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# Vanadium-51 NMR Line-broadening in the Mixture of Dioxovanadium(V) and Oxovanadium(IV) Ions in Perchloric Acid Solution

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## Abstract

Vanadium-51 NMR line-broadening in the mixture of dioxovanadium(V) $VO_2^+$ and oxovanadium(IV) $VO^{2+}$ ions has been studied in perchloric acid media. The line-broadening is attributed to the exchange reaction between $VO_2^+$ and a mixed-valence complex $VO_2^+–VO^{2+}$. The rate law is expressed by rate = $k_2K[VO^{2+}]_0[VO_2^+]_0^2/(1 + K[VO_2^+]_0)$ where $K$ and $k_2$ refer to the formation constant of $VO_2^+–VO^{2+}$ and the rate constant for the exchange reaction between $VO_2^+–VO^{2+}$ and $VO_2^+$, respectively, and $[\ ]_0$ denotes the initial concentration of each ion. The result differs from that of the earlier study by McConnell *et al.* who predicted a mechanism involving the formation of $VO_2^+–VO_2^+$.

## Introduction

The theory for the use of NMR spectroscopy to measure the rate of electron exchange reactions has been developed by McConnell and coworkers [1]. A number of electron exchange reactions have been studied by this method [2]. The rate of electron exchange reaction between oxovanadium(IV) and dioxovanadium(V) was first measured by Giuliano and McConnell by the $^{51}V$ NMR method [3]. They found that the rate was first-order in $VO^{2+}$ and second-order in $VO_2^+$, and proposed a mechanism involving a rapid monomer–dimer equilibrium as follows:

$$2V(V) \rightleftharpoons (V(V))_2 \qquad (1)$$

$$(V(V))_2 + V(IV) \rightleftharpoons (V(V))_2 + V(IV) \quad \text{(electron exchange)} \qquad (2)$$

On the other hand, Johnson and Murmann reported that the yl-oxygen exchange of $VO^{2+}$ with solvent water was catalyzed by $VO_2^+$ [4]. They explained that the electron exchange between $VO^{2+}$ and $VO_2^+$ passing through a mixed-valence dimer $VO_2^+–VO^{2+}$ (or $V_2O_3^{3+}$) caused the yl-oxygen exchange to increase. The existence of the mixed-valence complex $V_2O_3^{3+}$ was confirmed spectrophotometrically by Blanc *et al.* [5]. Recently, a dimer of $VO_2^+$, $V_2O_3^{4+}$, was also identified in concentrated acid media [6].

In order to examine the results of McConnell *et al.* we have studied the $^{51}V$ NMR line-broadening in the mixture of $VO^{2+}$ and $VO_2^+$ ions in various acid concentrations and discussed the mechanism of the line-broadening based on the results of recent studies.

## Experimental

### *Preparation of Solutions*

The vanadyl(IV) perchlorate solutions were prepared by mixing stoichiometric amounts of vanadyl sulfate and barium perchlorate (Wako Pure Chemical Ind. Ltd.) in aqueous solution and by filtering barium sulfate. Vanadyl perchlorate concentration was determined through titration with $KMnO_4$. The vanadium(V) stock solutions were prepared by mixing $HClO_4$ solution and $NaVO_3$ solution, where the latter is made by dissolving weighed $NH_4VO_3$ (Kanto Chemical Co., Inc.) in NaOH solution and by evaporating $NH_3$. The concentration of the vanadium(V) solution was determined from the amount of weighed $NH_4VO_3$. Anhydrous sodium perchlorate (Wako) was used to adjust the ionic strength of solutions.

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### *Spectrometric Measurements*

A JASCO UNIDEC Spectrophotometer with a thermostated cell compartment (±0.2 °C) was used for measurements of electronic spectra. One centimeter quartz cells were used. The concentration of $V_2O_3^{3+}$ ion was calculated by the use of molar extinction coefficients in the study of Blanc *et al.* [5] ($\epsilon_{813}$ = 118 and $\epsilon_{660}$ = 112 $M^{-1}$ $cm^{-1}$; 1 M = 1 mol $dm^{-3}$). Measurements of $^{51}V$ NMR spectra were carried out at 26.18 MHz on a JEOL JNM-FX 100 FT-NMR spectrometer equipped with a JNM-VT-3B temperature controller. For the line-width measurements, the spectra were fitted to single Lorentzian functions, the transverse relaxation rate $1/T_2$ being obtained from the full width at half height ($\pi\Delta\nu_{1/2}$). A Union Giken RA-401 stopped-flow spectrophotometer was used for kinetic measurements.

## Results

The $^{51}V$ NMR spectrum of $VO_2^+$ in acidic solutions gave a signal at −554 ppm with respect to $VOCl_3$ [7]. In the extreme narrowing conditions [8] the transverse relaxation time $T_{20}$ of $^{51}V$ for $VO_2^+$ in the absence of $VO^{2+}$ is described by,

$$1/T_{20} = \frac{3}{10}\,\frac{2I+3}{I^2(2I-I)}(1+\eta^2/3)(e^2qQ/\hbar)^2\tau_c \qquad (3)$$

where $I, Q, \eta$, and $eqQ/\hbar$ are spin number, the electric quadrupole moment of the nucleous, the asymmetry parameter of the electric field gradient tensor, and the quadrupole coupling constant, respectively. A reorientation correlation time $\tau_c$ is usually represented by an arrhenius-type function where

$$\tau_c = \tau_c^{\circ}\exp(E_r/RT) \qquad (4)$$

From eqns. (3) and (4) plots of $\ln(1/T_{20})$ *versus* $1/T$ are expected to be linear. Figure 1 shows that the plots are linear ($E_r$ = 18.3 kJ $mol^{-1}$) for solutions of low concentrations of $VO_2^+$ or/and perchloric acid whereas not linear for solutions of high concentrations of $VO_2^+$ and perchloric acid.

The transverse relaxation time $T_2$ of $^{51}V$ in the presence of $VO^{2+}$ ion is given as follows:

$$1/T_2 = 1/R_{20} + 1/\tau \qquad (5)$$

where $1/\tau$ is the line-broadening of $^{51}V$ caused by the interaction with $VO^{2+}$ ion and is defined by eqn. (6).

$$1/\tau = -\frac{d[VO_2^+]}{[VO_2^+]\,dt} \qquad (6)$$

In order to interprete the line-broadening of $^{51}V$ NMR due to the addition of $VO^{2+}$, ln $1/\tau$ is plotted against $1/T$ (Fig. 2). The plots exhibit an arrhenius-type relationship suggesting that the line-broadening is attributed to the chemical exchange between $VO_2^+$ and $VO^{2+}$. The dependence of $1/\tau$ on the concentration of perchloric acid, $VO^{2+}$ and $VO_2^+$ are shown in Figs. 3 and 4. The linear relationship with $VO^{2+}$ (Fig. 3) is consistent with the earlier result [3]. Figure 4 indicates that $\tau^{-1}$ depends on $[VO_2^+]$. However, unlike the result of earlier study, the plot deviates from linearity in the high $HClO_4$ solution.

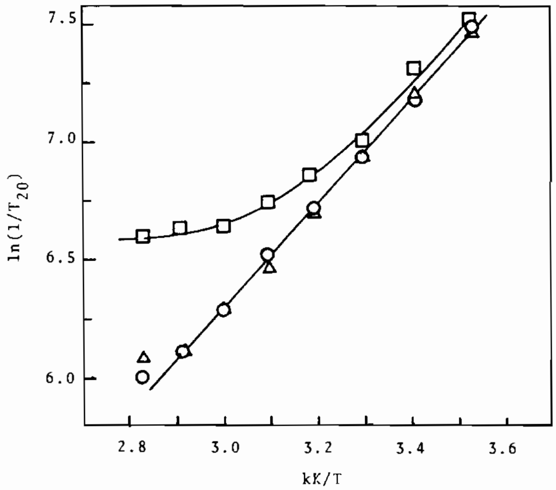


Fig. 1. Plots of $\ln(1/T_{20})$ of $^{51}V$ NMR signal against $1/T$ in solutions in the absence of $VO^{2+}$ ion: □, $[VO_2^+]_0$ = 0.20 M and $[H^+]$ = 5.4 M; ○, $[VO_2^+]_0$ = 0.20 M and $[H^+]$ = 1.5 M; △, $[VO_2^+]_0$ = 0.025 M and $[H^+]$ = 5.4 M.

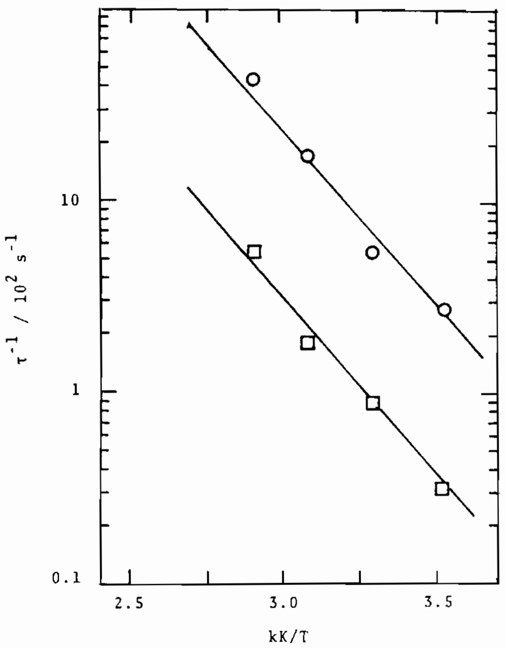


Fig. 2. Semilogarithmic plots of $1/\tau$ *vs.* $1/T$ in 1.5 (□) and 5.4 (○) M perchloric acid solutions. $[VO_2^+]$ = 0.20 M and $[VO^{2+}]$ = 0.02 M.

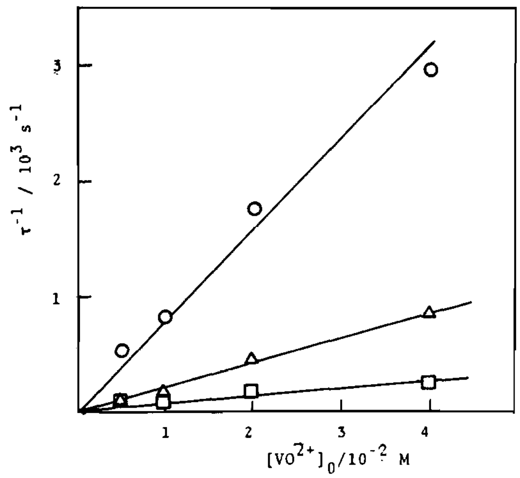


Fig. 3. Plots of $1/\tau$ vs. $[VO^{2+}]_0$ in 1.5 (□), 3.5 (△), and 5.4 (○) M perchloric acid solutions at 50 °C. $[VO_2^+]_0 = 0.20$ M (constant).

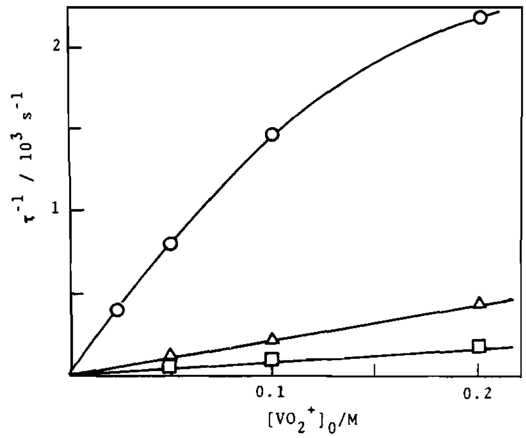


Fig. 4. Plots of $1/\tau$ vs. $[VO_2^+]_0$ in 1.5 (□), 3.5 (△), and 5.4 (○) M perchloric acid solutions at 50 °C. $[VO^{2+}]_0 = 0.02$ M (constant).

Blanc *et al.* [5] showed that the mixture of $VO^{2+}$ and $VO_2^+$ ions in perchloric, sulfuric, and hydrochloric acid solutions gave a mixed-valence cation–cation 1/1 complex, $V_2O_3^{3+}$ and the formation constant of the complex was dependent on the acid species and their concentrations. The complex formation can be written by eqn. (7).

$$VO^{2+} + VO_2^+ \overset{K}{\rightleftharpoons} V_2O_3^{3+} \tag{7}$$

We determined the formation constant $K$ by the spectrophotometric method as described by Blanc *et al.* [5] at various temperatures, ionic strength, and acid concentrations. The dependence of $K$ on acid concentration and ionic strength are shown in Figs. 5 and 6. The thermodynamic parameters for $K$ are listed in Table I.

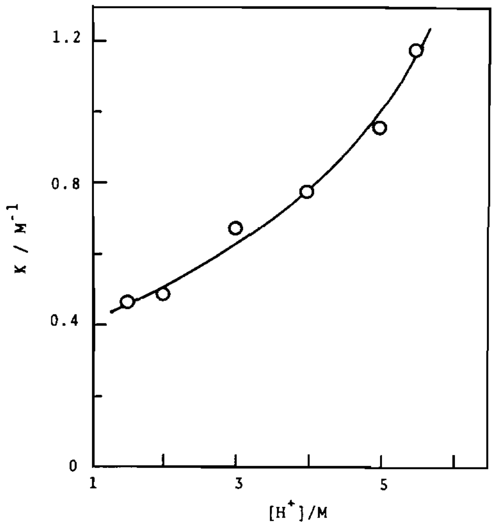


Fig. 5. Plot of the formation constant $K$ for $V_2O_3^{3+}$ vs. $[H^+]$ at 30 °C. Ionic strength = 5.4 M (constant).

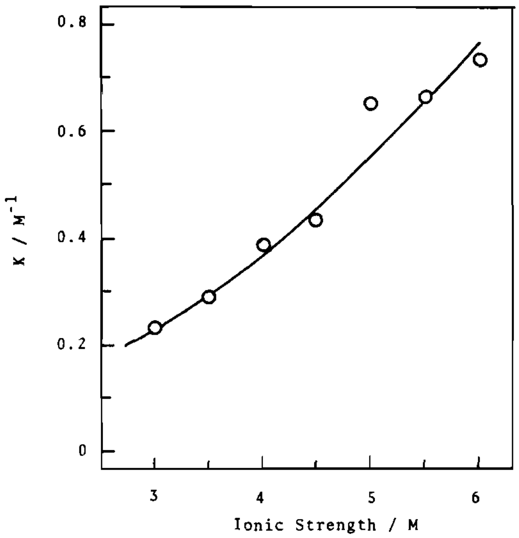


Fig. 6. Plot of the formation constant $K$ for $V_2O_3^{3+}$ vs. ionic strength at 30 °C. $[H^+] = 3.0$ M (constant).

TABLE I. Thermodynamic Parameters for the Formation Constants of $V_2O_3^{3+}$ Ion in Perchloric Acid Solution

| $[H^+]$ (M) | $\Delta H$ (kJ mol$^{-1}$) | $\Delta S$ (J K$^{-1}$ mol$^{-1}$) |
|---|---|---|
| 1.3 | $-4.97 \pm 0.19$ | $-30.3 \pm 0.6$ |
| 3.5 | $-4.73 \pm 0.32$ | $-26.8 \pm 1.1$ |
| 5.4 | $-9.26 \pm 0.30$ | $-32.0 \pm 1.0$ |

As seen in Figs. 5 and 6, the values of $K$ change markedly with the acid concentration and ionic strength. The tendency of the variation is similar to that of $\tau^{-1}$. This fact could imply that $\tau^{-1}$ is related

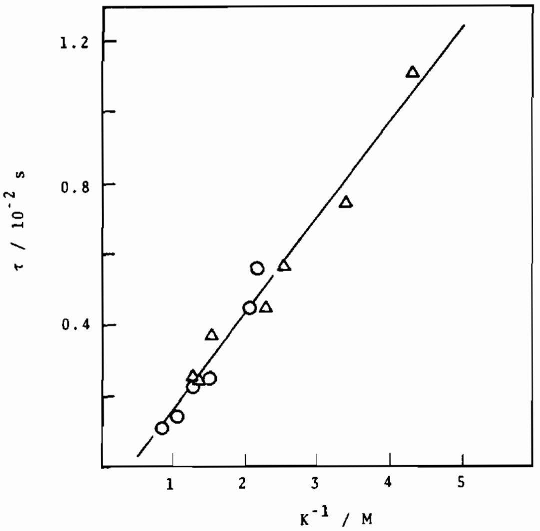
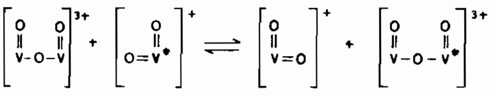


Fig. 7. Plots of $\tau$ *vs.* the reciprocal of the formation constant of $V_2O_3^{3+}$ at 30 °C: $[VO_2^+]_0 = 0.10$ M and $[VO^{2+}]_0 = 0.02$ M; (○), ionic strength = 5.4 M (constant) and $[H^+] = 1.5$–$5.5$ M; (△), $[H^+] = 3.0$ M (constant) and ionic strength = 3.0–6.0 M.

to $K$. Figure 7 demonstrates that $\tau$ is well correlated with $K^{-1}$.

It can be concluded from the above results that $^{51}V$ line-broadening in the mixture of $VO^{2+}$ and $VO_2^+$ ions is attributed to the formation of $V_2O_3^{3+}$ ion and that the value of $\tau^{-1}$ corresponds to the rate constant of the exchange reaction written as follows:



$$\left[\overset{O}{\overset{\|}{V}}-O-\overset{O}{\overset{\|}{V}}\right]^{3+} + \left[O=\overset{O}{\overset{\|}{V^*}}\right]^{+} \rightleftharpoons \left[\overset{O}{\overset{\|}{V}}=O\right]^{+} + \left[\overset{O}{\overset{\|}{V}}-O-\overset{O}{\overset{\|}{V^*}}\right]^{3+} \qquad (8)$$

where an asterisk is used to denote the exchanging species. A discussion of the transverse nuclear relaxation time in dilute solutions of paramagnetic ions has been given by Swift and Connick [9]. In the limit of slow exchange $\tau^{-1}$ is defined by

$$1/\tau = 1/T_2 - 1/T_{20} = p_M/\tau_M \qquad (9)$$

where $T_2$ and $T_{20}$ are the transverse relaxation times in the presence and in the absence of paramagnetic ions, respectively. In the present study the paramagnetic ion is regarded as $V_2O_3^{3+}$ in eqn. (8), and $\tau_M$ is the life time of $^{51}V$ staying in $V_2O_3^{3+}$ and $p_M$ is the mole fraction of $V_2O_3^{3+}$.

In the limit that $[VO_2^+]_0 \gg [V_2O_3^{3+}]$, the formation constant $K$ is expressed by

$$K = \frac{[V_2O_3^{3+}]}{[VO_2^+]_0([VO^{2+}]_0 - [V_2O_3^{3+}])} \qquad (10)$$

where $[VO_2^+]_0$ and $[VO^{2+}]_0$ are the initial concentrations of $VO_2^+$ and $VO^{2+}$, respectively.

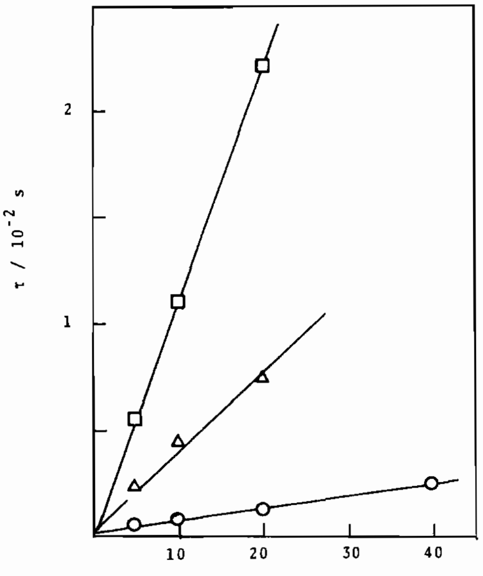


Fig. 8. Plots of $\tau$ *vs.* $1/[VO_2^+]_0$ in 1.5 (□), 3.5 (△), and 5.4 (○) M perchloric acid solutions at 50 °C. $[VO^{2+}]_0 = 0.02$ M (constant).

If the exchange reaction is assumed to be first-order in $V_2O_3^{3+}$ and first-order in $VO_2^+$, the rate is given by $k_2[V_2O_3^{3+}][VO_2^+]$. Therefore, $\tau^{-1}$ can be expressed in terms of $[VO_2^+]_0$ and $[VO^{2+}]_0$ from eqns. (6) and (10).

$$\tau^{-1} = \frac{\text{Rate}}{[VO_2^+]} = \frac{k_2K[VO^{2+}]_0[VO_2^+]_0}{1 + K[VO_2^+]_0} \qquad (11a)$$

$$\tau = \frac{1}{k_2K[VO^{2+}]_0}[VO_2^+]_0^{-1} + \frac{1}{k_2[VO^{2+}]_0} \qquad (11b)$$

Equation (11a) reveals that $\tau^{-1}$ is first-order in $VO^{2+}$ (see Fig. 3), but not first-order in $VO_2^+$ (see Fig. 4) unless $K[VO_2^+]_0 \ll 1$. It is expected in eqn. (11b) that the plot of $\tau$ against $K^{-1}$ is linear under the condition of constant $[VO^{2+}]_0$ and $[VO_2^+]_0$ (see Fig. 7) and the plot $\tau$ *versus* $[VO_2^+]_0^{-1}$ (Fig. 8) gives the formation constant $K$. The value of $K$ thus obtained by the NMR measurements is 1.1 $M^{-1}$ at $[H^+] = 5.4$ M. This value is considerably larger than 0.67 $M^{-1}$ determined spectrophotometrically under the same conditions. However, since large error is expected in the NMR method, the agreement in the values determined by the two methods is sufficient.

## Discussion

The value of $k_2K$, which corresponds to the overall rate constant, is determined to be $1.9 \times 10^5$ $M^{-2}$ $s^{-1}$ at $[H^+] = 5.4$ M. This value is well correlated with

TABLE II. Kinetic Parameters for the Exchange Reaction of $VO_2^+$ in the $V_2O_3^{3+}$ Ion with Free $VO_2^+$ Ion

| $[H^+]$ (M) | $\Delta H^{\ddagger}$ (kJ mol$^{-1}$) | $\Delta S^{\ddagger}$ (J K$^{-1}$ mol$^{-1}$) | $k_2$ (25 °C) $\times 10^4$ (M$^{-1}$ s$^{-1}$) |
|---|---|---|---|
| 1.5 | 39.4 ± 2.7 | −17.9 ± 8.8 | 9.02 |
| 5.4 | 44.1 ± 3.8 | 3.3 ± 12.2 | 17.3 |

the value of $1.5 \times 10^6$ M$^{-2}$ s$^{-1}$ for the electron exchange reaction between $VO^{2+}$ and $VO_2^+$ at $[H^+] = 6.5$ M by Giuliano and McConnell [3] in view of the difference in experimental conditions of these studies and also the difference in the NMR instrument which has been developed by use of the FT method.

Johnson and Murmann [4] studied the oxygen exchange between $VO^{2+}$ and water in the presence of $VO_2^+$ and estimated the rate constant of electron exchange between $VO_2^+$ and $VO^{2+}$ to be 3.91 M$^{-1}$ s$^{-1}$ at $[H^+] = 0.1$ M and 0 °C. On the other hand Macartney [10] evaluated the rate constant of electron exchange between $VO(OH)^{2+}$ and $VO(OH)^+$ to be $10^{-3}$ M$^{-1}$ s$^{-1}$ based on the Marcus theory on the assumption of outer-sphere redox process.

The apparent second-order rate constant $k_2K/[VO_2^+]_0$, first-order in both $VO^{2+}$ and $VO_2^+$, is calculated to be $1.9 \times 10^4$ M$^{-1}$ s$^{-1}$ at $[VO_2^+]_0 = 0.1$ M and $[H^+] = 5.4$ M in the present study. This value is much larger than those obtained by the indirect method in low acid solutions [4, 10]. As seen in eqn. (8), the electron exchange between $V_2O_3^{3+}$ and $VO_2^+$ appears to proceed more easily than the exchange between $VO^{2+}$ and $VO_2^+$, because both $V_2O_3^{3+}$ and $VO_2^+$ have similar V–O bonds resulting in a relatively smaller activation energy for the electron exchange through the oxygen bridge.

The monomer–dimer equilibrium in eqn. (7) is so fast that the $^{51}V$ relaxation of $VO_2^+$ is no longer controlled by reaction (7). As a matter of fact, any kinetic trace was not observed in the stopped-flow measurements, where $VO^{2+}$ and $VO_2^+$ solutions were mixed under the condition of high $[HClO_4]$. This fact indicates that the reaction was over within the mixing time of the instrument (2 ms). Similar behavior was observed in the $^{17}O$ NMR study of water exchange in $VO(H_2O)_5^{2+}$ [11]. The $^{17}O$ relaxation of bulk water is controlled by the water exchange at the equatorial positions, although the exchange rate is much faster at the axial position than at the equatorial positions.

A mechanism passing through a dimer of $VO_2^+$, $V_2O_4^{2+}$, (or $V_2O_3^{4+}$), can be ruled out, because the concentration of $V_2O_4^{2+}$ is extremely low compared with the concentration of mixed-valence complex under the conditions studied. According to Madic *et al.* [6] the existence of $V_2O_4^{2+}$ was observed in very high concentrations of $HClO_4$ solutions by electronic spectra, but undetectable in the solutions $[HClO_4] < 7$ M.

From the temperature dependence of $\tau^{-1}$ (Fig. 2) and the thermodynamic parameters for $K$ (Table I), the activation parameters for $k_2$ were determined. The results are listed in Table II. It should be noted that the values of $\Delta H^{\ddagger}$ for $k_2$ are smaller than that for the yl-oxygen exchange of $VO^{2+}$ ($\Delta H^{\ddagger} = 86$ kJ mol$^{-1}$) indicating that the V–O bond would not be broken during the electron exchange.

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