solvent exchange at high temperature and by outer-sphere relaxation at low temperature. Therefore¹⁰

$$(T_{2p}P_M)^{-1} = \tau_M^{-1} + T_{2o}^{-1} \quad (3)$$

where the solvent molecule lifetime in the first coordination sphere of iron(III) is given by the usual transition-state theory expression

$$\tau_M^{-1} = kT/h \exp\left(\frac{-\Delta H^\ddagger + T\Delta S^\ddagger}{RT}\right) \quad (4)$$

The outer-sphere relaxation time¹¹ (T_{2o}) is assumed to have a simple exponential temperature dependence given by

$$T_{2o}^{-1} = C_o \exp(E_o/RT) \quad (5)$$

After substitution of eq 4 and 5 into eq 3 a least-squares best-fit of the temperature dependence of $(T_{2p}P_M)^{-1}$ was used to obtain values of ΔH^\ddagger , ΔS^\ddagger , C_o , and E_o .

The results of various fitting procedures are summarized in Table I for both of the CH_3 and the CH resonances. The results for the CH proton are considered to be more accurate because the line broadenings are larger and they are not subject to any error which might result from the least-squares resolution of the two CH_3 line widths. For these reasons the

(9) Values have been calculated using a coordination number $n = 6$.

(10) The data show no indication of leveling which would indicate inner-sphere relaxation rate (T_{2M}^{-1}) control in the high-temperature extreme. A consideration of other DMF systems in which the dipolar mechanism controls T_{2M}^{-1} shows that it should be about four times greater than T_{2o}^{-1} . On this basis a leveling would have been expected especially for the CH_3 protons. These observations indicate that T_{2M} must be dominated by a scalar interaction, as might be expected for octahedral iron(III) with an electron spin relaxation time of 10^{-2} – $10^{-10} \text{ sec}^{-1}$ (M. Rubenstein, *et al.*, *Mol. Phys.*, **20**, 67 (1971)).

(11) Z. Luz and S. Meiboom, *J. Chem. Phys.*, **40**, 1066 (1964).

Table I. Least-Squares Best-Fit Parameters for Fe(DMF)₆³⁺ in DMF

	ΔH^\ddagger , kcal mol ⁻¹	ΔS^\ddagger , cal mol ⁻¹ deg ⁻¹	C_o , sec ⁻¹	E_o , kcal mol ⁻¹
CH proton	9.98	-16.4	20.6	2.66
CH ₃ , low field	9.15	-19.4	12.6	2.57
	9.98 ^a	-17.2	10.8	2.66 ^a
CH ₃ , high field	11.4	-13.8	33.5	2.22
	9.98 ^a	-17.3	14.3	2.66 ^a

^a Fixed at the value indicated by the CH proton fit.

ΔH^\ddagger and E_o from the CH proton fit were fixed in one of the fits of the CH₃ proton data. The calculated smooth curves in Figure 1 clearly show that the latter fits are entirely consistent with the CH₃ proton data. This is further indicated by the fact that the ΔS^\ddagger values are in good agreement when ΔH^\ddagger is fixed at 9.98 kcal mol⁻¹.

FeTPP⁺ in *N,N*-Dimethylformamide. This system was studied at concentrations of FeTPP⁺ in the range 1.0×10^{-2} – 4.0×10^{-2} *m*. Line broadenings of 10–80 Hz and chemical shifts of up to 20 Hz were observed and found to be directly dependent on the FeTPP⁺ concentration.

The temperature dependence of $(T_{2P}P_M)^{-1}$ for this system is shown in Figure 2. P_M was calculated assuming $n = 1$ for reasons given in the Discussion section.

Table II. Least-Squares Best-Fit Parameters for Fe(TPP)⁺ in DMF

	— $(T_{2P}P_M)^{-1}$ data—			— $\Delta\omega$ data—	
	A	B	C	D	E
ΔH^\ddagger , kcal mol ⁻¹	8.01	9.78	9.37	9.19	9.37 ^d
ΔS^\ddagger , cal mol ⁻¹ deg ⁻¹	-2.09	4.43	3.11	3.47	4.22
$10^{-3}C_M$, sec ⁻¹	4.16	3.82	4.74	4.74 ^d	4.74 ^d
E_M , kcal mol ⁻¹	1.44	1.37 ^b	1.31	1.31 ^d	1.31 ^d
C_o , sec ⁻¹	2.20×10^{-3}	822	36.4		
E_o , kcal mol ⁻¹	6.67	1.37 ^b	2.66 ^c		
$10^{-7}C_\omega$, radians sec ⁻¹ deg	2.04 ^a	2.04 ^a	2.04 ^a	2.05	2.04

^a Fixed at value indicated by $\Delta\omega$ data. ^b E_M set equal to E_o . ^c Fixed at value obtained from Fe(DMF)₆³⁺ system, Table I. ^d Fixed at value given by fit C.

These results were ultimately fitted to the complete two site equation developed by Swift and Connick.¹²

$$(T_{2P}P_M)^{-1} = \frac{1}{\tau_M} \times \left(\frac{(T_{2M})^{-2} + (\tau_M T_{2M})^{-1} + \Delta\omega_M^2}{\left(\frac{1}{T_{2M}} + \frac{1}{\tau_M}\right)^2 + \Delta\omega_M^2} \right) + T_{2o}^{-1} \quad (6)$$

The last term describes the outer-sphere contribution as in eq 3 and 5. Qualitative analyses of the data in Figure 2 indicate that the $\Delta\omega_M^2$ terms could be dropped in eq 6 for this system and this was done in preliminary fits of the data. However, the independent chemical shift measurements show that the $\Delta\omega_M^2$ terms make a 10–15% contribution near the maximum of the curve in Figure 2, and they have been included in the final analysis.

The temperature dependence of the relaxation time

(12) T. J. Swift and R. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

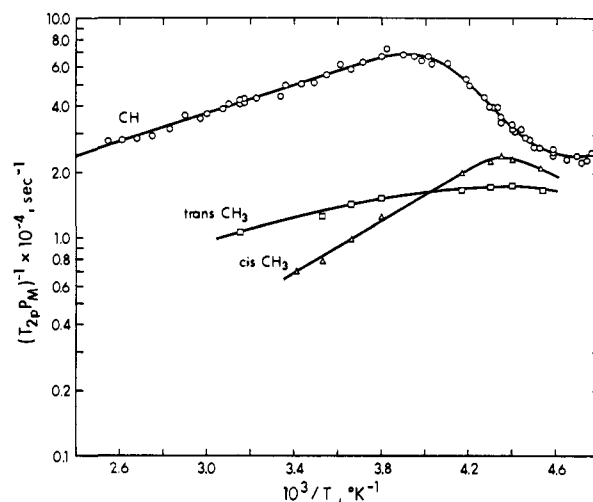


Figure 2. Temperature dependence of $(T_{2P}P_M)^{-1}$ for solutions of FeTPP⁺ in *N,N*-dimethylformamide. Smooth curve for CH proton is calculated from fit C (Table II).

in the first coordination sphere is assumed to be given by

$$T_{2M}^{-1} = C_M \exp(E_M/RT) \quad (7)$$

The temperature dependence of the chemical shift in the first coordination sphere is assumed to be given

by the expression developed by Bloembergen¹³

$$\Delta\omega_M = -\left(\frac{A}{\hbar}\right) \frac{\omega_0 \mu_{\text{eff}} \beta \sqrt{S(S+1)}}{3kT\gamma_I} = -\frac{C_\omega}{T} \quad (8)$$

The results of various least-squares fits of the data to eq 6 are summarized in Table II. The outer-sphere contribution is not well defined by the data and this is evident from the anomalous E_o value in fit A. As a result fits B and C were attempted in which the value of E_o was constrained. The results from fit C are considered to be the most reliable because the E_o is based on the experimental value from the Fe(DMF)₆³⁺ system and is also consistent with values in the range of 2.3–2.8 found for NiTAAB²⁺ in DMF.¹⁴

The observed chemical shift ($\omega_{\text{sample}} - \omega_{\text{solvent}}$) is given by¹²

$$-\frac{\Delta\omega_{\text{obsd}}}{P_M} = \frac{\Delta\omega_M}{\left(\frac{\tau_M}{T_{2M}} + 1\right)^2 + (\tau_M \Delta\omega_M)^2} \quad (9)$$

(13) N. Bloembergen, *ibid.*, **27**, 572 (1957).

(14) L. L. Rusnak, J. E. Letter, Jr., and R. B. Jordan, *Inorg. Chem.*, **11**, 199 (1972).

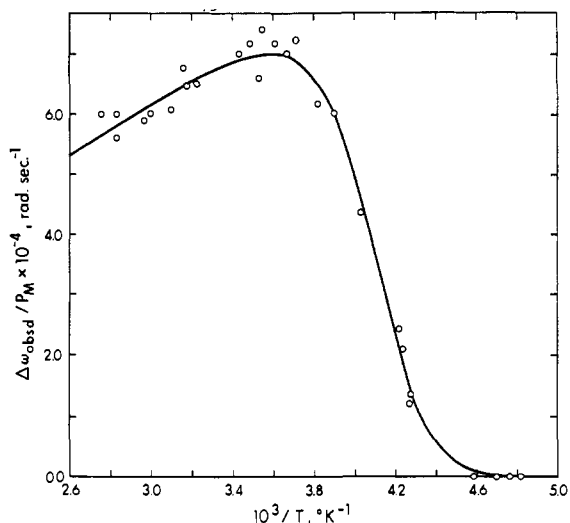


Figure 3. Temperature dependence of $\Delta\omega_{\text{obsd}}/P_M$ for solutions of FeTPP^+ in *N,N*-dimethylformamide. Smooth curve is calculated from fit E (Table II).

The temperature dependence of $\Delta\omega_{\text{obsd}}$ is shown in Figure 3. The chemical shifts are not sufficiently precise to permit a complete fit to eq 9. However, if C_M and E_M are fixed, then the least-squares fit (D in Table II) yields values for ΔH^\ddagger and ΔS^\ddagger in reasonable agreement with those from the $(T_{2P}P_M)^{-1}$ data. Fit E and the curve drawn in Figure 3 show that the shift and line-broadening results are compatible with the same exchange rate parameters.

It should be noted that C_ω is relatively insensitive to the ΔH^\ddagger and ΔS^\ddagger values, since it is well defined by the limiting chemical shift at high temperature. The value of C_ω can be used in eq 8 to calculate a value for the hyperfine coupling constant (A/\hbar) of 3.70×10^6 radians sec^{-1} , based on an effective magnetic moment of 5.9 BM.¹⁵

The inner-sphere relaxation rate (T_{2M}^{-1}) of the CH proton is calculated to be $4.32 \times 10^4 \text{ sec}^{-1}$ at 25° from the parameters of fit C of Table II. This value is consistent with relaxation by the dipolar mechanism¹⁶ with an inner-sphere interaction distance of 3 Å and a correlation time of $3.2 \times 10^{-11} \text{ sec}$. This correlation time is much shorter than the rotational correlation time of $\sim 1.2 \times 10^{-10} \text{ sec}$ estimated for vanadyl in DMF.¹⁷ Therefore the correlation time is probably the electron spin relaxation time (τ_e) of the high-spin iron(III) complex. This proposal is consistent with the failure of Wolberg and Manassen¹⁸ to observe a room temperature epr spectrum for FeTPP^+ . The somewhat low value of E_M is also consistent with this assumption.

The line-broadening results for the methyl protons of DMF are plotted also in Figure 2. These results show little effect of chemical exchange and therefore are not helpful in better defining ΔH^\ddagger and ΔS^\ddagger . The results are included only because they show an unusual relaxation effect in that the line broadening for the high-field trans CH_3 group has a much lower activa-

(15) C. Maricondi, W. Swift, and D. K. Straub, *J. Amer. Chem. Soc.*, **91**, 5205 (1969).

(16) R. E. Connick and D. Fiat, *J. Chem. Phys.*, **44**, 4103 (1966).

(17) N. S. Angerman and R. B. Jordan, *ibid.*, **54**, 837 (1971).

(18) A. Wolberg and J. Manassen, *J. Amer. Chem. Soc.*, **92**, 2982 (1970).

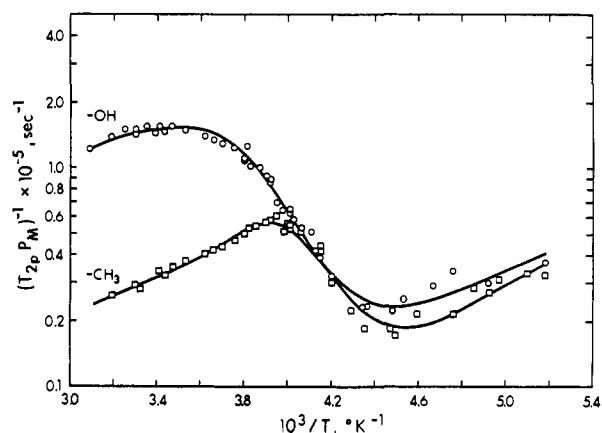
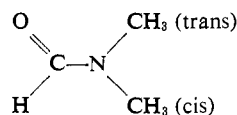


Figure 4. Temperature dependence of $(T_{2P}P_M)^{-1}$ for solutions of FeTPP^+ in methanol. Smooth curves are calculated from fits D and G (Table III).

tion energy ($E_M \approx 1.0 \text{ kcal mol}^{-1}$) than the cis CH_3 ($E_M \approx 2.8 \text{ kcal mol}^{-1}$).



If the dipolar broadening¹⁶ is dominant then the trans CH_3 is expected to have a larger $(T_{2P}P_M)^{-1}$ because the interaction distance to the metal ion is shorter.¹⁹ However, in the FeTPP^+ system below -20° , the trans CH_3 has a smaller $(T_{2P}P_M)^{-1}$ value. The effect is clearly evident in the spectra since the trans CH_3 resonance has a higher maximum than the cis below -20° , while normally the cis resonance is higher. Therefore the effect does not arise from some difficulty in the least-squares fitting used to resolve the line widths of these two resonances.

The problem is to explain why the relaxation rate for the trans CH_3 is less than that predicted from the cis CH_3 . Additional relaxation mechanisms will not explain the results. The only qualitative explanation seems to be that some faster correlation time is operative for the trans CH_3 dipolar interaction which is not operative for the cis CH_3 . This explanation is consistent with the differences in E_M for the two sets of protons but requires a new correlation time shorter than $\sim 3 \times 10^{-11} \text{ sec}$. It should be noted that this phenomenon was not observed in the previous study of manganese(III) protoporphyrin(IX) dimethyl ester in DMF.¹

FeTPP⁺ in Methanol. Four samples were studied with FeTPP^+ concentrations in the range 9.2×10^{-3} – $1.5 \times 10^{-2} \text{ M}$. Line broadenings in the range of 5–20 Hz and chemical shifts of up to 6 Hz were observed. The accuracy of the results from this system is considerably limited by the low solubility of FeTPP^+ in methanol.

The temperature dependencies of $(T_{2P}P_M)^{-1}$ for the OH and CH_3 protons are shown in Figure 4. Initially these results were fitted to a modified form of eq 6 in which the $\Delta\omega_M^2$ terms were neglected. This gave preliminary values of ΔH^\ddagger , ΔS^\ddagger , C_M , and E_M , which were used to fit the chemical shift results in Figure 5 to determine values for C_ω . As can be seen from fits J and K in Table III, C_ω is not very sensitive to ΔH^\ddagger ,

(19) N. A. Matwiyoff, *Inorg. Chem.*, **5**, 788 (1966).

Table III. Least-Squares Best-Fit Parameters for FeTPP⁺ in Methanol

	$(T_{2P}P_M)^{-1}$ data							$\Delta\omega$ data				
	OH proton				CH ₃ protons			OH proton		CH ₃ protons		
	A	B	C	D	E	F	G	H	I	J	K	L
ΔH^\ddagger , kcal mol ⁻¹	11.63	12.89	11.37	11.28	12.89 ^f	11.63 ^h	11.28 ⁱ	11.62 ^a	11.28 ^j	11.63 ^h	12.89 ^f	11.28 ⁱ
ΔS^\ddagger , cal mol ⁻¹ deg ⁻¹	10.17	15.51	9.32	8.97	16.09	10.95	9.52	10.28	8.98	10.36	15.2	8.92
$10^{-2}C_M$, sec ⁻¹	97.5	575	162	150	28.4	26.3	25.7	97.4 ^a	150 ⁱ	6.03 ^g	28.4 ^d	25.7 ^k
E_M , kcal mol ⁻¹	1.59 ^c	0.53	1.30 ^d	1.35 ^e	1.30	1.35	1.37	1.59 ^a	1.35 ^j	2.14 ^e	1.30 ^d	1.37 ^k
C_ω , sec ⁻¹	577	315	192	186	65.5	40.2	34.2					
E_ω , kcal mol ⁻¹	1.59 ^c	1.86	2.05	2.06	2.42	2.61	2.68					
$10^{-7}C_\omega$, sec ⁻¹	2.27 ^b	2.27 ^b	2.27 ^b	2.27 ^b	2.11 ^g	2.10 ⁱ	2.10 ⁱ	2.27	2.28	2.10	2.08	2.12

^a Fixed at value from preliminary fit neglecting $\Delta\omega_M^2$ terms. ^b Fixed at value from fit H. ^c E_M set equal to E_ω . ^d Fixed at value from fit E. ^e Fixed at value from fit F. ^f Fixed at value from fit B. ^g Fixed at value from preliminary fit not shown. ^h Fixed at value from fit A. ⁱ Fixed at value from fit J. ^j Fixed at value from fit D. ^k Fixed at value from fit G.

ΔS^\ddagger , C_M , and E_M , and therefore good estimates can be obtained in this way. This procedure is justified further by the fact that the $\Delta\omega_M^2$ terms make <5% contribution to the OH proton $(T_{2P}P_M)^{-1}$ values although they can affect the CH₃ proton values by about 20%.

The values of C_ω were fixed and the complete eq 6 was used to obtain least-squares best-fit values of the other parameters. It should be noted that ΔH^\ddagger and ΔS^\ddagger are best defined by the OH proton $(T_{2P}P_M)^{-1}$ data while E_M is best defined by the CH₃ proton results. The latter can be seen from fits E, F, and G which show that E_M is relatively insensitive to the ΔH^\ddagger and ΔS^\ddagger values. It seemed reasonable to expect that E_M would be the same for both types of protons and therefore that the E_M from fit B is meaningless because the value is poorly defined by the OH proton line-broadening data. The fitting was continued until reasonable self-consistency of E_M and ΔS^\ddagger was obtained as represented by fits D and G, and then final fits I and L of the shift data were obtained.

The main assumption which has been used in evaluating the results is that E_M is the same for both the OH and CH₃ protons. Experience in previous work indicates that this is a reasonable assumption. However, the results from the two CH₃ protons in the FeTPP⁺-DMF system cast some doubt on this assumption. It is possible that the unexplained phenomenon which causes the two CH₃ groups to have different apparent E_M values could also cause different E_M values for the OH and CH₃ protons in methanol. Therefore it is not possible to completely disregard fit B which gave $\Delta H^\ddagger = 12.9$ kcal mol⁻¹ and $\Delta S^\ddagger = 15.5$ cal mol⁻¹ deg⁻¹. However, the latter parameters give $\tau_M^{-1}(25^\circ) = 5.3 \times 10^6$ sec⁻¹, not qualitatively different from the value of 3.1×10^6 sec⁻¹ calculated with $\Delta H^\ddagger = 11.28$ kcal mol⁻¹ and $\Delta S^\ddagger = 9.0$ cal mol⁻¹ deg⁻¹.

The chemical shift results, which are given in Figure 5, are not very accurate because the maximum observable shift was only 6 Hz. The shifts show the expected temperature dependence and have been fitted to eq 9 as described above. The C_ω values in Table III can be used to calculate hyperfine coupling constants (A/h) of 1.4×10^6 sec⁻¹ and 1.3×10^6 sec⁻¹ for the hydroxy and methyl protons, respectively, based on an effective magnetic moment of 5.9.¹⁵

The results from fits D and G predict inner-sphere relaxation rates of 1.47×10^5 and 2.58×10^4 sec⁻¹ for the hydroxy and methyl protons, respectively. These results are consistent with relaxation by a dipolar

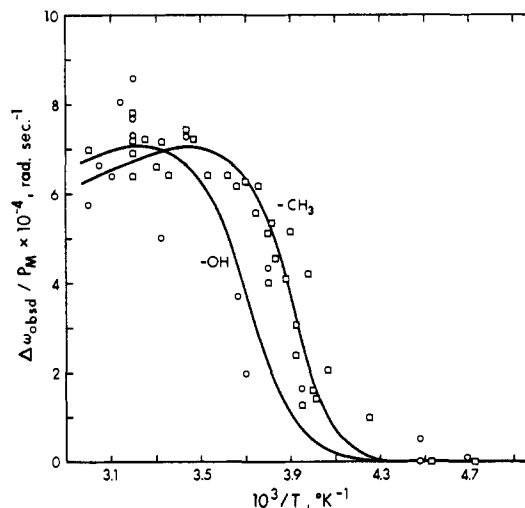


Figure 5. Temperature dependence of $\Delta\omega_{\text{obsd}}/P_M$ for solutions of FeTPP⁺ in methanol. Smooth curves are calculated from fits I and L (Table III).

mechanism with interaction distances of 3.0 and 4.0 Å for the hydroxy and methyl protons, respectively, and a correlation time of 1.06×10^{-10} sec⁻¹. The calculated T_{2M}^{-1} values are 1.46×10^5 sec for the OH proton and 2.61×10^4 sec⁻¹ for the CH₃ protons. The correlation time is three times longer than that found in DMF but could be either the electron spin relaxation time or the rotational tumbling time of the molecule.

Discussion

The kinetic results from this and previous related work are summarized in Table IV. In the Fe(DMF)₆³⁺-DMF system the observations reported here are qualitatively similar to those found previously by Breivogel.²⁰ However, the $(T_{2P}P_M)^{-1}$ values are consistently smaller than those from the earlier work, by as much as a factor of 2-3 in the low-temperature outer-sphere region. The differences in the kinetic parameters are due largely to the differences in the correction for the outer-sphere effects. The outer-sphere activation energy (E_ω) of 3.5 kcal mol⁻¹ found by Breivogel is higher than values found for several systems in these laboratories and is also higher than the activation energy for viscosity of DMF (~ 2.8 kcal mol⁻¹).

The very negative ΔS^\ddagger for DMF exchange with

(20) F. W. Breivogel, Jr., *J. Phys. Chem.*, **73**, 4203 (1969).

