

# Proton and Deuteron Relaxation in Aqueous Solutions of Vanadyl(IV). Effects of Electron Spin Relaxation and Chemical Exchange

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**Abstract:** Proton and deuteron relaxation times in aqueous solutions of vanadyl(IV) sulfate have been studied as a function of temperature. The "excess" nuclear relaxation in this system is governed by both the relaxation time of a nucleus in the first hydration shell,  $T_{2M}$ , and its mean residence time,  $\tau_M$ . These quantities have been separated by comparing the proton and deuteron transverse relaxation times in the same solution, taking advantage of the fact that  $T_{2M^H}/T_{2M^D} = (\gamma_D/\gamma_H)^2$ . The temperature dependence of  $T_{2M}$ , governed by the variation of the electron relaxation rate, has thus been obtained. The observed behavior closely follows that predicted by the Kivelson theory of electron spin relaxation. It is, thus, demonstrated that reliable results for the electron relaxation and its temperature dependence may be obtained from nuclear relaxation studies. This approach has also yielded more accurate values for the kinetic parameters of the acid-catalyzed hydrogen ion exchange between the vanadyl(IV) aquo complex and the uncoordinated water molecules. A deuterium isotope effect on the rate constants has been observed, and its relation to the reaction mechanism is discussed.

Oxygen-17 nmr studies have given a detailed picture of the nature of the aquo complex of vanadyl(IV) present in solution.<sup>1,2</sup> Thus, it has been found that four water molecules are tightly bound to the central ion,<sup>1</sup> whereas a fifth molecule, if present in the first coordination sphere, has to have a very short residence time.<sup>1,2</sup> Some insight into the nature of the chemical bonding of the four equatorial molecules has recently been gained from the ligand nuclear hyperfine coupling constants, which have been determined by chemical shift measurements at elevated temperatures.<sup>3</sup> The values of the deuteron and proton hyperfine coupling constants are  $(4.9 \pm 0.8) \times 10^5$  Hz and  $(3.2 \pm 0.5) \times 10^6$  Hz, respectively.<sup>3</sup> The square of the hyperfine coupling constant enters in the corresponding term of the transverse relaxation rate,  $1/T_{2M}$ , of a nucleus in the first coordination sphere, and it is now possible to estimate its value. It appears that the nuclear relaxation of the coordinated molecules is an important mechanism for the observed relaxation in the bulk of the solution, but it has not always been considered in previous studies. The nuclear relaxation in aqueous vanadyl(IV) solutions has in fact been subject to some controversy.<sup>4</sup>

Proton and deuteron relaxation in vanadyl(IV) solutions has recently been investigated by Mazitov and Rivkind.<sup>5</sup> The interpretation of the results given by these authors seems, however, to be rather qualitative and bears some shortcomings. The main difficulties are: (a) the hyperfine coupling constant was unknown at that time and the contribution of  $T_{2M}$  to the observed relaxation times could not be quantitatively accounted; (b) most of their results were obtained with relatively concentrated solutions (0.16 and 0.5 M), and the electron relaxation time was probably affected by electron

spin-exchange interactions (*vide infra*); (c) the acid concentration was neither stated nor considered, although it was known that the nuclear relaxation in these solutions is affected by acids. The above comments do not invalidate the conclusion that the mean residence time of a hydrogen nucleus in the first coordination sphere of  $VO^{2+}$  is governed by protolytic reactions and that the exchange of the whole water molecule is slower.<sup>5</sup> This conclusion has been substantiated by more recent studies.<sup>1,2,6</sup> A more detailed investigation of the acid-catalyzed proton exchange in vanadyl(IV) solutions has been carried out by Swift, *et al.*<sup>6</sup> It has been found that the effective rate constant,  $k_M$ , obtained from the proton line width can be expressed as

$$k_M = k_1 + k_2[H^+] \quad (1)$$

where the constants  $k_1$  and  $k_2$  are of the order of magnitude  $10^{-4} \text{ sec}^{-1}$  and  $10^{-5} \text{ sec}^{-1} M^{-1}$ , respectively.<sup>6</sup> However, these authors have not considered the contribution of  $T_{2M}$  to the observed relaxation times and have assumed in their calculations a hydration number of five.<sup>6</sup> These comments as well as a discussion of the potentialities of deuteron magnetic resonance for studying solutions of paramagnetic ions<sup>7</sup> brought us to the conclusion that further investigation of proton and deuteron relaxation in vanadyl(IV) solutions may lead to a better and more detailed understanding of the nuclear relaxation processes in this system.

Undertaking this study, we have anticipated that our task should be facilitated by the already accumulated knowledge on the system, namely the detailed nature of the vanadyl aquo complex, the proton and deuteron hyperfine coupling constants, and, of course, the published work of other authors. The problem was approached along the guide lines summarized for convenience in the next section.

(1) J. Reuben and D. Fiat, *Inorg. Chem.*, **6**, 579 (1967).

(2) K. Wüthrich and R. E. Connick, *ibid.*, **6**, 583 (1967); **7**, 1377 (1968).

(3) J. Reuben and D. Fiat, submitted for publication.

(4) A. I. Rivkind, *Zh. Strukt. Khim.*, **4**, 664 (1963), and references cited therein; see also J. Selbin, *Chem. Rev.*, **65**, 153 (1965).

(5) R. K. Mazitov and A. I. Rivkind, *Dokl. Akad. Nauk SSSR*, **166**, 654 (1966). These authors refer also to previous work on the subject.

(6) T. J. Swift, T. A. Stephenson, and G. R. Stein, *J. Am. Chem. Soc.*, **89**, 1611 (1967).

(7) J. Reuben and D. Fiat, *ibid.*, **91**, 1242 (1969).

## Outline of the Approach

The isotropic shift,  $\Delta\omega_M$ , of a nucleus in a paramagnetic complex is related to the hyperfine coupling constant,  $A$ , by the well-known Bloembergen formula

$$\Delta\omega_M/\omega_0 = -Ah(\gamma_e/\gamma_n)S(S+1)/3kT \quad (2)$$

where  $A$  is in frequency units (Hz),  $\omega_0$  is the applied resonance frequency,  $h$  is the Planck constant,  $\gamma_e$  and  $\gamma_n$  are the electronic and nuclear magnetogyric ratios, respectively,  $S$  is the resultant electronic spin angular momentum (in  $\hbar$  units),  $k$  is the Boltzmann constant, and  $T$  is the absolute temperature.<sup>8</sup> It can be shown, that for  $\text{VO}^{2+}$ , where the electron relaxation time,  $\tau_e$ , is of the order of  $10^{-8}$  sec, the relation<sup>9</sup> for the transverse relaxation rate,  $1/T_{2M}$ , of a nucleus in the first coordination sphere of a paramagnetic ion simplifies to

$$1/T_{2M} = (1/3)S(S+1)(2\pi A)^2\tau_e \quad (3)$$

Calculations show that for protons and deuterons (as well as for oxygen-17) in the vanadyl aquo complex  $(1/T_{2M})^2 \gg \Delta\omega_M^2$ . In this case the general equation of Swift and Connick<sup>10</sup> describing the "excess" relaxation,  $1/T_{2p}$  (*i.e.*, the observed relaxation minus that of the pure solvent) in dilute solutions of paramagnetic ions reduces to

$$1/T_{2p} = P_M/(T_{2M} + \tau_M) \quad (4)$$

where  $P_M$  is the fraction of nuclei in the first coordination sphere, and therefore its calculation requires the knowledge of the hydration number, and  $\tau_M$  is the mean residence time of a nucleus in the complex. It is related to the over-all rate constant by  $\tau_M = 1/k_M$ . The rate constants are expected to obey Eyring's formula

$$k_i = (kT/h) \exp[-(\Delta H_i^\ddagger/RT) + (\Delta S_i^\ddagger/R)] \quad (5)$$

where  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are respectively the enthalpy and entropy of activation and  $i = 1$  or  $2$ .

The observed quantity is  $1/T_{2p}$ . In order to interpret it properly an estimate of the relative contributions of  $T_{2M}$  and  $\tau_M$  is needed. This can be done by calculating  $T_{2M}$  from eq 3 using simplifying assumptions with regard to the electron relaxation time. In some cases, at lower temperatures,  $\tau_M \gg T_{2M}$ , and therefore extrapolation of low-temperature data to higher temperatures, using eq 5, may also lead to a satisfactory separation of terms. We have used another approach suggested by a recent discussion of the deuteron nmr parameters in solutions of paramagnetic ions.<sup>7</sup>

It can be shown<sup>7</sup> that

$$T_{2M}^D/T_{2M}^H = (\gamma_H/\gamma_D)^2 \simeq 42.5 \quad (6)$$

Therefore, measurements of proton and deuteron relaxation in solutions of the same ion should permit separation of the terms as far as  $\tau_M$  remains unchanged by isotopic substitution. This may be expected to be so for processes of ligand exchange. For protolytic reactions, however, where the rate-determining step usually involves the transfer of a hydrogen ion, it is expected that  $\tau_M^D > \tau_M^H$ . This obstacle can be eliminated by

(8) N. Bloembergen, *J. Chem. Phys.*, **27**, 595 (1957).

(9) R. E. Connick and D. Fiat, *ibid.*, **44**, 4103 (1966); A. Abragam, "The Principles of Nuclear Magnetism," Clarendon Press, Oxford, 1961.

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

investigating the nuclear relaxation (both proton and deuteron) in  $\text{H}_2\text{O}-\text{D}_2\text{O}$  mixtures. We refer, for example, to a solution of  $\text{VO}^{2+}$  in 90%  $\text{D}_2\text{O}$ -10%  $\text{H}_2\text{O}$  mixture. Considering the statistical nature of the exchange process and having in mind that of the eight hydrogen atoms in the first hydration shell at most one can be proton, it is a good approximation to assume that in this solution  $\tau_M^D = \tau_M^H$ . The exchange rate observed in this solution should closely approach that expected for 100%  $\text{D}_2\text{O}$  solutions. Thus, there is a means to obtain reliable values for  $T_{2M}$  and  $\tau_M$  from the experimental transverse relaxation times.

$$\begin{aligned} P_M T_{2p}^H &= T_{2M}^H + \tau_M \\ P_M T_{2p}^D &= T_{2M}^D + \tau_M \end{aligned} \quad (7)$$

The following relations are obtained using eq 6

$$\begin{aligned} T_{2M}^D &= \frac{P_M T_{2p}^D - P_M T_{2p}^H}{1 - (1/42.5)} \\ \tau_M &= \frac{P_M T_{2p}^H - (P_M T_{2p}^D/42.5)}{1 - (1/42.5)} \end{aligned}$$

or, approximately (introducing an error of less than 2.5%)

$$T_{2M}^D \simeq P_M T_{2p}^D - P_M T_{2p}^H \quad (8)$$

$$\tau_M \simeq P_M T_{2p}^H - (P_M T_{2p}^D/42.5) \quad (9)$$

## Experimental Section

Proton resonance was usually observed on a Varian A-60 spectrometer. A small amount (<1 mole %) of *t*-butyl alcohol was added to the samples, and its narrow methyl resonance served as an internal reference for adjusting the magnetic field homogeneity. The 0.377 *m*  $\text{VOSO}_4$  sample was measured at 56.4 MHz on a Varian DP-60 nmr spectrometer. This instrument operating at 8.13 MHz was used to obtain the deuteron spectra. In this case the samples contained small amounts of  $(\text{CD}_3)_2\text{SO}$  for referencing purposes.

The pure absorption mode was recorded, and the transverse relaxation rate  $1/T_{2p}$  was obtained from the full width at half-height of the water signal corrected for broadening from other sources by subtracting the line width of the reference signal.

Other experimental details are similar to those published in our previous communications.<sup>1,3</sup>

## Results and Discussion

**Preliminary Considerations.** The quantity  $P_M T_{2p}$  of deuterons in 89.4 mole %  $\text{D}_2\text{O}$  solutions of  $\text{VOSO}_4$  is plotted against the inverse absolute temperature,  $1/T$ , in Figure 1. Solution A was 0.044 *m* in  $\text{VOSO}_4$  with no acid added. In this case the temperature range was rather limited owing to oxidation of the vanadyl(IV) in neutral solutions and elevated temperatures. Solution B was 0.043 *m* in  $\text{VOSO}_4$  and 0.42 *m* in perchloric acid. We note the different magnitudes and temperature dependence of  $P_M T_{2p}$  in these two solutions. In the presence of acid the rate of exchange is increased and its effect on  $P_M T_{2p}$  diminished. The quantity  $P_M T_{2p}$  of the protons in solution B is shown in Figure 2. It is seen that the behavior is different from that observed for deuterons. The ratio  $P_M T_{2p}^D/P_M T_{2p}^H$  varies between 2.9 at  $1/T = 3.36 \times 10^{-3} \text{ }^\circ\text{K}^{-1}$  and 8.1 at  $1/T = 2.72 \times 10^{-3} \text{ }^\circ\text{K}^{-1}$ . Approximate values of  $T_{2M}^D$  can be obtained by setting in eq 4 for the deuterons  $\tau_M = P_M T_{2p}^H$ , *i.e.*, using eq 8. It appeared from the results that  $T_{2M}^D$  has a flat minimum at about 55°. Of the quantities governing  $T_{2M}$  the one expected to be temperature dependent is  $\tau_e$ . In our case  $\tau_e$  may be identified with the longitudinal elec-

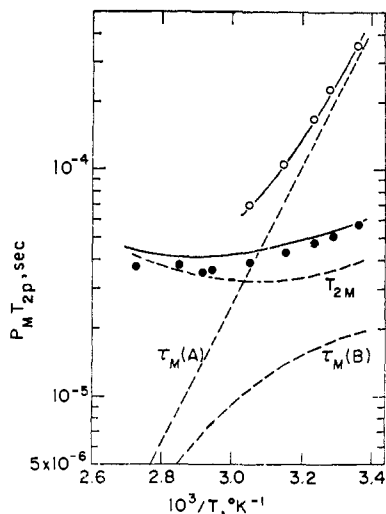


Figure 1. The normalized relaxation time,  $P_M T_{2p}$ , of deuterons in 89.4 mole %  $D_2O$  solutions of  $VOSO_4$  vs.  $1/T$ . Concentrations: (A) 0.044  $m$ , no acid ( $\circ$ ); (B) 0.043  $m$ , 0.42  $m$  in  $HClO_4$  ( $\bullet$ ). The curves are calculated (see text). The full curve represents  $\tau_M + T_{2M}$ .

tron relaxation time  $T_{1e}$ .<sup>9</sup> Hence  $T_{2M} \propto 1/T_{1e}$  and the increase in  $T_{2M}^D$  with increasing the temperature above  $55^\circ$  is clearly due to a decrease in  $T_{1e}$ . Of the various contributions to the electron relaxation in dilute solutions of paramagnetic ions the spin-rotational mechanism has been shown to have a temperature dependence similar to that obtained now in the interpretation of the nuclear relaxation times.<sup>11,12</sup>

**Electron Relaxation in Vanadyl Solutions.** The theory of electron relaxation in solutions of paramagnetic complexes has been discussed in detail by Kivelson. For convenience we refer to two recent articles from his laboratory.<sup>11,12</sup>

The esr line width,  $\Delta H$ , related to  $1/T_{1e}$ , may be expressed as

$$\Delta H = \alpha' + \alpha'' + \beta M + \gamma M^2 + \delta M^3 \quad (10)$$

where  $M$  is the projection of nuclear spin (in our case vanadium-51,  $I = 7/2$ ) along the quantization axis and  $\alpha'$ ,  $\alpha''$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  are constants obtained empirically from the esr spectrum.  $\alpha'$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  arise from the modulation of the anisotropic  $g$  and hyperfine (of the  $^{51}V$  nucleus) tensors by the molecular reorientational motions. Therefore, they are dependent on the magnitude of the applied external magnetic field and are proportional to the reorientational correlation time  $\tau_R$ . It is often assumed that  $\tau_R$  can be expressed by the BPP formula<sup>13</sup>

$$\tau_R = 4\pi\eta r^3/3kT \quad (11)$$

where  $\eta$  is the viscosity of the medium and  $r$  is the hydrodynamic radius of the complex. It has been shown that  $\alpha''$  arises from the interaction of the electronic spin with the magnetic moment associated with the rotation of the complex.<sup>11,12</sup>

In the analysis and discussion of the results we shall refer only to the  $\alpha'$  and  $\alpha''$  components of the electron relaxation. The reasoning is that, in the magnetic fields

(11) R. Wilson and D. Kivelson, *J. Chem. Phys.*, **44**, 154 (1966).

(12) P. W. Atkins and D. Kivelson, *ibid.*, **44**, 169 (1966).

(13) N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, **73**, 679 (1948).

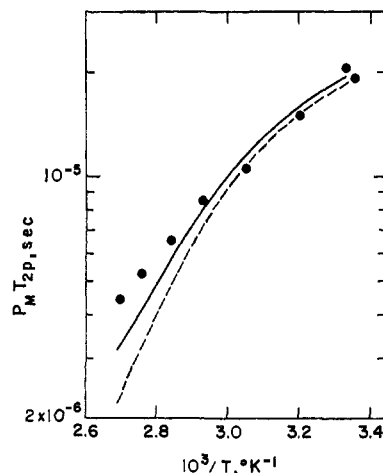


Figure 2. The normalized relaxation time,  $P_M T_{2p}$ , of protons in solution B (see Figure 1). The broken curve represents  $\tau_M$  and the full curve  $\tau_M + T_{2M}$ .

used to obtain resonance conditions for the protons (14100 G, 60 MHz) and the deuterons (12450 G, 8.13 MHz),  $\alpha'$  is much greater than  $\beta$ ,  $\gamma$ , and  $\delta$ . The calculations were done using the formulas given by Wilson and Kivelson (Tables III and IV of ref 11) and the constants of the spin-Hamiltonian reported by McCain and Myers.<sup>14</sup> An additional point is that it may be expected that the vanadium-51 relaxation time is much shorter than that of the ligand nuclei, and hence the effects of the components of  $1/T_{1e}$  containing  $M$  on the relaxation times of the ligand nuclei is averaged out.

Among the various terms contributing to  $\alpha'$ , the dominating is the secular term given by<sup>11</sup>

$$(1/T_{1e})_{\alpha'} = (4/45)(\Delta\gamma H_0)^2 \tau_e \quad (12)$$

where  $\Delta\gamma = \Delta g\beta/\hbar$  and  $H_0$  is the magnitude of the external magnetic field. All other terms give a total contribution of a few per cent. The relaxation due to the spin-rotational interaction is field independent and is given by<sup>12</sup>

$$(1/T_{1e})_{\alpha''} = (1/9)(\Delta g_{||}^2 + 2\Delta g_{\perp}^2)/\tau_R \quad (13)$$

The quantities  $\Delta g$ ,  $\Delta g_{||}$ , and  $\Delta g_{\perp}$  are defined in Table I, where the constants of the spin-Hamiltonian of the hydrated vanadyl ion obtained from a glass solution are listed.<sup>14</sup>

**Table I.** The Constants of the Spin-Hamiltonian of the Hydrated Vanadyl(IV) Ion<sup>a</sup>

$g_{\perp} = 1.9778$	$g_{  } = 1.9312$
$g = (1/3)(g_{  } + 2g_{\perp}) = 1.9623$	
$\Delta g = g_{  } - g_{\perp} = -0.0466$	
$\Delta g_{  } = g_{  } - 2.0023 = -0.0711$	
$\Delta g_{\perp} = g_{\perp} - 2.0023 = -0.0245$	
$a/g\beta = (1/3g\beta)(A_{  } + 2A_{\perp}) = 119.5$ G	
$b/g\beta = (2/3g\beta)(A_{  } - 2A_{\perp}) = 86.0$ G	

<sup>a</sup> From ref 14.

These data were used to calculate the electron relaxation rates,  $(1/T_{1e})_{\alpha'}$  and  $(1/T_{1e})_{\alpha''}$ , from eq 12, 13, and 11. In the calculation the molecular radius was taken as  $r = 3.1$  Å, conforming with the structure of the aquo

(14) D. C. McCain and R. J. Myers, *J. Phys. Chem.*, **71**, 192 (1967).

**Table II.** The Parameters of Hydrogen Ion Exchange from the First Hydration Sphere of Vanadyl(IV) at 25°

	D <sub>2</sub> O	H <sub>2</sub> O	Ref 6
$k_1, \text{sec}^{-1}$	$3.3 \times 10^3$	$7.7 \times 10^3$	$10 \times 10^3$
$\Delta H_1^\ddagger, \text{kcal/mole}$	$14 \pm 1$	$12 \pm 1$	$8 \pm 1$
$\Delta S_1^\ddagger, \text{eu}$	$2.4 \pm 2$	$0 \pm 2$	$-14 \pm 4$
$k_2, \text{sec}^{-1} M^{-1}$	$1.2 \times 10^6 \pm 20\%$	$2.2 \times 10^6 \pm 20\%$	$2.0 \times 10^6$
$\Delta H_2^\ddagger, \text{kcal/mole}$	$1.7 \pm 0.4$	$2.5 \pm 1$	$2 \pm 1$
$\Delta S_2^\ddagger, \text{eu}$	$-12 \pm 2$	$-10 \pm 2$	$-26 \pm 4$

complex of vanadyl(IV). A similar value ( $r = 3.17 \text{ \AA}$ ) has recently been obtained for the hydrated copper(II) ion from analysis of esr results.<sup>15</sup> Viscosity data were

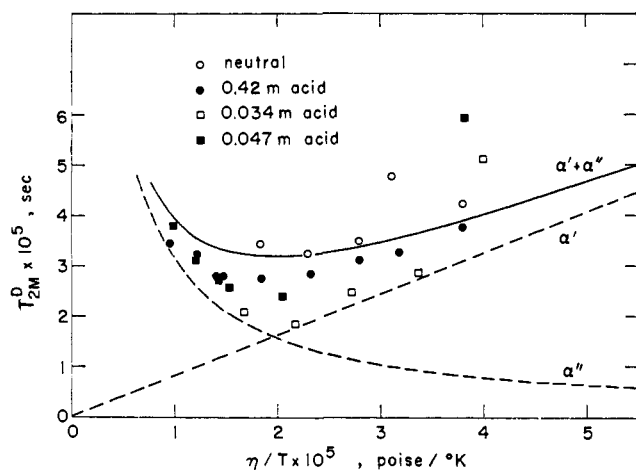


Figure 3. The deuteron transverse relaxation time,  $T_{2M}^D$ , in the hydration shell of vanadyl(IV) plotted against  $\eta/T$ . The curves are calculated (see text).

taken from the literature.<sup>16</sup> The correlation time calculated from eq 11 is  $\tau_R = 2.74 \times 10^{-11}$  sec in H<sub>2</sub>O at 25°. The two contributions,  $\alpha'$  and  $\alpha''$ , to the nuclear relaxation time  $T_{2M}^D$  were calculated from eq 3. The results of these calculations are graphically represented by the curves in Figure 3 as a function of  $\eta/T$ . The calculated electron relaxation time is of the order of  $10^{-8}$  sec, in good agreement with that obtained from esr measurements.<sup>14</sup>

**Analysis of the Proton and Deuteron Relaxation.** In the semilogarithmic plots of the concentration normalized proton line widths vs.  $1/T$  in solutions of low acidity, a deviation from linearity is observed at lower temperatures (see Figure 4). This deviation was absent in similar plots of the deuteron line width. A plausible origin for this broadening of the proton lines is the proton relaxation arising from the dipolar interaction of the fifth axial water molecule in the vanadyl aquo complex. We may regard the observed relaxation rate in this region as given by  $1/T_{2p} = P_{M,eq}/\tau_M + P_{M,ax}/T_{2M,ax}$ , where  $1/T_{2M,ax}$  is given by<sup>9</sup>

$$1/T_{2M,ax} = (1/15)\gamma_n^2 g^2 \beta^2 S(S+1)r^{-6} \times [7\tau_c + 13\tau_c/(1 + \omega_e^2 \tau_c^2)] \quad (14)$$

(15) W. B. Lewis, M. Alei, Jr., and L. O. Morgan, *J. Chem. Phys.*, **44**, 2409 (1966).

(16) (a) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth & Co., Ltd., London, 1959; (b) R. C. Hardy and R. L. Cottingham, *J. Chem. Phys.*, **17**, 509 (1949).

$\tau_c$  being the correlation time for dipolar interaction.  $1/T_{2M,ax}$  is expected to be, by a factor of 42.5, smaller for deuterons than for protons. The contribution of  $1/T_{2M,ax}$  was calculated (it is shown in Figure 4 by the broken curve), assuming  $\tau_c = \tau_R$ , and taken into account in estimating the rate constants of hydrogen ion exchange and their temperature dependence.

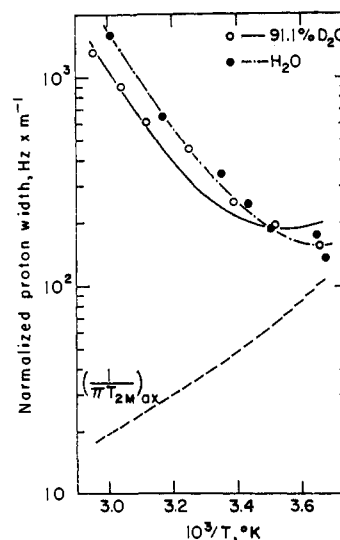


Figure 4. The proton line width divided by the concentration of VOSO<sub>4</sub> vs.  $1/T$ . Concentrations: (●) 0.012 m, 0.016 m in HClO<sub>4</sub>; (○) 0.0335 m, 0.042 m in HClO<sub>4</sub>.

The rate constants of hydrogen ion exchange from the first coordination sphere of vanadyl(IV) in H<sub>2</sub>O solutions as well as in H<sub>2</sub>O–D<sub>2</sub>O mixtures were obtained from the proton relaxation times. The values of  $T_{2M}^H$  were calculated in a manner similar to that used for  $T_{2M}^D$ . The contribution of  $T_{2M}^H$  in the region important for the determination of  $k_2$  did not exceed 20% of the experimental  $P_M T_{2p}$  values, and we may regard this as the maximum uncertainty in  $k_2$  and its activation parameters. The results obtained for the rate constants and their enthalpies and entropies of activation are summarized in Table II.

Using the data in Table II,  $\tau_M$  for each case may now be calculated from eq 1. The experimental relaxation times,  $P_M T_{2p}^D$ , and the calculated  $\tau_M$  values may be used to obtain values of  $T_{2M}^D$ . These are shown as experimental points in Figure 3. The agreement with the calculated curve is encouraging. The qualitative behavior is clearly revealed. The deviation may be ascribed in part to the large uncertainty in the hyperfine coupling constant, the square of which enters in the calculation. The full curves shown in Figures 1, 2, 4, and

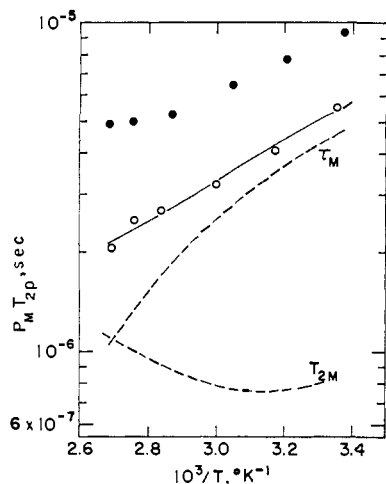


Figure 5. The normalized relaxation time,  $P_M T_{2p}$ , of protons in aqueous solutions of  $VOSO_4$  vs.  $1/T$ . Concentrations: (O) 0.024  $m$ , 0.97  $m$  in  $HClO_4$ ; (●) 0.377  $m$ , 0.47  $m$  in  $HClO_4$ .

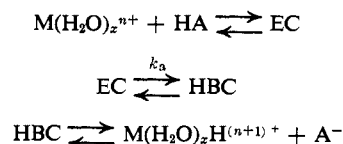
5 were calculated using the theoretical  $T_{2M}$  values. Again the agreement is satisfactory.

At higher concentrations of  $VOSO_4$  ( $>0.1 m$ ) electron spin-exchange interactions may become important and give rise to a shortening of the electron relaxation time.<sup>14,17</sup> In this case  $T_{2M}$  is expected to increase. Indeed (see Figure 5) the observed relaxation times,  $P_M T_{2p}$ , in a 0.377  $m$  solution of  $VOSO_4$  are greater than anticipated. It may therefore be concluded that in this system reliable results may be obtained only from nuclear relaxation studies of dilute solutions ( $<0.1 m$ ). Now it is possible to rationalize the inconsistency observed by Mazitov and Rivkind in comparing  $\tau_M$  values obtained in 0.05 and 0.5  $m$  solutions.<sup>5</sup> They ascribed it to the mutual interaction between the  $VO^{2+}$  ions leading to "loosening" of the hydration shells and thereby increasing the rate of exchange. This process seems to be improbable, or at least very ineffective.

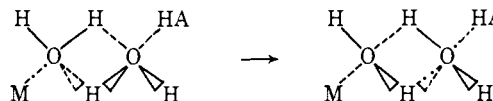
**The Kinetics of Hydrogen Ion Exchange.** The kinetic and thermodynamic parameters for the reaction of proton exchange between the vanadyl aquo complex and the solvent water molecules are in qualitative agreement with the values reported by Swift, *et al.*<sup>6</sup> The main disagreements are in the enthalpy and entropy of activation (see Table II). It seems that the origin of the discrepancy is not in the experimental results but rather in their interpretation. Two important points in this regard are: (a) Swift, *et al.*, assumed that the effective hydration number is five (we use four); (b) these authors have not considered any other relaxation mechanisms besides the mean residence time of a nucleus in the first hydration shell. Nevertheless, our results, showing the existence of an isotope effect on the rate constants,

(17) G. P. Vishnevskaya and P. G. Tishkov, *Dokl. Akad. Nauk SSSR*, **142**, 841 (1962).

do not invalidate the mechanism proposed by Swift, *et al.*, for the protonation step of the hydrated ion that is characterized by  $k_2$ .<sup>6</sup> This mechanism consists of the following three substeps



where HA is an acid, EC is an encounter complex, and HBC is a hydrogen-bonded complex.<sup>6</sup> It has been suggested that the substep characterized by  $k_a$  is rate determining. This, however, is not the only mechanism which can explain the results. Any concerted (cooperative) mechanism involving a water molecule from the second hydration shell may also conform with the observed rate constants. For example<sup>18</sup>



The existence of an isotope effect and the acid catalysis indicate in this case that in the rate-determining step there is a hydrogen ion transfer.<sup>19</sup> Hydrogen-bonded complexes of a type similar to that shown in the above scheme have been considered in a more recent discussion of the kinetics of proton transfer involving aquated cations.<sup>20</sup>

## Conclusions

The study of proton and deuteron relaxation in solutions of vanadyl(IV) in  $H_2O$ - $D_2O$  mixtures has shown that the contributions of the two main parameters,  $T_{2M}$  and  $\tau_M$ , governing the nuclear transverse relaxation times of water may be separated. Encouraging agreement has been obtained between experimental  $T_{2M}$  values and those calculated using electron relaxation rates predicted by theory. This suggests that reliable results for electron relaxation rates and their temperature dependence may be obtained from studies of nuclear relaxation times (both proton and deuteron). This approach should be in particular useful and straightforward in cases where the rate of hydrogen exchange is determined by the rate of ligand exchange, and isotope effects are absent.

The hydrogen ion exchange between the hydrated vanadyl(IV) ion and the water in bulk is acid catalyzed and is found to be slower in  $D_2O$ , suggesting that the rate-determining step involves the transfer of a hydrogen ion.

(18) A discussion of such mechanism has recently been given by M. Eigen, *Discussions Faraday Soc.*, **39**, 7 (1965).

(19) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959.

(20) T. A. Stephenson, T. J. Swift, and J. B. Spencer, *J. Am. Chem. Soc.*, **90**, 4291 (1968).