

Scheme II. II is an associative intermediate involving H_2O_2 bonded as a monodentate at a face of the octahedron of $\text{VO}_2(\text{nta})^{2-}$. The rearrangement to the distorted pentagonal-bipyramidal transition state (III) from the associative complex (II) is enhanced by the protonation to an oxo group in the k_2 path.

There is no direct evidence to distinguish whether oxo oxygen or oxygen in hydrogen peroxide is released as a water molecule from the transition state (III). The oxygen exchange on vanadium(V) ion is very slow,¹⁸ and mostly the oxygen exchange of oxyanion is not first order but second order in hydrogen ion concentration.^{19,20} The strength of the $\text{V}=\text{O}$

bond in vanadium(V) complexes estimated from IR spectra does not correspond to the reactivity of vanadium(V) complexes with H_2O_2 .¹ Thus as shown in Scheme II it is likely that the peroxy in the product results from an oxo group of the $\text{V}(\text{V})$ -NTA complex and an oxygen atom of hydrogen peroxide.

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Kinetics of Solvent Water Exchange on Iron(III)

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Pulsed NMR methods have been used to measure the transverse and longitudinal relaxation rates of oxygen-17 in aqueous solutions of iron(III) (8.20×10^{-3} – 0.315 *m*) and perchloric acid (0.34 – 3.89 *m*) from 0 to 140 °C. The results have been used to determine the kinetic parameters for solvent water exchange from $\text{Fe}(\text{OH}_2)_6^{3+}$ and $\text{Fe}(\text{OH})_5(\text{OH})^{2+}$. The values of k (s^{-1} , 25 °C), ΔH^\ddagger (kcal mol^{-1}), and ΔS^\ddagger ($\text{cal mol}^{-1} \text{ deg}^{-1}$) are $(1.6 \pm 0.2) \times 10^2$, 15.3 ± 0.6 , and 2.9 ± 1.6 for $\text{Fe}(\text{OH}_2)_6^{3+}$ and $(1.2 \pm 0.1) \times 10^5$, 10.14 ± 0.35 , and 1.26 ± 0.95 for $\text{Fe}(\text{OH})_5(\text{OH})^{2+}$. The solvent exchange rates and various ligand substitution rates are most consistent with associative activation for substitution on $\text{Fe}(\text{OH}_2)_6^{3+}$ and dissociative activation for $\text{Fe}(\text{OH})_5(\text{OH})^{2+}$.

A standard method of determining the mechanism of ligand substitution on a metal ion is to compare the solvent exchange rate with the ligand substitution rate.² After correction for ion pair formation it has been found, at least for cobalt(II) and nickel(II), that the dissociative mechanism suggested by Eigen and Wilkins³ is most consistent with the results. There have been a number of studies of ligand substitution on iron(III), but the mechanistic conclusions remain uncertain because of the lack of published water exchange rate data. The iron(III) system is complicated by the ease with which the $\text{Fe}(\text{OH}_2)_6^{3+}$ ion hydrolyzes and polymerizes.

This paper reports the results of oxygen-17 pulsed NMR relaxation time measurements on aqueous iron(III) perchloric acid solutions. The temperature and hydrogen ion dependence of the water solvent exchange rate has been determined.

Experimental Section

Materials. Ferric perchlorate stock solutions were prepared from two sources of iron. First, ammonium ferric sulfate (BDH AnalaR grade) was treated with an excess of concentrated NaOH solution, and the precipitated hydrated ferric oxide was dissolved in excess perchloric acid. After concentration of the resulting solution and cooling, crystals of $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$ were obtained and washed with concentrated perchloric acid. The damp crystals were dissolved in 1 M perchloric acid to give a stock solution about 0.7 M in iron(III) and 1.8 M in HClO_4 . Second, high-purity iron (Alfa Products; 99.998% considering metallic impurities) was dissolved in concentrated nitric acid, and the solution was fumed with concentrated perchloric

acid. The resulting crystals were treated as above to give a stock solution of similar composition.

The stock solutions were analyzed for iron both volumetrically by reduction to iron(II) with stannous chloride and by reoxidation with standard potassium dichromate⁴ and spectrophotometrically as the tris(1,10-phenanthroline)iron(II) complex after reduction with hydroxylamine.⁵ The methods gave concordant results. Manganese(II) is known to be a common impurity of iron compounds, and the very effective NMR line-broadening characteristics of the ion make it a highly undesirable contaminant. The two iron(III) stock solutions were analyzed for manganese spectrophotometrically as MnO_4^- after oxidation of the solution with periodate. The manganese concentration of the stock solutions was less than 2×10^{-6} M, and at these levels no contribution to the ^{17}O relaxation times from manganese(II) is possible.⁶ The solutions were also analyzed for iron(II); the tests were negative, and $[\text{iron(II)}]/[\text{iron(III)}] \leq 5 \times 10^{-3}$.

The acid content of the stock solutions was measured by titration of the solutions with standard NaOH by using phenolphthalein⁷ as indicator and verified by displacement of H^+ from a cation-exchange resin in the H^+ form.

Aluminum perchlorate was prepared from the nitrate salt (Fisher) by fuming a concentrated aqueous solution with concentrated perchloric acid. When the mixture was cooled, white crystals of $\text{Al}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ were precipitated and were washed with perchloric acid and dried at 100 °C for several hours. A stock solution in water was analyzed for aluminum gravimetrically as tris(8-quinolinolato)aluminum⁴ and for perchloric acid by ion-exchange displacement of H^+ .

Reagent grade sodium perchlorate (G. F. Smith) was recrystallized twice, and a 1 M solution was prepared and analyzed by cation

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exchange. Other reagents were reagent grade and were used as supplied. Water enriched to 10% in ^{17}O was obtained from Prochem/Isotopes and distilled in vacuo before use.

Sample Preparation. Hindman et al.⁸ have reported that, in order to obtain reproducible ^{17}O spin-lattice relaxation times, careful cleaning of glassware is necessary. Accordingly all glassware was treated with a hot solution of sodium ethylenediaminetetraacetate in concentrated NaOH and then with hot concentrated hydrochloric acid. The glassware was rinsed with distilled water and then methanol. Samples were prepared by the addition of known volumes of perchloric acid (1 M or concentrated), 1 M NaClO₄, 1 M NaHCO₃ (if required), and iron(III) or aluminum(III) stock solution, in that order. The excess water was distilled off at room temperature and oil pump pressure (no perchloric acid distills under these conditions). The amount of water remaining in the mixture was measured by weight difference. A known volume of H₂¹⁷O was added to the mixture which was then transferred to a 10-mm o.d. Pyrex tube. The solution was degassed on the vacuum line by the freeze-thaw technique and then sealed under vacuum.

NMR Measurements. These were performed on a Bruker SXP pulse spectrometer operating at 8.4 MHz. A 14-kG Varian electromagnet and V3506 flux stabilizer were used. The experiments were controlled by a Nicolet Instrument Corp. Model 1180 computer and 293A programmable pulser. Relaxation time data were collected and analyzed by using programs developed in these laboratories. Chemical shifts were measured by using Fourier transform software provided by Nicolet Corp. The sample volume (0.8 cm³) was less than that of the H₁ coil to avoid problems associated with inhomogeneity in the H₁ field. Temperature was controlled to ± 0.3 K by the Bruker B-ST 100/700 temperature control unit and was measured by a thermocouple inserted into glycerol contained in an NMR sample tube.

Spin-Lattice Relaxation Times (T_1). These were measured by the standard $180^\circ\text{-}\tau\text{-}90^\circ$ pulse sequence by using fifteen τ values in the range 0.2–4 T_1 and accumulating the data from 10 measurements at each value of τ . Final data analysis was by a standard least-squares method. The precision of the T_1 data was about 1%.

Spin-Spin Relaxation Times (T_2). These were normally measured by the Carr-Purcell-Meiboom-Gill pulse sequence.⁹ At least 80 echo trains were accumulated under computer control, and two or more values of the 180° pulse separation were used. The data were analyzed by a least-squares method. The T_2 values had a standard deviation of 4–7%. For very short relaxation times ($T_2 < 1$ ms) the pulse echo method was not reliable, and in these cases T_2^* was obtained from the time constant for free induction decay, the signal:noise ratio of the trace being improved by averaging about 1000 transients. A correction of not more than 10% of T_2 was made to T_2^* to allow for the effect of field inhomogeneity.

Shift measurements were made relative to an external standard for pure H₂¹⁷O placed concentrically just above the iron(III) solution. Spectra were obtained by Fourier transformation after a 90° pulse with use of the commercial program NTCFT-1180. Shifts were measured in a 0.315 *m* iron(III) solution in 0.37 and 0.89 *m* HClO₄. The magnitude of the shifts was ~ 430 Hz, varying with temperature and reproducible to ± 4 Hz.

Results

Relaxation Times in the Absence of Iron(III). The oxygen-17 transverse (T_2) and longitudinal (T_1) relaxation times have been measured in blank solutions of 1.0 *m* HClO₄, 2.0 *m* HClO₄, 1.0 *m* NaClO₄, and 0.5 *m* HClO₄ + 0.5 *m* HClO₄. The two relaxation times were the same within the experimental uncertainty and were essentially the same for the four solutions. Values were measured at about 10 °C intervals from –6 to +136 °C, and it was found that the values are given to within $\pm 2\%$ by function 1. The form of this equation was

$$T_1 = 1.975 \times 10^{-4} T \exp(-5.436 \times 10^7 / T^3) \quad (1)$$

chosen on the assumption that the relaxation time depends on a viscosity-dependent correlation time.^{10,11} The values of T_1

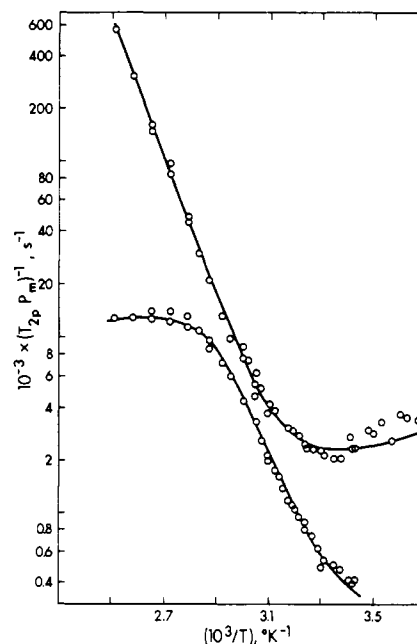


Figure 1. Variation of the solvent water oxygen-17 relaxation rates $(T_{2p}P_m)^{-1}$ (upper curve) and $(T_{1p}P_m)^{-1}$ (lower curve) with temperature for iron(III) in 0.95 *m* perchloric acid.

agree ($\pm 3\%$) with those in pure water of Hindman et al.⁸ above 40 °C, but our T_1 values are increasingly longer below 40 °C. For example, at 25 °C our results give $T_1 = 7.58 \times 10^{-3}$ s, while Hindman et al. obtained 6.85×10^{-3} s.

The small relaxation effect of iron(III) at low temperatures makes a knowledge of the blank T_1 and T_2 values rather critical. For this reason relaxation times were measured on a solution of 0.37 *m* Al(ClO₄)₃ and 0.70 *m* HClO₄ between –0.2 and +46.1 °C. The results are described by eq 2, and

$$T_1 = 1.998 \times 10^{-4} T \exp(-5.818 \times 10^7 / T^3) \quad (2)$$

the relaxation times are about 15% shorter than in the HClO₄–NaClO₄ solutions.

Relaxation Times in the Presence of Iron(III). The solvent water oxygen-17 relaxation times were measured in 13 solutions with various concentrations of iron(III) (8.20 $\times 10^{-3}$ –0.315 *m*) and perchloric acid (0.340–3.89 *m*) and ionic strength, adjusted with NaClO₄, between 1.05 and 4.03 *M*. Most samples were checked for irreversible effects of heating and aging on the relaxation rate. No such effects could be detected.

The results are given in terms of $(T_{2p}P_m)^{-1}$, where

$$\frac{1}{P_m T_{1,2p}} = \frac{[\text{solvent}] - 6[\text{iron(III)}]}{6[\text{iron(III)}]} \{ (T_{1,2})_{\text{Fe}}^{-1} - (T_{1,2})_{\text{sol}}^{-1} \} \quad (3)$$

and $(T_{1,2})_{\text{Fe}}$ is the value of T_1 or T_2 in the presence of iron(III) and $(T_{1,2})_{\text{sol}}$ is the analogous value in the absence of iron(III). It was found that $T_{1,2p}^{-1}$ was directly dependent on iron(III) as predicted by eq 3, and ionic strength had a minor effect on $(T_{1,2p}P_m)^{-1}$.

The temperature dependence of $(T_{1,2p}P_m)^{-1}$ in 0.95 *m* HClO₄ is shown in Figure 1. These results are quite representative of the behavior at other acidities. The $(T_{2p}P_m)^{-1}$ data are clearly divided into two regions; at high temperatures ($10^3/T \lesssim 3.1$) there is a high apparent activation energy of ~ 18 kcal mol^{–1} typical of chemical-exchange control of $(T_{2p}P_m)^{-1}$, while at low temperature exchange is slow and nuclear relaxation

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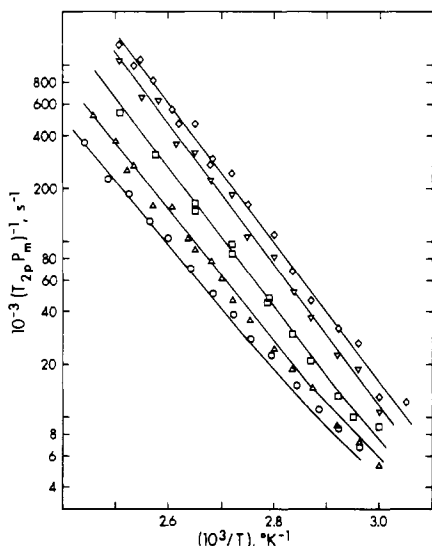


Figure 2. Temperature dependence of $(T_{2p}P_m)^{-1}$ at varying acidities of 0.34 *m* (\diamond), 0.495 *m* (∇), 0.95 *m* (\square), 1.87 *m* (Δ), and 3.89 *m* (\circ).

in the outer sphere controls $(T_{2p}P_m)^{-1}$ with a typical low activation energy of 2–3 kcal mol⁻¹. Therefore

$$(T_{2p}P_m)^{-1} = \tau_m^{-1} + T_{20}^{-1} \quad (4)$$

where τ_m is the exchange lifetime of a solvent molecule from the first coordination sphere of iron(III) and T_{20} is the transverse relaxation time for outer-sphere solvent molecules.

The $(T_{1p}P_m)^{-1}$ results in Figure 1 are consistent with chemical exchange as well since¹²

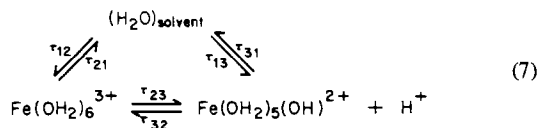
$$(T_{1p}P_m)^{-1} = (\tau_m + T_{1m})^{-1} + T_{10}^{-1} \quad (5)$$

At high temperature ($10^3/T \lesssim 2.7$) $\tau_m < T_{1m}$ to give a region of low activation energy with $(T_{1p}P_m)^{-1} \approx T_{1m}^{-1}$. As the temperature decreases, $\tau_m > T_{1m}$, and τ_m becomes the controlling factor until finally at low temperature the slight bending can be attributed to the T_{10}^{-1} contribution.

Unfortunately, the analysis is not as straightforward as the above discussion might indicate because τ_m has a significant acid dependence. This can be seen from the results in Figures 2 and 3, which show $(T_{2p}P_m)^{-1}$ values in the temperature range where $(T_{2p}P_m)^{-1} = \tau_m^{-1}$. It is clear from Figure 3 that

$$\tau_m^{-1} = k_0 + k_1[H^+]^{-1} \quad (6)$$

The inverse hydrogen ion dependence of τ_m^{-1} is consistent with solvent exchange from both $\text{Fe}(\text{OH}_2)_6^{3+}$ and $\text{Fe}(\text{OH}_2)_5(\text{OH})^{2+}$. Then the results should be considered as a three-site problem such as eq 7.



The expression for $(T_{2p})^{-1}$ for this system has been developed.^{13,14} From the work of Eyring and co-workers¹⁵ it is possible to estimate that $\tau_{23}^{-1} \approx 2 \times 10^7$ s⁻¹ and $\tau_{32}^{-1} \approx (0.3-2) \times 10^9$ s⁻¹ depending on the acidity. As discussed subsequently, the relaxation rates for H₂¹⁷O on $\text{Fe}(\text{OH}_2)_6^{3+}$ (T_{22}^{-1}) and on $\text{Fe}(\text{OH}_2)_5\text{OH}^{2+}$ (T_{23}^{-1}) are expected to be $\sim 10^7$ s⁻¹ so that it is reasonable to assume that $\tau_{32}^{-1} \gg T_{23}^{-1} + \tau_{31}^{-1}$ and, since the results indicate that $\tau_{21}^{-1} < 10^6$ s⁻¹, then $T_{22}^{-1} + \tau_{23}^{-1} \gg$

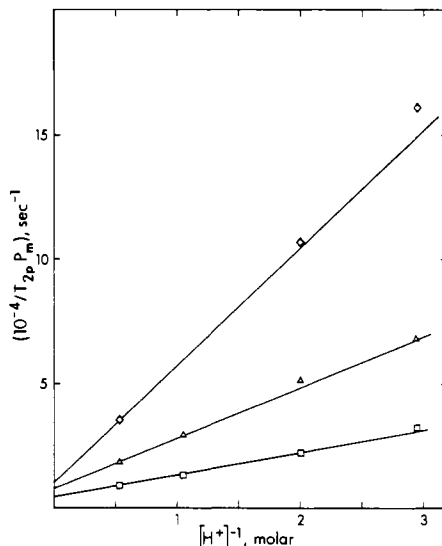


Figure 3. Variation of the solvent water oxygen-17 relaxation rate $(T_{2p}P_m)^{-1}$ with $[\text{H}^+]$ at 69 °C (\square), 79 °C (Δ), and 91 °C (\diamond). The data are within ± 1 °C of the stated temperature and at varying ionic strengths.

τ_{21}^{-1} . The equation given by Angerman and Jordan¹³ reduces to

$$T_{2p}^{-1} = \left(\frac{P_m}{\tau_m} \right) \frac{A(\tau_{32}^{-2}T_{2m}^{-1}) + B}{A^2\tau_{32}^{-2} + B} + T_{20}^{-1} \quad (8)$$

where

$$A = T_{2m}^{-1} + \tau_m^{-1}$$

$$B = \left(\frac{\Delta\omega_2}{\tau_{32}} \right)^2 + \left\{ \Delta\omega_3 \left(\frac{1}{T_{22}} + \frac{1}{\tau_{23}} \right) \right\}^2 + \frac{2\Delta\omega_2\Delta\omega_3}{\tau_{23}\tau_{32}} + (\Delta\omega_2\Delta\omega_3)^2$$

$$T_{2m}^{-1} = T_{22}^{-1} + \frac{5[\text{Fe}(\text{OH}_2)_5\text{OH}]}{6[\text{Fe}(\text{OH}_2)_6]} T_{23}^{-1} = T_{22}^{-1} + \frac{5K_{23}}{6[\text{H}^+]} T_{23}^{-1}$$

and the $5/6$ factor assumes, in the absence of evidence to the contrary, that the water molecules on $\text{Fe}(\text{OH}_2)_5\text{OH}^{2+}$ are equivalent.

$$\tau_m^{-1} = \tau_{21}^{-1} + \frac{5[\text{Fe}(\text{OH}_2)_5\text{OH}]}{6[\text{Fe}(\text{OH}_2)_6]} \tau_{31}^{-1} = \tau_{21}^{-1} + \frac{5K_{23}}{6[\text{H}^+]} \tau_{31}^{-1}$$

$$T_{20}^{-1} = [\text{Fe}(\text{OH}_2)_6](T_{22})_0^{-1} + [\text{Fe}(\text{OH}_2)_5\text{OH}](T_{23})_0^{-1} = [\text{Fe}]_{\text{tot}} \left\{ (T_{22})_0^{-1} + \frac{K_{23}}{[\text{H}^+]} (T_{23})_0^{-1} \right\}$$

$$P_m = 6[\text{Fe}(\text{OH}_2)_6] / \{ [\text{H}_2\text{O}]_0 - 6[\text{Fe}(\text{OH}_2)_6] \} = 6[\text{Fe}]_{\text{tot}} / [\text{H}_2\text{O}]_0$$

$$[\text{Fe}]_{\text{tot}} = [\text{Fe}(\text{OH}_2)_6] + [\text{Fe}(\text{OH}_2)_5(\text{OH})]$$

and

$$K_{23} = [\text{Fe}(\text{OH}_2)_5\text{OH}][\text{H}^+] / [\text{Fe}(\text{OH}_2)_6]$$

These expressions have made use of the condition that $[\text{H}^+] \gg K_{23}$ and that the solvent concentration $[\text{H}_2\text{O}]_0 \gg 6[\text{Fe}]_{\text{tot}}$ for the conditions of this study.

The observations are consistent with eq 2 if either $(A/\tau_{32}^2 T_{2m}) \gg B$ or $B \gg (A/\tau_{32}^2 T_{2m})$, since in either case

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$$(P_m T_{2p})^{-1} = \tau_m^{-1} + \frac{[H_2O]_0}{6} T_{20}^{-1} \quad (9)$$

and

$$(P_m T_{2p})^{-1} = \tau_{21}^{-1} + \frac{5K_{23}}{6[H^+]} \tau_{31}^{-1} + (T_{20}')^{-1} \quad (10)$$

Equations 9 and 10 are consistent with the observations as expressed by eq 4 and 6. It may be noted that T_{20}^{-1} is predicted to show an $[H^+]^{-1}$ dependence; however, none was observed. This is reasonable if $(T_{22})_0 \approx (T_{23})_0$, since at low temperature $K_{23} \approx 1.5 \times 10^{-3} M$,¹⁷ so that $K_{23}/[H^+] \ll 1$, and then $(T_{22})_0^{-1} \ll K_{23}/\{[H^+](T_{23})_0\}$.

The equation for T_{1p}^{-1} can be derived directly from eq 8 when it is recognized that changes in precessional frequency ($\Delta\omega$) do not contribute to longitudinal relaxation. Therefore $B = 0$ ¹⁶ and

$$(P_m T_{1p})^{-1} = (T_{1m} + \tau_m)^{-1} + (T_{10}')^{-1} \quad (11)$$

where T_{1m} and T_{10}' are defined analogously to T_{2m} and T_{20}' . No $[H^+]$ dependence of T_{1m}^{-1} could be detected probably for the reasons given above for the lack of $[H^+]$ dependence of T_{20}^{-1} . This observation, combined with the high-temperature value of K_{23} ($\sim 10^{-2} M$) and lowest $[H^+]$ studied (0.34 *m*), is consistent with $T_{13}^{-1} \lesssim 5T_{12}^{-1}$.

The temperature dependences of $(T_{2p}P_m)^{-1}$ and $(T_{1p}P_m)^{-1}$ have been fitted to eq 10 and 11 after substitution of appropriate functions. The variation of K_{23} with temperature and ionic strength was determined from Matijevic et al.¹⁷ (eq 12).

$$\begin{aligned} \Delta H_{23}^\circ &= 8014 - 171(\mu - 1.00) \\ \Delta S_{23}^\circ &= 13.85 - 0.832(\mu - 1.00) \\ K_{23} &= \exp\{(-\Delta H_{23}^\circ + T\Delta S_{23}^\circ)/RT\} \end{aligned} \quad (12)$$

The usual transition-state theory equation was used for the temperature dependence of τ_{21} and τ_{31} . The outer-sphere relaxation rate was assumed to have the same temperature dependence as the solvent, so that

$$(T_{1,2}')_0^{-1} = ((C_{1,2})_0/T) \exp(E_0/T^3) \quad (13)$$

and similarly for the inner-sphere T_{1m}

$$(T_{1m})^{-1} = (C_{1m}/T) \exp(E_m/T^3) \quad (14)$$

As shown by Figure 1, the T_{2p} results define τ_m over a much larger temperature range than the T_{1p} results. The latter also suffer from complete uncertainty about the outer-sphere contribution at low temperature and some uncertainty in the temperature dependence of T_{1m} at high temperature. As a result only the T_{2p} data have been used to evaluate the solvent-exchange-rate parameters. These parameters were fixed in the analysis of the T_{1p} data, and the resultant fit simply shows that the two data sets are compatible with the same exchange-rate parameters.

The results of nonlinear least-squares analysis of the data are summarized in Table I. The results for τ_{31} are much better characterized than those for τ_{21} because τ_{31} makes the dominant contribution to τ_m . This can be seen clearly from the relatively small intercept values in Figure 3. The uncertainty in E_0 also contributes significantly to that in τ_{21} because both T_{20} and τ_{21} are important in the low-temperature region. For example, if E_0 is changed from 2.92×10^7 to 5.44×10^7 , then ΔH_{21}^\ddagger decreases by 1.3 kcal mol⁻¹ and τ_{21}^{-1} (25 °C)

Table I. Least-Squares Best-Fit Parameters^a for Iron(III) in Water

	Fe(OH ₂) ₆ ³⁺	Fe(OH ₂) ₅ OH ²⁺
$\tau_{21}^{-1}, \tau_{31}^{-1}$ (25 °C), s ⁻¹	$(1.6 \pm 0.2) \times 10^2$	$(1.4 \pm 0.1) \times 10^5$
ΔH^\ddagger , kcal mol ⁻¹	15.3 ± 0.6	10.14 ± 0.35
ΔS^\ddagger , cal mol ⁻¹ deg ⁻¹	2.9 ± 1.6	1.26 ± 0.95
C_{02} , s ⁻¹ deg	$(1.99 \pm 0.49) \times 10^5$	
$E_{02} = E_m$, ^b deg ³	$(2.92 \pm 0.57) \times 10^7$	
C_{1m} , s ⁻¹ deg	$(3.04 \pm 0.08) \times 10^6$	
C_{01} , s ⁻¹ deg	$(1.52 \pm 0.23) \times 10^4$	

^a Errors quoted are 1 standard deviation, and 95% confidence limits are ~ 3 times these values. ^b Fixed in fitting the T_{1p} results.

Table II. Oxygen-17 Chemical Shifts in Aqueous Fe(ClO₄)₃ Solutions

<i>T</i> , K	[H ⁺], <i>m</i>	$10\Delta\nu/\nu_0 P_m$ ^{a, b}
272	0.37	1.19
273	0.89	1.18
282	0.37	1.11
282	0.89	1.12
292	0.37	1.07
293	0.89	1.09
302	0.37	1.03
304	0.89	1.05
312	0.37	1.03
313	0.89	1.01

^a $\Delta\nu$ is referenced to pure H₂¹⁷O and $\nu_0 = 8.43$ MHz. ^b P_m is calculated by assuming eight water molecules in the second coordination sphere of Fe(OH₂)₆³⁺.

changes from 157 to 246 s⁻¹, whereas the corresponding values for τ_{31} change by less than 1%.

The E_0 value which best fits the $(T_{2p}P_m)^{-1}$ results is much smaller than that found for the solvent blanks. This behavior seems to be typical of systems in which the electron spin relaxation time is the correlation time for the nuclear relaxation.¹⁸ This observation is consistent with the subsequent discussion of the outer-sphere relaxation mechanism.

Outer-Sphere Chemical Shift. A significant solvent oxygen-17 chemical shift was studied between 0 and 40 °C. The shift must be due to a scalar interaction with second coordination sphere solvent nuclei because inner-sphere exchange is so slow at these temperatures. The same effect has been observed with chromium(III) in water.¹⁹ The observed shift should be related to the mole fraction of second coordination sphere solvent molecules (P_0) and the chemical shift in the second coordination sphere ($\Delta\omega_0$) by eq 15. The scalar

$$\Delta\omega_{\text{obsd}} = -P_0(\Delta\omega_0) \quad (15)$$

coupling constant (A/\hbar) can be calculated from the usual expression (eq 16). Values of $\Delta\omega_{\text{obsd}}$ (Table II) have the

$$\Delta\omega_0 = -(A/\hbar)(\omega_{1g}\beta(S)(S+1)/3kT\gamma_1) \quad (16)$$

expected temperature dependence. If a second sphere coordination number of 8 is assumed, then $A/\hbar = (3.1 \pm 0.1) \times 10^6$ rad s⁻¹. A value of 2×10^6 rad s⁻¹ can be calculated from Alei's data on chromium(III),¹⁹ while nickel(II) gives 4×10^5 rad s⁻¹ from the data of Hunt et al.²⁰

Outer-Sphere Relaxation. The results clearly show that $(T_2)_0^{-1} \gg (T_1)_0^{-1}$. Even though the latter is not well-defined, the magnitude of 100–200 s⁻¹ is consistent with a dipolar relaxation mechanism with an interaction distance of $\sim 4 \text{ \AA}^{21}$ and a correlation time of $\sim 4 \times 10^{-11}$ s.²²

The difference between T_2^{-1} and T_1^{-1} is normally ascribed to a scalar contribution to T_2^{-1} , given by eq 17, where $\tau_c^{-1} =$

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$$(T_{20})^{-1} = (A/\hbar)_0^2 \frac{(S)(S+1)}{3} \left\{ \tau_{1c} + \frac{\tau_{2c}}{1 + \omega_e^2 \tau_{2c}^2} \right\} \quad (17)$$

$T_{1e}^{-1} + \tau_m^{-1}$, $\tau_{2c}^{-1} = T_{2e}^{-1} + \tau_m^{-1}$, τ_m is the residence time of a solvent molecule in the second coordination sphere, and T_{1e} and T_{2e} are the transverse and longitudinal electron spin relaxation times respectively. Since $(A/\hbar)_0 = 3.1 \times 10^6$ rad s^{-1} , the magnitude of $(T_{20})^{-1}$ ($\sim 2 \times 10^3$ s $^{-1}$) requires that the scalar correlation time be $\sim 1 \times 10^{-10}$ s. This value is consistent with the T_{2e} values for $\text{Fe}(\text{OH}_2)_6^{3+}$ and implies that the outer-sphere $\tau_m > 10^{-10}$ s. Wuthrich and Connick²⁴ came to the same conclusion for the outer-sphere lifetime of VO^{2+} in water.

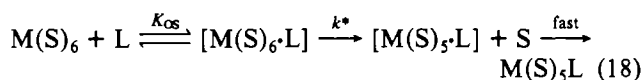
Inner-Sphere Relaxation. The known Fe-O interaction distance²¹ and a reasonable correlation time of 4×10^{-11} s give a dipolar $(T_{1m})^{-1} = 1.3 \times 10^4$ s $^{-1}$ compared to the extrapolated experimental value of 3×10^4 s $^{-1}$. A scalar contribution to $(T_{1m})^{-1}$ of 1.4×10^4 s $^{-1}$ is possible if $T_{1e} = T_{2e} = 2.6 \times 10^{-10}$ s²³ and $A/\hbar = 2 \times 10^8$ rad s $^{-1}$. This coupling constant gives a scalar contribution to $(T_{2m})^{-1} = 3 \times 10^7$ s $^{-1}$, which is at least consistent with one of the possible conditions which give eq 10; i.e., $(T_{2m})^{-1} \gg \tau_m^{-1}$.

It is also possible to obtain eq 10 if $B \gg A^2 \tau_{32}^{-2}$. Reasonable assumptions indicate that $B \approx \Delta\omega_2^2 / \tau_{32}^2$ so that eq 10 requires $\Delta\omega_2^2 \gg (\tau_m^{-1} + T_{2m}^{-1})^2$ or that at least $\Delta\omega_2^2 \gg \tau_m^{-2}$. The observed value of $(T_{2p} P_m)^{-1}$ at the highest temperature (140 °C) gives $\Delta\omega_2^2 \gtrsim 10 \times 10^6$ or $\Delta\omega_2 \gtrsim 3 \times 10^6$ rad s $^{-1}$. This value can be used to estimate a scalar coupling constant of $\gtrsim 2 \times 10^8$ rad s $^{-1}$. This value is consistent with that required to give a significant scalar contribution to T_{1m}^{-1} .

Inner-Sphere Chemical Shift. This should be a short analysis because no inner-sphere shift was observed. This is consistent with the above estimates because the line width would be 3 times larger than the shift at high temperature. At low temperature the shift is greatly reduced because the system is in the slow-exchange region. For example, at 55 °C in a 0.1 M iron(III) solution the inner-sphere shift is calculated to be ~ 0.1 Hz.

Discussion

Ligand substitution reactions are often analyzed in terms of the dissociative ion pair (DIP) mechanism proposed by Eigen and Wilkins.³ This mechanism can be tested by a comparison of the rates of ligand substitution and solvent exchange. The mechanism can be formulated as eq 18, where



K_{OS} is the formation constant for the outer-sphere precursor complex and k^* is the rate constant for dissociative solvent elimination. Normally the measured rate constant for ligand substitution is $k_{\text{obsd}} = k^* K_{\text{OS}}$, and an estimate of K_{OS} is used to calculate k^* . Then, after statistical correction,²⁵ k^* is compared to the solvent exchange rate (k_{ex}), and if $k^* \approx k_{\text{ex}}$, the result is taken to support the DIP mechanism. However, the statistical factor is somewhat uncertain,^{26,27} and calculation of K_{OS} ,²⁸ especially at the high ionic strengths used in most iron(III) studies, is of doubtful validity.²⁹ Therefore, it seems more meaningful to compare k_{obsd} values with the expectation that they will be fairly constant for a particular ligand charge

Table III. Ligand-Substitution Rate Constants on Iron(III) in Water

ligand	k_{obsd} , M $^{-1}$ s $^{-1}$ (25 °C)	
	$\text{Fe}(\text{OH}_2)_6^{3+}$	$\text{Fe}(\text{OH}_2)_5\text{OH}^{2+}$
SO_4^{2-} ^a	2.3×10^3	1.14×10^5
Cl^- ^b	4.8	5.5×10^3
Br^- ^c	1.58	2.8×10^3
NCS^- ^d	90	5×10^3
$\text{Cl}_2\text{CCO}_2^-$ ^e	63	7.8×10^3
$\text{Cl}_2\text{CHCO}_2^-$ ^e	118	1.9×10^4
$\text{ClCH}_2\text{CO}_2^-$ ^e	1.5×10^3	4.1×10^4
$\text{CH}_3\text{CO}_2\text{H}$ ^f	27	$\leq 2.8 \times 10^3$
$\text{C}_6\text{H}_5\text{OH}$ ^g		1.5×10^3
$\text{H}_3\text{CC}(\text{O})\text{NH}(\text{OH})$ ^h	1.2	2.0×10^3
H_2O ⁱ	1.6×10^2	1.4×10^5

^a Cavasino, F. P. *J. Phys. Chem.* 1968, 72, 1378. ^b Reference 37. ^c Reference 40. ^d Funahashi, S.; Adachi, S.; Tanaka, M. *Bull. Chem. Soc. Jpn.* 1973, 46, 479. ^e Reference 30. ^f Pandey, R. N.; M. Smith, W. *Can. J. Chem.* 1972, 50, 194. ^g Cavasino, F. P.; DiDio, E. *J. Chem. Soc. A* 1970, 1151. ^h Monzyk, B.; Crumblis, A. L. *J. Am. Chem. Soc.* 1979, 101, 6203. ⁱ This work; units are s $^{-1}$.

because K_{OS} depends strongly on the reactant charge product.

Values of k_{obsd} for some ligand systems are given in Table III, and more complete tabulations can be found elsewhere.^{30,31} The results for $\text{Fe}(\text{OH}_2)_5\text{OH}^{2+}$ conform to the expectations of the DIP mechanism, in that k_{obsd} changes from $\sim 1 \times 10^5$ to $\sim 5 \times 10^3$ to $\sim 2 \times 10^3$ M $^{-1}$ s $^{-1}$ as the ligand charge changes from -2 to -1 to 0. Similar changes are observed for $\text{Ni}(\text{OH}_2)_6^{2+}$ ³² for which the DIP mechanism is well established, although the value of k_{obsd} for a uninegative ion is 2-3 times smaller than k_{ex} for $\text{Ni}(\text{OH}_2)_6^{2+}$ whereas it is ~ 20 times smaller for $\text{Fe}(\text{OH}_2)_5\text{OH}^{2+}$. This difference could be ascribed to the higher ionic strength normally used with iron(III) (~ 1 M) compared to nickel(II) (~ 0.1 M). Higher ionic strength should decrease K_{OS} . It is also possible that the nonreacting (OH^-) ligand may affect K_{OS} and/or the probability of ligand substitution from the ion pair.

The results for dichloro- and monochloroacetate seem to be exceptions to the above discussion in that the k_{obsd} values are larger than expected for a uninegative ion. The same effect has been observed for these ions and acetate ion, reacting with nickel(II) in methanol.³³ Hoffmann³⁴ has suggested an internal hydrolysis mechanism for the latter case, and a similar suggestion was made by Perlmutter-Hayman and Tapuhi^{24,30} for the iron(III) system. A hydrogen bonding contribution to K_{OS} would also seem to be a possibility with the more basic acetates.

The reactions of $\text{Fe}(\text{OH}_2)_6^{3+}$ do not show the simple correlation of k_{obsd} with ligand charge. The substantial entering-group dependence is indicative of an associative activation process for substitution on $\text{Fe}(\text{OH}_2)_6^{3+}$.³⁵ Similar effects have been noted by Swaddle and Lo³⁶ for substitution on $\text{Cr}(\text{DMF})_6^{3+}$, and other evidence points to associative activation for substitution on chromium(III).³⁵ The large dependence of k_{obsd} on the basicity of the acetate ligands and the fact that $k_{\text{obsd}} \gg k_{\text{ex}}$ for chloroacetate are most easily understood in terms of an associative mechanism.

Volumes of activation also are consistent with the above mechanistic suggestions. The values of ΔV^\ddagger for reaction of $\text{Fe}(\text{OH}_2)_5(\text{OH})^{2+}$ with Cl^- and NCS^- are +8 and +7 cm³ mol $^{-1}$, respectively.^{37,38} Similar values have been found for

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substitution on $\text{Ni}(\text{OH}_2)_6^{2+}$,³⁹ and they are consistent with a dissociative mechanism. In contrast, the ΔV^\ddagger values for reaction of Cl^- ,³⁷ NCS^- ,³⁸ and Br^- with $\text{Fe}(\text{OH}_2)_6^{3+}$ are -5, -1, and $-19 \text{ cm}^3 \text{ mol}^{-1}$, respectively, and are consistent with an associative mechanism.

In conclusion, the comparison of ligand-substitution rate constants with varying ligands and the water solvent exchange

rate seems more consistent with dissociative activation for substitution on $\text{Fe}(\text{OH}_2)_5(\text{OH})^{2+}$ and associative activation for $\text{Fe}(\text{OH}_2)_6^{3+}$.

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Photoaquation of *trans*- and *cis*- $[\text{Cr}(\text{NH}_3)_4\text{F}_2]^+$

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The photoaquation of *trans*- and *cis*- $[\text{Cr}(\text{NH}_3)_4\text{F}_2]^+$ in acidic aqueous medium at 22 °C leads to efficient ammonia aquation ($\phi = 0.36$ and 0.45, respectively, for irradiation in the lowest quartet state) with minor yields of fluoride. The quantum yields or quantum yield ratios show small wavelength dependencies. The observed products from *trans*- $[\text{Cr}(\text{NH}_3)_4\text{F}_2]^+$ were 1,6-difluoro-2-aquotriamminechromium(III) (*mer* FWF) and 1,2-difluoro-6-aquotriamminechromium(III) (*mer* WFF) in a 1:2.5 ratio, while the *cis* compound yielded these two products in a 1:1.5 ratio, with the addition of small, wavelength-dependent amounts of 1,2-difluoro-3-aquotriamminechromium(III) ion. The results for the *trans* compound are consistent with both the edge displacement model of photostereochemistry and a recent theory invoking dissociative, symmetry-restricted photoreaction. In contrast the results for the *cis* compound do not fit at all well with the edge displacement model but are consistent with the symmetry-restricted, dissociative model, despite some difficult ambiguities which arise in its application.

Introduction

The development of theoretical models¹⁻⁷ for the photochemical modes of reaction of chromium(III) and other metal complexes and recently their photostereochemistry⁸ has been and continues to be a vigorous area of research. Of at least equal importance is the continued and further exploration of the behavior of actual systems under a variety of conditions to provide a background of data to explore validity of the theories. In particular emphasis should be on the need to provide data which will test and discriminate between the models with the maximum stringency wherever possible.

For a large number of the chromium complexes studied to date the different models give very similar predictions, so the data, although interesting and valuable in their own right, do not provide the desired discrimination. A satisfying exception has been the data on fluoroammine complexes of chromium(III); it was an early elegant study² of *trans*- $[\text{Cr}(\text{en})_2\text{F}_2]^+$ that first showed that, while many complexes underwent the photoreaction mode predicted by Adamson's rules,^{1,5} this was not universal. More recently a comparison⁹ of the photochemistry

of $[\text{Cr}(\text{NH}_3)_5\text{F}]^{2+}$ and *trans*- $[\text{Cr}(\text{en})_2\text{NH}_3\text{F}]^{2+}$ has provided a test of the recent Vanquickenborne and Ceulemans (VC) models.^{7,8} These satisfactorily accounted for the reaction modes but gave correct predictions of the photostereochemistry only if it was assumed^{10,11} that the theory could be extended to allow reaction of the postulated five-coordinate trigonal-bipyramidal intermediate in an electronically excited state.

For extension of the range of compounds studied and hopefully for further useful background data, a study of the photoreaction modes and stereochemistry of *trans*- and *cis*- $[\text{Cr}(\text{NH}_3)_4\text{F}_2]^+$ has been undertaken and is reported here. The photochemistry of the analogous *trans*- $[\text{Cr}(\text{en})_2\text{F}_2]^+$ has been the subject of a dispute^{2,12} over whether or not the photo and thermal products of ethylenediamine aquation are identical and therefore over the stereoretivity of the process. The analogous amine compounds with their fewer, more readily identifiable product isomers offered an excellent potential for clear-cut product isomer analysis, and therefore a more definite verdict as to whether the photoaquation of the equatorial ammonia is, by analogy, stereoretentive as originally suggested.² These compounds in addition provide an opportunity of a further test of the VC theory of photostereochemistry.

Experimental Section

Preparation of Complexes. Both *trans*- and *cis*- $[\text{Cr}(\text{NH}_3)_4\text{F}_2]^+$ were most conveniently prepared by fluoride anation^{13,14} in acidified

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