

tortions imposed on the molecular configuration of the complex by the presence of the solvated molecules at crystallographic sites. The first mechanism, however, is rejected on the grounds of experimental evidence. Infrared spectra of solvates as well as solutions of (morphdte)<sub>3</sub>Fe studied in the 4000-700-cm<sup>-1</sup> region showed no spectral changes indicative of solute-solvent linkages, e.g., coordination, hydrogen bonding, etc. Moreover, the solution effective magnetic moment of the complex dissolved in benzene or dichloromethane was measured by the NMR method and it was found the same,  $\mu_{\text{eff}}(300 \text{ K}) = 4.5 \pm 0.1 \mu_{\text{B}}$ , in both solutions. This constitutes further evidence that there are no solute-solvent interactions strong enough to induce changes in the spin-state equilibrium of the ferric ion, at least in the liquid phase. The absence of complex-solvated solvent linkages has also been suggested by X-ray studies of (Budtc)<sub>3</sub>Fe·C<sub>6</sub>H<sub>6</sub> monocrystals.<sup>50</sup> The second mechanism of the solid-state forces affecting the spin equilibrium of the paramagnetic center appears more relevant in view of the experimental data mentioned above and also from earlier studies on the pressure dependence of the solution  $\mu_{\text{eff}}(300 \text{ K})$  of several Fe(III) dithiocarbamates.<sup>3</sup> It was found that application of external pressures up to 5000 atm on chloroform solutions of ((alkyl)<sub>2</sub>dte)<sub>3</sub>Fe complexes shifts the high-spin-low-spin equilibrium toward the low-spin state. This shift has been associated with a shortening of the Fe-S bond by ca. 0.1 Å, amounting to a volume decrease of the order of 5 cm<sup>3</sup>/mol of dithiocarbamate complex.<sup>3</sup> In a similar fashion the solvated solvent can be assumed to distort the complex by pure lattice forces and induce a decrease in the Fe-S bond length analogous to the decrease caused by the external pressure. In fact, in FeM·2PhH, the mean Fe-S bond length at 300 K is 2.318 Å<sup>26</sup> compared to Fe-S = 2.430 Å<sup>25</sup> in FeM·DCM. Accord-

ingly, the former solvate exhibits high-spin-low-spin equilibrium at room temperature whereas the latter is in a predominantly high-spin state. Since the inclusion of solvent molecules at crystallographic sites seems to be very common in iron(III) dithiocarbamate crystals, combined X-ray and magnetic studies of these solvates can provide valuable information concerning the relationship between the spin state of Fe<sup>3+</sup> and the exact structure of the FeS<sub>6</sub> core. The magnetic properties of several other solvated ferric dithiocarbamates are now under investigation in our laboratory along with their crystal structures at 300 and 77 K.

We conclude with a final remark concerning the previously published<sup>26</sup>  $S = 3/2$  assignment for (morphdte)Fe·CH<sub>2</sub>Cl<sub>2</sub>. The temperature dependence of  $\mu_{\text{eff}}(T)$  reported earlier<sup>26</sup>, which contradicts the low-temperature Mössbauer data presented here, as well as our magnetic susceptibility measurements, probably arises from partial desolvation of the FeM·DCM and FeM·2PhH samples used in ref 26. In fact samples of dichloromethane-solvated crystals that were left at room temperature for few days produced liquid helium Mössbauer spectra consisting of two superimposed patterns, one exhibiting hyperfine structure identical with the spectrum of FeM·DCM and one exhibiting the doublet corresponding to the desolvated complex. The effective moment of those samples was indeed 5.5  $\mu_{\text{B}}$  at 300 K and close to 4  $\mu_{\text{B}}$  at 77 K. After complete removal of the solvent by heating and pumping the Mössbauer spectra demonstrated only the doublet of the desolvated complex while the magnetic susceptibility dropped to 5.2  $\mu_{\text{B}}$  at 300 K and 3.3  $\mu_{\text{B}}$  at 77 K.

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**Registry No.** FeM, 14285-01-9; FeM·2PhH, 59568-15-9; FeM·DCM, 53179-06-9.

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## High-Pressure NMR Evidence for an Associative Interchange Mechanism, I<sub>a</sub>, for Solvent Exchange on Iron(III)<sup>1-3</sup>

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Variable-pressure 60-MHz <sup>1</sup>H NMR transverse relaxation rate measurements have been made on iron(III) perchlorate solutions in dimethyl sulfoxide (Me<sub>2</sub>SO), dimethylformamide (DMF), and methanol. For the two former solvents, the cation is hexasolvated whereas in methanol, even in acidic solutions, the cation is Fe(CH<sub>2</sub>OH)<sub>5</sub>(OCH<sub>3</sub>)<sup>2+</sup>. The derived volumes of activation ( $\Delta V^*$ ) for solvent exchange are interpreted in terms of an associative interchange I<sub>a</sub> for Me<sub>2</sub>SO (-3.1 ± 0.3 cm<sup>3</sup> mol<sup>-1</sup>) and DMF (-0.9 ± 0.2 cm<sup>3</sup> mol<sup>-1</sup>) but a dissociative interchange I<sub>d</sub> for the hydrolyzed cation in methanol (+6.4 ± 0.2 cm<sup>3</sup> mol<sup>-1</sup>). The reasons for the difference in mechanism between the hexasolvated and the hydrolyzed species are discussed. The results for the hexasolvated ion exchange are compared with those available for other first-row transition-metal trivalent-ion solvent exchanges and are interpreted in terms of a gradual mechanistic change from I<sub>a</sub> to I<sub>d</sub> on going from left to right across the periodic table. A similar trend for the divalent ions has also recently been reported.

### Introduction

In a recent article,<sup>2</sup> the effect of pressure on the rate of water exchange on iron(III) has been studied up to 240 MPa. The pressure dependence shows marked variation with pH and yields a negative volume of activation for the water exchange

with Fe(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> and a positive volume of activation for water exchange with Fe(H<sub>2</sub>O)<sub>5</sub>OH<sup>2+</sup>. However, the work was complicated since it was necessary to work at very high ionic strengths and acidities and to correct for changes in hydrolysis with pressure.

In a series of recent articles,<sup>4-9</sup> we have shown that the

(1) This is part 14 of the series, "High-Pressure NMR Kinetics".  
 (2) Part 13 is to be taken as: Swaddle, T. W.; Merbach, A. E. *Inorg. Chem.* 1981, 20, 4212.  
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relative volumes of activation for solvent exchange on the divalent transition-metal ions  $Mn^{2+}$  to  $Ni^{2+}$  do not show large variation with solvent and all show the change from negative to positive values on going from left to right across the periodic table. It was thus decided to study the pressure dependence of nonaqueous solvent exchange on iron(III) in order to shed further light on the solvent exchange and ligand substitution kinetics, an area that has produced much controversy.

### Experimental Section

**Preparation of Materials and Samples.** Dimethyl sulfoxide ( $Me_2SO$ ) was purified and  $[Fe(Me_2SO)_6](ClO_4)_3$  was prepared as described previously.<sup>10</sup> Solutions ( $7.8 \times 10^{-2}$  and  $8.0 \times 10^{-2}$  mol of complex/kg of solvent) were prepared in a glovebox (water content  $<5$  ppm) and contained no internal reference.

Dimethylformamide (DMF) (Fluka, for UV) was dried by reflux over BaO for 10 h and then distilled and stored over 4-Å molecular sieves (Merck). Cyclohexane (Fluka, purum) was dried by reflux over Na for 3 h, distilled, and stored over 4-Å molecular sieves. Chloroform (Fluka, puriss, p.a.) was stored over 4-Å molecular sieves.  $[Fe(DMF)_6](ClO_4)_3$  was prepared from  $Fe(ClO_4)_3 \cdot 9H_2O$  (Fluka, pract.) according to the method of Hodgkinson and Jordan.<sup>11</sup> It was twice purified by being dissolved in the minimum quantity of DMF followed by removal of the solvent by vacuum distillation. Anal. Found (calcd): C, 27.26 (27.10); H, 5.33 (5.26); N, 10.45 (10.50); O, 36.42 (36.31); Cl, 13.20 (13.41); Fe, 6.82 (7.04). For variable-temperature work, three solutions ( $1.8 \times 10^{-2}$ ,  $3.1 \times 10^{-2}$ , and  $4.9 \times 10^{-2}$  mol  $kg^{-1}$ ) were prepared, each containing 1% of either cyclohexane or chloroform as internal reference. The solutions were contained within the capillary of a Wilmad 5-mm coaxial cell with a deuterium-containing lock substance (either  $Me_2SO-d_6$  or acetone- $d_6$ , each with one drop of  $CH_3NO_2$ ) in the annulus. For variable-pressure work four solutions ( $3.3 \times 10^{-2}$ ,  $4.7 \times 10^{-2}$ ,  $4.7 \times 10^{-2}$ , and  $6.0 \times 10^{-2}$  mol  $kg^{-1}$ ) were prepared, each containing 1% cyclohexane as internal reference.

Methanol was dried over anhydrous calcium sulfate (water content by Karl Fischer titration  $<50$  ppm). Two solutions of anhydrous  $FeCl_3$  (Fluka, purum) ( $1.22 \times 10^{-2}$  and  $1.37 \times 10^{-2}$  mol  $kg^{-1}$ ) were prepared, each containing 1%  $Me_4Si$  as internal reference. The chloride ion was eliminated by reaction of the solution with a slight excess of anhydrous  $AgClO_4$  prepared from  $AgClO_4 \cdot H_2O$  (Fluka, puriss) according to the method of Radell et al.<sup>12</sup> The solutions were then filtered and used immediately.

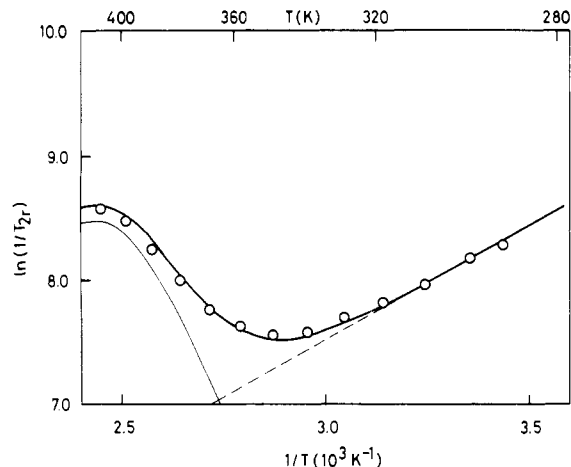
**NMR Measurements.** Variable-temperature measurements were performed on a Bruker WP-60 spectrometer using an internal deuterium lock. The homogeneity was controlled by using the proton signal of the lock substance. The temperature was measured by using a substitution technique using a 100-Ω Pt resistor as the temperature-measuring device.<sup>13</sup>

Variable-pressure measurements were performed on a Bruker WP-60 spectrometer using high-pressure NMR probes similar to those previously described.<sup>3</sup> An external  $^{19}F$  lock was used and, where feasible, the magnetic field inhomogeneity was taken into account from the observed internal reference line width.

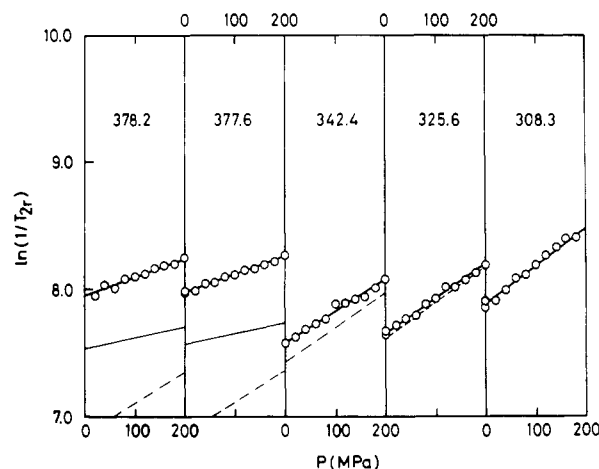
For both variable-pressure and -temperature measurements, the reduced transverse relaxation rate  $1/T_{2r}$  ( $s^{-1}$ ) was obtained from the inhomogeneity-corrected line width  $\Delta\nu_{cor}$  (Hz) by means of the expression  $1/T_{2r} = \pi(\Delta\nu_{cor})/P_m$ , where  $P_m$  is the mole fraction of bound solvent.

### Data Treatment and Results

**Dimethyl Sulfoxide Exchange.** In a recent publication,<sup>10</sup> we have reported a variable-frequency proton (8–360 MHz)



**Figure 1.** Relaxation rates ( $s^{-1}$ ) of  $[Fe(Me_2SO)_6](ClO_4)_3$  solutions in dimethyl sulfoxide as a function of temperature (—) together with the chemical exchange (—) and outer-sphere relaxation (---) contributions.



**Figure 2.** Relaxation rates ( $s^{-1}$ ) of  $[Fe(Me_2SO)_6](ClO_4)_3$  solutions in dimethyl sulfoxide as a function of pressure at various temperatures (—) together with the chemical exchange (—) and outer-sphere relaxation (---) contributions.

and carbon-13 (50 MHz) NMR study of both bound and free solvent for solutions of  $[Fe(Me_2SO)_6](ClO_4)_3$  in  $Me_2SO$  as a function of temperature, undertaken in order to obtain values for the rate and activation parameters for solvent exchange. The 13 data sets were analyzed by a simultaneous nonlinear least-squares procedure with 12 unknown parameters. It was clear that our variable-pressure free-solvent  $T_{2r}$  study at 60 MHz would be unable to define the pressure dependence of the three correlation times and of the solvent-exchange rate. We were thus required to adopt a different analysis. Figure 1 shows the 60-MHz  $1/T_{2r}$  values as a function of temperature. Experimentally it is clear that, at low temperatures, the outer-sphere contribution obeys a reasonable Arrhenius behavior, and thus the temperature dependence was assumed to be of the form<sup>9</sup>

$$\frac{1}{T_{2os}} = \frac{1}{T_{2os}(298)} \exp \left[ \frac{E}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right] \quad (1)$$

where  $1/T_{2os}(298)$  is the contribution at 298.15 K and  $E$  is the activation energy. A new fit of only the 60-MHz  $^1H$  NMR  $1/T_{2r}$  data was made by using the full Swift–Connick equation<sup>10,14</sup> with bound-solvent relaxation given by both scalar and dipolar relaxation but with  $1/T_{2os}$  given by eq 1. All parameters were fixed at the values obtained previously,<sup>10</sup> and just

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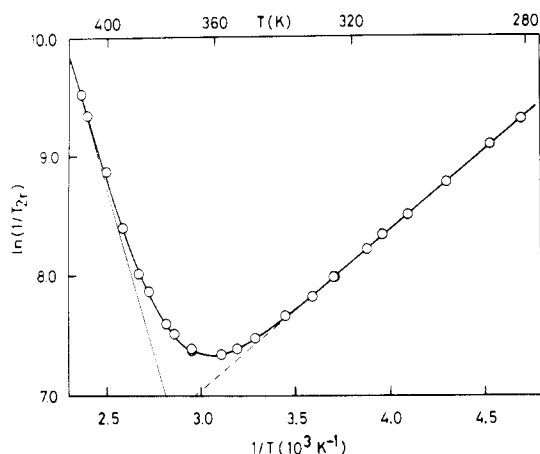
**Table I.** Zero-Pressure Rate Constants and Outer-Sphere Relaxation Rates with their Standard Deviations for  $[\text{Fe}(\text{Me}_2\text{SO})_6](\text{ClO}_4)_3$  Solutions in Dimethyl Sulfoxide from Variable-Pressure Studies at Different Temperatures

$T$ , K	$(1/T_{2\text{os}}^i)^0$ , $\text{s}^{-1}$	$k_i^0$ , $\text{s}^{-1}$
378.2	957 <sup>a</sup>	2082 ± 7
377.6	964 <sup>a</sup>	2161 ± 28
342.4	1682 ± 14	276 <sup>a</sup>
325.6	2012 ± 16	84 <sup>a</sup>
308.3	2639 ± 21	22 <sup>a</sup>

$$\Delta V^* = -3.1 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$$

$$\Delta V_{\text{os}}^* = -7.6 \pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$$

<sup>a</sup> Fixed parameter.

**Figure 3.** Relaxation rates ( $\text{s}^{-1}$ ) of  $[\text{Fe}(\text{DMF})_6](\text{ClO}_4)_3$  solutions in dimethylformamide as a function of temperature (—) together with the chemical exchange (---) and outer-sphere relaxation (· · ·) contributions.

$1/T_{2\text{os}}(298)$  and  $E$  were allowed to vary. The values obtained were  $1/T_{2\text{os}}(298) = 3520 \pm 80 \text{ s}^{-1}$  and  $E = 15.3 \pm 0.6 \text{ kJ mol}^{-1}$ . The smooth curve in Figure 1 shows the calculated values. The variable-pressure  $1/T_{2r}$  measurements (Figure 2) were performed at five different temperatures, and it is clear that, particularly at the three higher temperatures, both the kinetic term and  $1/T_{2\text{os}}$  contribute to the relaxation. For each of the five data sets ( $i = 1-5$ ), the pressure dependences of both  $1/T_{2\text{os}}^i$  and  $k_i$  were assumed to be of the forms

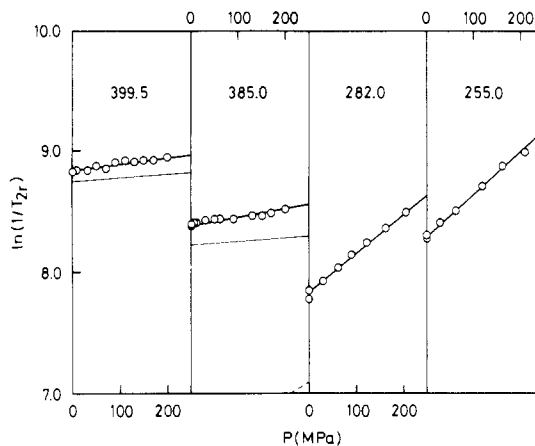
$$\ln(1/T_{2\text{os}}^i) = \ln(1/T_{2\text{os}}^i)^0 + (\Delta V_{\text{os}}^*)P/RT \quad (2)$$

$$\ln k_i = \ln k_i^0 + (\Delta V^*)P/RT \quad (3)$$

where  $(1/T_{2\text{os}}^i)^0$  and  $k_i^0$  are the zero-pressure outer-sphere relaxation and rate constants, respectively, and  $\Delta V_{\text{os}}^*$  and  $\Delta V^*$  are the activation volumes for outer-sphere relaxation and solvent exchange, respectively. In principle, there are 12 unknowns,  $(1/T_{2\text{os}}^i)^0$  and  $k_i^0$  ( $i = 1-5$ ) and  $\Delta V_{\text{os}}^*$  and  $\Delta V^*$ ,<sup>15</sup> but it is clear that, for the lowest three temperatures, the data would not define  $k_i^0$  and, at the highest two, the data would not define  $(1/T_{2\text{os}}^i)^0$ . These five parameters were thus fixed at the values obtained from the variable-temperature analysis. The results of the least-squares data analysis are given in Table I, and the calculated relaxation rates together with their exchange and outer-sphere contributions are the smooth curves given in Figure 2.

**Dimethylformamide Exchange.** Figure 3 shows the temperature dependence of the  $^1\text{H}$  NMR transverse relaxation

(15) In principle, the zero-pressure rate constants  $k_i^0$  and outer-sphere contributions  $(1/T_{2\text{os}}^i)^0$  could all be set to the values obtained from the above variable-temperature analysis. In practice, small variations in concentration, homogeneity corrections, and differences in temperature calibration between the variable-temperature and -pressure experiments could cause nonrandom errors in the  $\Delta V^*$  measurements.<sup>5,6</sup>

**Figure 4.** Relaxation rates ( $\text{s}^{-1}$ ) of  $[\text{Fe}(\text{DMF})_6](\text{ClO}_4)_3$  solutions in dimethylformamide as a function of pressure at various temperatures (—) together with the chemical exchange (---) and outer-sphere relaxation (· · ·) contributions.**Table II.** Zero-Pressure Rate Constants and Outer-Sphere Relaxation Rates with their Standard Deviations for  $[\text{Fe}(\text{DMF})_6](\text{ClO}_4)_3$  Solutions in Dimethylformamide from Variable-Pressure Studies at Different Temperatures

$T$ , K	$(1/T_{2\text{os}}^i)^0$ , $\text{s}^{-1}$	$k_i^0$ , $\text{s}^{-1}$
399.5	590 <sup>a</sup>	6284 ± 46
385.0	669 <sup>a</sup>	3922 ± 28
282.0	2509 ± 21	20.8 <sup>a</sup>
255.0	3952 ± 36	2.8 <sup>a</sup>

$$\Delta V^* = -0.9 \pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$$

$$\Delta V_{\text{os}}^* = -7.5 \pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$$

<sup>a</sup> Fixed parameter.

times of solutions of  $[\text{Fe}(\text{DMF})_6](\text{ClO}_4)_3$  in dimethylformamide. The outer-sphere contribution appears to obey reasonable Arrhenius behavior and was assumed to follow eq 1. Up to the highest temperature studied (423 K) there was no evidence of approaching the Swift–Connick maximum and thus the Swift–Connick equation was simplified to<sup>6,14</sup>

$$1/T_{2r} = 1/T_{2\text{os}} + k \quad (4)$$

where  $k$  is the solvent-exchange rate constant. It has been clearly demonstrated that this simplified equation can yield erroneous results for  $\Delta H^*$  and  $\Delta S^*$ , where accurate characterization of both the slope and  $1/T = 0$  intercept is necessary.<sup>5</sup> Attempts to measure the bound-solvent chemical shift and line width directly in order to be able to use the full, accurate Swift–Connick equations were unsuccessful. The values obtained from this single-frequency, free-solvent  $1/T_{2r}$  study are as follows:  $k(298)$  ( $\text{s}^{-1}$ ) =  $59 \pm 2$ ;  $\Delta H^*$  ( $\text{kJ mol}^{-1}$ ) =  $42.57 \pm 0.39$ ;  $\Delta S^*$  ( $\text{J K}^{-1} \text{ mol}^{-1}$ ) =  $-68.21 \pm 1.00$ ;  $1/T_{2\text{os}}(298)$  ( $\text{s}^{-1}$ ) =  $1832 \pm 12$ ;  $E$  ( $\text{kJ mol}^{-1}$ ) =  $11.07 \pm 0.07$ . They are essentially identical with those obtained by Hodgkinson and Jordan<sup>11</sup> over a narrower temperature range. We wish to emphasize that one should not give too much weight to these rate parameters and as in the case of iron(III)– $\text{Me}_2\text{SO}$  exchange,<sup>10</sup> accurate evaluation of these parameters would require a multinuclear and variable-frequency study. However, it has also been well established<sup>5</sup> that the simplified equation gives reliable values for  $\Delta V^*$ . The variable-pressure transverse relaxation rate measurements (Figure 4) were performed at four different temperatures. As with the  $\text{Me}_2\text{SO}$  results, for each of the four data sets ( $i = 1-4$ ) the pressure dependence of both  $1/T_{2\text{os}}^i$  and  $k_i$  in eq 4 were given by eq 2 and 3. At the two lowest temperatures  $k_i^0$  was fixed at the value calculated from the variable-temperature analysis, and at the two highest  $(1/T_{2\text{os}}^i)^0$  was fixed. The results of the data analysis are given in Table II, and the calculated relaxation rates are

Table III. Rate Constants and Activation Parameters for Solvent Exchange on Iron(III)

	$k_{298}, \text{s}^{-1}$	$k_{373}, \text{s}^{-1}$	$\Delta H^*, \text{kJ mol}^{-1}$	$\Delta S^*, \text{J K}^{-1} \text{mol}^{-1}$	$\Delta V^*, \text{cm}^3 \text{mol}^{-1}$
$\text{Fe}(\text{H}_2\text{O})_6^{3+ a, b}$	$(1.6 \pm 0.2) \times 10^2$	$3.6 \times 10^4$	$64.0 \pm 2.5$	$+12.1 \pm 6.7$	$-5.4 \pm 0.4$
$\text{Fe}(\text{DMF})_6^{3+ c, d}$	61	$2.3 \times 10^3$	$42.3 \pm 4$	$-69.0 \pm 13$	$-0.9 \pm 0.2$
$\text{Fe}(\text{Me}_2\text{SO})_6^{3+ e, d}$	$9.3 \pm 1.6$	$1.8 \times 10^3$	$62.5 \pm 1.9$	$-16.7 \pm 5.2$	$-3.1 \pm 0.3$
$\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+ a, b}$	$(1.4 \pm 0.1) \times 10^5$	$1.7 \times 10^7$	$42.4 \pm 1.5$	$+5.3 \pm 4.0$	$+7.0 \pm 0.5$
$\text{Fe}(\text{CH}_3\text{OH})_5(\text{OCH}_3)^{2+ f, d}$	$2.4 \times 10^3$	$1.3 \times 10^5$	44.7	-29	$+6.4 \pm 0.2$
$\text{Fe}(\text{CH}_3\text{CH}_2\text{OH})_5(\text{OCH}_2\text{CH}_3)^{2+ f}$	$2.0 \times 10^4$	$2.2 \times 10^5$	$25.9 \pm 6.3$	$-75 \pm 21$	

<sup>a</sup> Variable temperature; ref 18. <sup>b</sup> Variable pressure; ref 2. <sup>c</sup> Variable temperature; ref 11. <sup>d</sup> Variable pressure; this work. <sup>e</sup> Variable temperature; ref 10. <sup>f</sup> Variable temperature; ref 16.

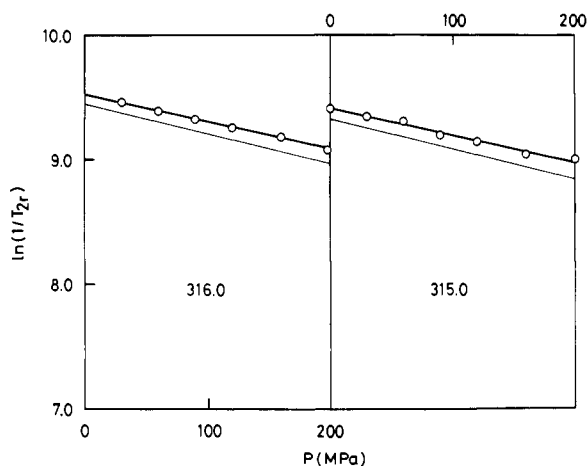


Figure 5. Relaxation rates ( $\text{s}^{-1}$ ) of iron(III) perchlorate solutions in methanol as a function of pressure at two temperatures (K) (—) together with the chemical exchange (—) contribution.

the smooth curves given in Figure 4.

**Methanol Exchange.** Breivogel<sup>16,17</sup> has studied the temperature dependence of the proton  $1/T_{2r}$  of the methyl resonance of  $[\text{Fe}(\text{CH}_3\text{OH})_6](\text{ClO}_4)_3$  solutions in methanol. His results suggest that for this system, as for the dimethylformamide exchange, the simplified equation (4) may also be used. Furthermore, in the temperature range suitable for performing variable-pressure kinetic measurements, the outer-sphere contribution to  $1/T_{2r}$  is small (only 10% at 315 K) and its pressure dependence may be neglected.<sup>7</sup> Two variable-pressure experiments were performed at closely similar temperatures (315 and 316 K) and were fitted to eq 3 and 4 ( $i = 1, 2$ ) with a fixed value of  $1/T_{2os}$  of  $1000 \text{ s}^{-1}$  read from the diagram of Breivogel's paper.<sup>17</sup> The derived parameters are as follows:  $k_1^0(315 \text{ K}) (\text{s}^{-1}) = 11 186 \pm 100$ ;  $k_2^0(316 \text{ K}) (\text{s}^{-1}) = 12 639 \pm 141$ ;  $\Delta V^* (\text{cm}^3 \text{mol}^{-1}) = +6.4 \pm 0.2$ . The experimental and calculated relaxation rates are given in Figure 5. The approximate nature of the subtraction of the outer-sphere contribution is open to some criticism but even altering the value by  $\pm 50\%$  results in a change in  $\Delta V^*$  of only  $\pm 0.3 \text{ cm}^3 \text{mol}^{-1}$ , which is of the same order as the reported standard deviation.

### Discussion

Table III summarizes the rate constants and variable-temperature and -pressure activation parameters for solvent exchange on iron(III). The results have been separated into two groups. The first group contains solvent exchange on hexasolvated ions while the second contains exchange on partially hydrolyzed ions (see below).

The volumes of activation for the solvent exchange on the hexasolvated ions are all negative, implying an associative activation mode. The values are less negative than those expected for a limiting associative A mechanism, leading to the assignment of an associative interchange  $I_a$  mechanism.

The observed exchange rates are all slow by paramagnetic NMR standards. As was mentioned above, the dimethylformamide variable-temperature results may be in error since they were obtained by using a simplified Swift-Connick analysis and more reliable values would require a multinuclear and variable-frequency study. Notwithstanding this problem, a detailed inspection of the rate for the three systems shows that the extrapolation of the Eyring equation from temperatures where meaningful kinetic results may be obtained to 298.15 K is long even for water and thus the  $k_{298}$  values may not be very reliable. For example, for the  $\text{Me}_2\text{SO}$  system, we have recently reported<sup>10</sup> a serious error correlation of  $k_{298}$  with  $\Delta H^*$ . In view of this, it might be advisable to choose a higher temperature, e.g., 373 K, at which to make comparisons of complex formation and solvent-exchange rates. This comparison is important if one wishes to confirm the associative interchange mechanism by detecting an effect of the incoming ligand on the rate of the ligand-interchange step. For water, there is high-pressure  $T$ -jump evidence that the anation reactions of  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$  with  $\text{SCN}^-$ ,<sup>19</sup>  $\text{Cl}^-$ ,<sup>20</sup> and  $\text{Br}^-$ <sup>21</sup> are associative. The overall activation volumes  $\Delta V^*$  are respectively  $0 \pm 5$ ,  $-4.5 \pm 1.1$ , and  $-8 \pm 4 \text{ cm}^3 \text{mol}^{-1}$ . Noting that  $\Delta V^* = \Delta V_{os} + \Delta V_1^*$ , where  $\Delta V_{os}$  is the reaction volume of outer-sphere association and  $\Delta V_1^*$  is the volume of activation for the interchange step,  $\Delta V_1^*$  must be negative since  $\Delta V_{os}$  is a positive quantity of similar magnitude for ligands of the same charge type.

The solvent-exchange rates on the hydrolyzed ions are very much faster than on the unhydrolyzed ions, e.g., by a factor of 1000 in water. The presence of the  $\text{RO}^-$  group clearly has a profound effect on the exchange reaction. The experimental evidence for the hydrolyzed nature of alcohol solutions of iron(III) is compelling. It is well established that, in water, one must work at very high concentrations of acid in order to ensure that the exchange on  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$  is the predominant process.<sup>18,22</sup> One could expect that hydrolysis in methanol would be even more severe due to its lower dielectric constant, and one might never be able to work at high enough acidities to ensure that exchange on  $\text{Fe}(\text{CH}_3\text{OH})_6^{3+}$  is predominant. In acid media, aqueous solutions of iron(III) are almost colorless whereas, as the pH is raised, the solutions become yellow-brown due to the large absorbance of  $\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ . Solutions of iron(III) in anhydrous methanol even in the presence of acid are also yellow-brown, and as early as 1942 Rabinowitch and Stockmayer<sup>23</sup> suggested that the color could be due to hydrolysis. More recently, Horne<sup>24</sup> has studied the UV-visible spectra of iron(III) in alcohol-water mixtures and concludes that the strong yellow color in alcohol-rich solutions

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**Table IV.** Volumes of Activation  $\Delta V^\ddagger$  ( $\text{cm}^3 \text{mol}^{-1}$ ) for Solvent Exchange on Hexasolvated Trivalent Metal Ions

	scandium, $d^0$	chromium, $d^3$	iron, $d^5$	gallium, $d^{10}$
H <sub>2</sub> O		-9.3 <sup>a</sup>	-5.4 <sup>b</sup>	
DMF		-6.3 <sup>c</sup>	-0.9	+7.9 <sup>d</sup>
Me <sub>2</sub> SO		-11 <sup>e</sup>	-3.1	+13.1 <sup>d</sup>
(CH <sub>3</sub> O) <sub>3</sub> PO	-20.7 <sup>f</sup>			+20.7 <sup>g</sup>
mechanism	A, I <sub>a</sub>	I <sub>a</sub>	I <sub>a</sub>	I <sub>d</sub>

<sup>a</sup> Reference 25. <sup>b</sup> Reference 2. <sup>c</sup> Reference 26. <sup>d</sup> Reference 27. <sup>e</sup> Reference 28. <sup>f</sup> Reference 29. <sup>g</sup> Reference 30.

is due to a hydrolysis product. We have made a qualitative study of anhydrous solutions of iron(III) in methanol as a function of added perchloric acid. The solutions in each case contained an excess of methyl orthoformate to remove water. Even at 5 M acid, the solutions were still strongly colored. Addition of water removed the color, and subsequent addition of more methyl orthoformate restored the color. No quantitative measurements were made due to the extremely hazardous nature of perchloric acid/methanol mixtures due to the slow formation of the very explosive methyl perchlorate. Thus, after observation, the solutions were immediately diluted with excess water. We are thus confident that the predominant species in solution is a hydrolysis product, probably  $\text{Fe}(\text{CH}_3\text{OH})_5(\text{OCH}_3)^{2+}$ . Similar conclusions can be drawn from the work of Horne for the higher alcohols. The alcohol data in Table III have not been corrected for the fact that there are only five exchanging solvent molecules and this will alter the value of  $k_{298}$  and  $\Delta S^\ddagger$ . Such a correction would also assume that there are no differences in lability between cis and trans solvents, which is unlikely. It is clear from the table that the volumes of activation for the hydrolyzed species are positive, and we are thus confident that the reactions occur via a dissociative activation mode. In water this is also borne out<sup>2</sup> by the overall volumes of activation for anation reactions of  $\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$  by  $\text{Cl}^-$  and  $\text{NCS}^-$ , which are also positive (+7.8 and +7.1  $\text{cm}^3 \text{mol}^{-1}$ , respectively). One may readily explain the much greater rate of solvent exchange of the hydrolyzed species over the hexasolvated species and the change of mechanism using the fact that a strongly bound ligand (i.e.,  $\text{RO}^-$ ) will weaken the remaining ion-solvent bonds, most probably the trans solvent molecule, thus giving rise to a faster solvent-exchange rate. This bond weakening is also large enough that bond breaking becomes more important than bond making at the transition state, giving rise to a mechanistic change.

Table IV gives the available volumes of activation for solvent exchange on trivalent hexasolvated first-row transition-metal ions. It is clear that for these high-spin ions there is a gradual change of mechanism on going from left to right across the series. For scandium, there are currently insufficient data available to decide whether the exchange is associative interchange I<sub>a</sub> or limiting associative A. For gallium, however, it is clear that we have not reached the limiting dissociative

D mechanism since aluminum gives larger volumes of activation and is thus more dissociative than gallium.<sup>27,30</sup> We thus assign gallium as dissociative interchange I<sub>d</sub>. The available data for both aqueous<sup>9</sup> and nonaqueous<sup>7</sup> solvent exchanges on the high-spin, first-row divalent transition-metal ions show identical trends, and for both series the changeovers occur after  $d^5$ , i.e., after  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$ . This result is surprising since one might expect the mechanism to be dominated by two opposing effects. First, one would expect more highly charged ions to favor an associative transition state, and second, one would expect smaller ions to favor a dissociative transition state. It is clear that as one descends a column of the periodic table the reactions become more and more associative. For example, between  $\text{Al}^{3+}$  and  $\text{In}^{3+}$ , the volumes of activation of TMPA change from +22.5 to -21.4  $\text{cm}^3 \text{mol}^{-1}$ .<sup>30</sup> It is conceivable that, for the first-row metal ions, the loss of associativity on going from divalent to trivalent ions due to decrease in ionic size is exactly compensated by the gain in associativity due to the increase in charge. We have recently suggested that the change of mechanism along the first-row divalent metal ions from  $\text{Mn}^{2+}$  to  $\text{Ni}^{2+}$  is due to changes in the occupancy of the  $t_{2g}$  electron orbitals. The  $t_{2g}$  electrons, being nonbonding, point between adjacent ligands, and increasing occupancy of these orbitals would inhibit formation of a seven-coordinate transition state. However, the mechanistic changes also mirror changes in ionic radii, and for the divalent ions it is not yet possible to separate the two effects. However, for the trivalent ions we have more information. The fact that  $\text{Cr}^{3+}$  is more associative than  $\text{Fe}^{3+}$  suggests that  $e_g$  orbital occupancy is also important in dictating the mechanism; this is readily explainable when one considers that the  $e_g$  orbitals are antibonding.  $\text{Cr}^{3+}$  and  $\text{Ga}^{3+}$  have similar ionic radii (0.62 Å), and the very large difference in mechanism is strong evidence that on going across the series the number of d electrons seems to be the dominating factor in determining the mechanism.<sup>31</sup>

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**Registry No.** [ $\text{Fe}(\text{Me}_2\text{SO})_6$ ]( $\text{ClO}_4$ )<sub>3</sub>, 14245-13-7; [ $\text{Fe}(\text{DMF})_6$ ]( $\text{ClO}_4$ )<sub>3</sub>, 33247-87-9; [ $\text{Fe}(\text{CH}_3\text{OH})_6$ ]( $\text{ClO}_4$ )<sub>3</sub>, 79872-87-0;  $\text{Fe}(\text{CH}_3\text{OH})_5(\text{OCH}_3)^{2+}$ , 79872-88-1.

**Supplementary Material Available:**  $1/T_{2r}$  data for the variable-pressure Fe(III)-Me<sub>2</sub>SO (Table S1), variable-temperature (Table S2) and -pressure Fe(III)-DMF (Table S3), and variable-pressure Fe(III)-methanol systems (Table S4) (9 pages). Ordering information is given on any current masthead page.

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