

hydroxyaquo ion has a half-life of about 25 min at 25°. It seems unlikely that the NCO<sup>-</sup> ion will greatly accelerate the water exchange rate, and the latter figure probably imposes a maximum rate on the entry of NCO<sup>-</sup> by the anation mechanism. At the same time it requires NCO<sup>-</sup> to be an unusually good competitor

for the coordination position to be vacated; water usually competes about three times as well as a mononegative anion under similar circumstances<sup>9</sup> (1 M NCO<sup>-</sup> and 55 M H<sub>2</sub>O). Both the rate and competition factor militate against the anation mechanism. In addition it has been shown unequivocally that NCO<sup>-</sup> adds to the coordinated water in the Co(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>3+</sup> ion.

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## The Kinetics of Protonation of Nickel and Chromium Hexaaquo Cations in Aqueous Solution

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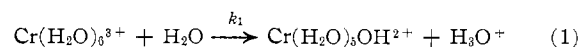
A detailed study of the kinetics of acid dissociation of Cr(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> in aqueous solution was performed by the application of proton magnetic resonance. The rate constant for the transfer of protons from Cr(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> ions to bulk water was found to be of the form  $k = k_1 + k_2[\text{H}^+]$ . Further investigation revealed that this is also the form of the rate constant for proton transfer involving Ni(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> in aqueous solution. The rate constants,  $k_1$  and  $k_2$ , were found to be  $7.0 \pm 0.1 \times 10^4 \text{ sec}^{-1}$  and  $5.0 \pm 0.2 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$ , respectively, for chromic ion at 298°K. The values of  $k_1$  and  $k_2$  for nickelous ion at the same temperature were found to be  $9 \pm 1 \times 10^4 \text{ sec}^{-1}$  and  $1.3 \pm 0.2 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ , respectively. A mechanism is proposed for the acid-dependent proton-transfer process revealed by these studies, and this mechanism involves the protonation of the hexaaquo cations as the principal step.

### Introduction

It has recently been demonstrated that the exchange of water molecules between the bulk of an aqueous solution and the primary hydration sphere of a managanous ion in solution may be used to study the primary hydration of cations in solution. At least in principle other reactions exist which may be employed in a similar manner as independent checks on the results obtained by Swift and Sayre.<sup>1</sup> One such reaction of some promise has been reported previously by Bloembergen and Morgan.<sup>2</sup> The authors have studied the temperature and frequency dependences of proton relaxation in aqueous solutions containing each of several paramagnetic cations.

The relaxation produced by one of the ions, Cr(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>, appears to be controlled at lower temperatures by the rate of a chemical-exchange process. Since the rate of water molecule exchange between the bulk and the primary hydration sphere of a Cr(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> ion is relatively slow at these temperatures,<sup>3</sup> the

authors<sup>2</sup> concluded that the exchange process revealed by their studies is



This reaction and the line broadening produced by it form exactly the type of basis sought for the hydration number technique. Water molecules are directly involved in the reaction, kinetic distinguishability may be realized through the anticipated difference in basicity between bulk water molecules and waters in the primary hydration spheres of cations, and the reaction is directly and simply related to a precisely measurable line width.

Because of this potentially important application the detailed investigation of the line-broadening effect of Cr(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> was undertaken in this laboratory.

### Experimental Section

Stock solutions of Cr<sup>3+</sup> and Ni<sup>2+</sup> were prepared from analytical grade nitrate salts, and these stock solutions were subsequently analyzed for the metal ions. Solutions of various concentrations of acid were prepared in the following manner. Those solutions in which the acid concentration was less than 10<sup>-1</sup> M were prepared by dropwise addition of dilute HNO<sub>3</sub>, and the pH was measured with a Beckman pH meter. Those solutions in which

(1) T. J. Swift and W. G. Sayre, *J. Chem. Phys.*, **44**, 3567 (1966).  
 (2) N. Bloembergen and L. O. Morgan, *ibid.*, **34**, 842 (1961).  
 (3) J. P. Hunt and H. Taube, *ibid.*, **18**, 757 (1950).

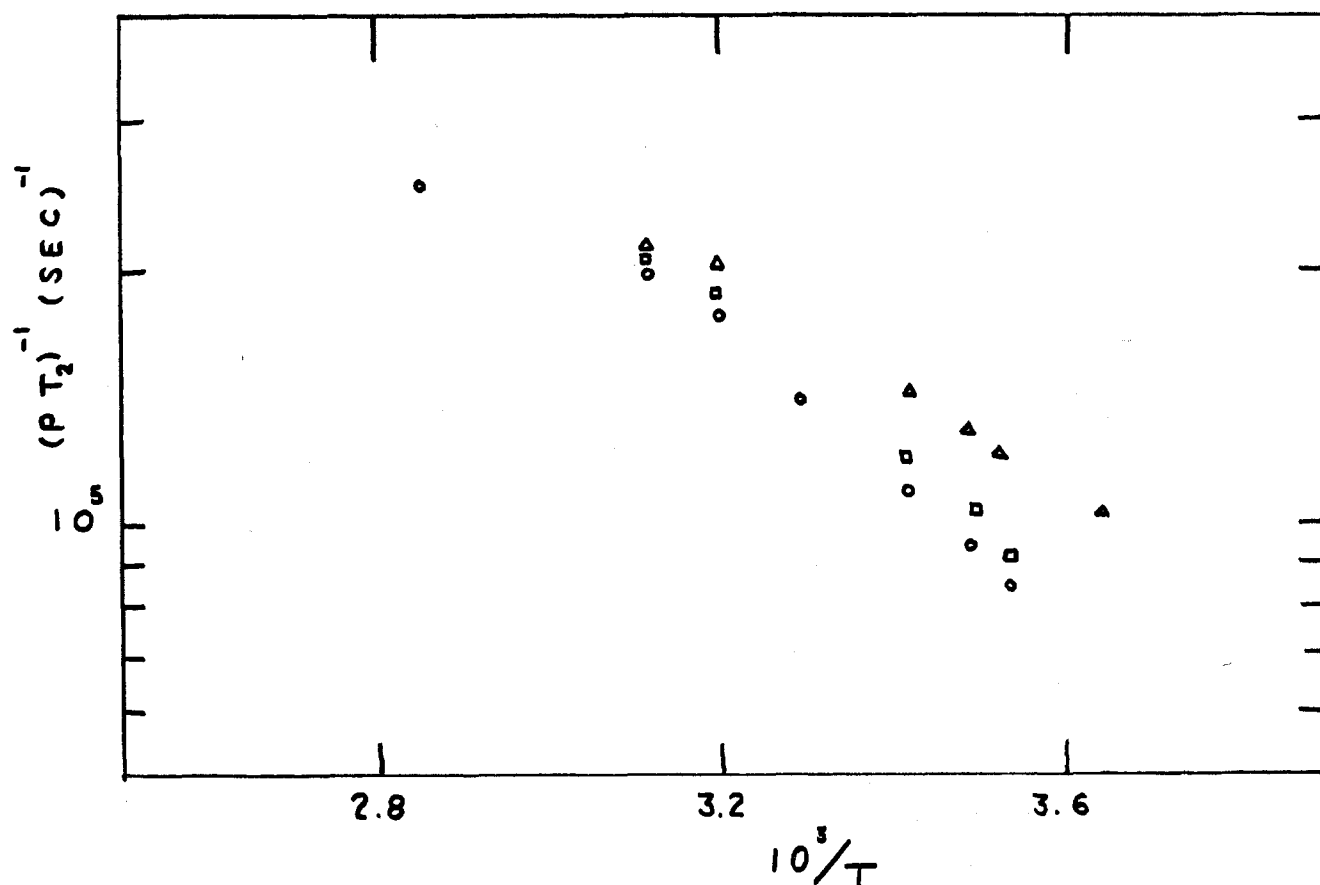


Figure 1.—Graph of  $-\log PT_2$  vs.  $10^3/T$  for  $0.0600 M Cr(NO_3)_3$  solutions at the following concentrations of  $H^+$ : O,  $1.10 M$ ; □,  $1.29 M$ ; Δ,  $1.80 M$ .

the acid concentration was greater than  $10^{-1} M$  were prepared through dilution of a standardized solution of  $HNO_3$ .

Concentrations of water in each of the solutions were calculated from the densities, which were measured with a Westphal balance.

Spectra were recorded on both a Varian A-60 proton resonance spectrometer and a Varian A-60A spectrometer. The temperature was varied through use of a Varian V-6040 temperature-control unit.

Much care was taken in the recording of the spectra to avoid instrument line broadening, and the detector phase was painstakingly adjusted to ensure that each absorption signal was truly Lorentzian in shape. Values of  $T_2$  were obtained from the line widths.

### Results

Spin-spin relaxation times,  $T_2$ , as a function of temperature for three chromic nitrate solutions are given in Figure 1. The term  $P$  is the concentration factor,  $12[Cr^{3+}]/(2[H_2O] + [H^+])$ , where  $[H_2O]$  is the concentration of bulk water. The data in Figure 1 are in good agreement with the results of previous investigators,<sup>2,4</sup> with the addition of one quite unexpected effect which appeared as a function of the acid concentration.

The general shape of any of the three curves in Figure 1 has been explained<sup>2,4</sup> as arising from the competition between chemical exchange control at lower temperatures and relaxation control at higher temperatures. The term  $PT_2$  is given to a good approximation by<sup>5</sup>

$$PT_2 = T_{2Cr} + \tau_{Cr} \quad (2)$$

where  $T_{2Cr}$  is the transverse relaxation time for protons in the primary hydration sphere of a chromic ion and  $\tau_{Cr}$  is the mean lifetime of a proton in this state.

It is clear from the data given in Figure 1 that  $T_2$  is dependent on  $[H^+]$  and/or  $[NO_3^-]$ . Relaxation times were measured for all three solutions of Figure 1 at temperatures between  $80$  and  $100^\circ$ . Values of  $T_2$  for the three solutions were virtually identical in this temperature range and were within  $\pm 1\%$  of each other at  $100^\circ$ . From these results it was apparent that  $T_{2Cr}$  is independent of  $[H^+]$  and  $[NO_3^-]$  within the limits given above and that the spread in relaxation times at lower temperatures may be ascribed to changes in  $\tau_{Cr}$ .

The lifetime,  $\tau_{Cr}$ , was shown to depend primarily on  $[H^+]$  by means of the following experiments. A  $0.0600 M Cr(NO_3)_3$  solution was prepared in which the concentration of  $HNO_3$  was  $1.10 M$  and in which the concentration of  $NaNO_3$  was  $2.00 M$ . Values of  $T_2$  for this solution as a function of temperature deviated by only a few per cent from the values given in Figure 1 for the solution in which  $[H^+]$  was  $1.10 M$ .

This type of experiment was repeated several times with  $NaNO_3$ ,  $Mg(NO_3)_2$ , and  $Ca(NO_3)_2$ . In all cases the relaxation times were found to be closely related to  $[H^+]$  and to be virtually independent of  $[NO_3^-]$ .

As an additional check relaxation times as a function of temperature were obtained for  $Cr(NO_3)_3$  solutions

(4) R. Hausser and G. Laukien, *Z. Physik*, **153**, 394 (1959).

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

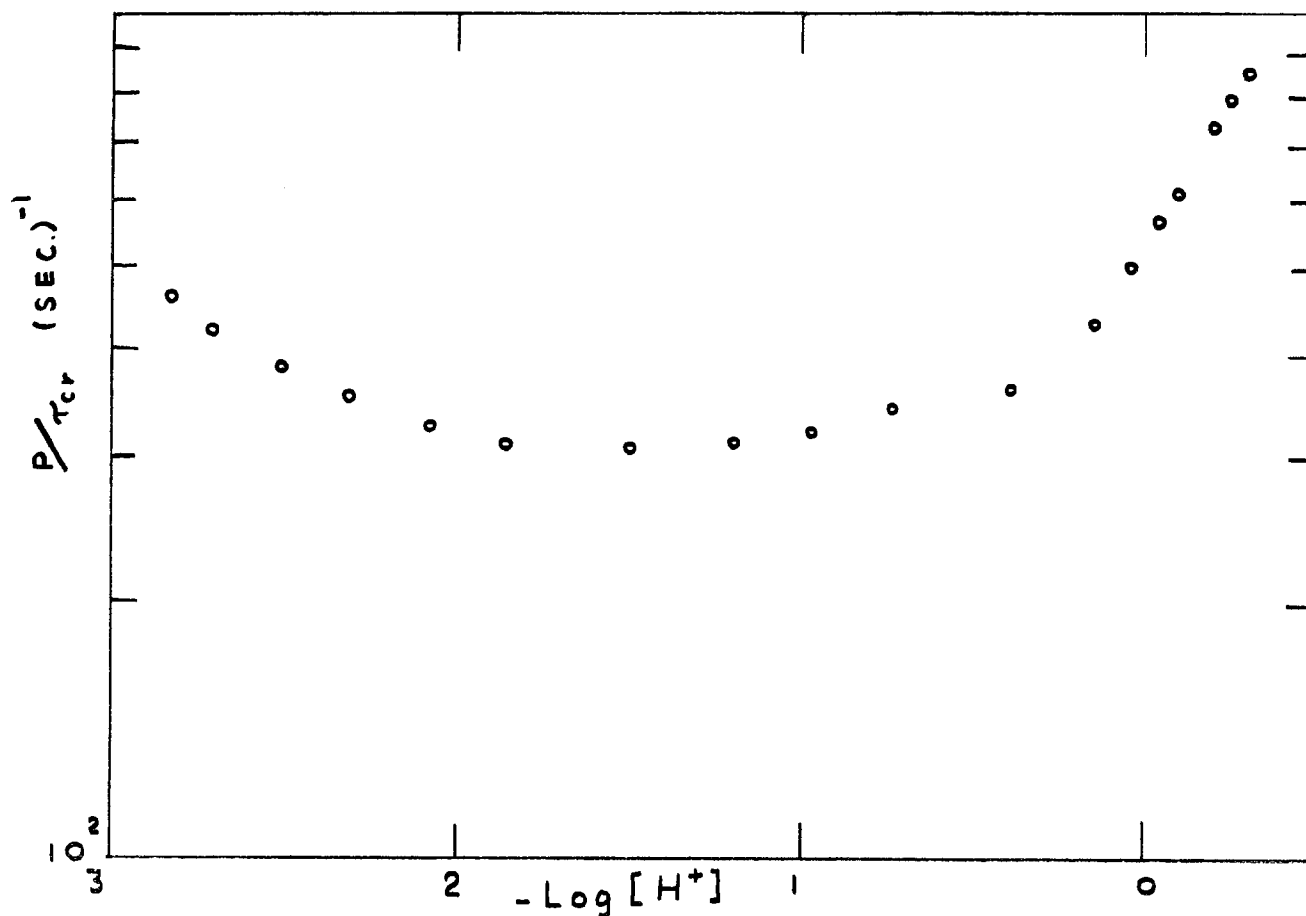


Figure 2.—Graph of  $\log P/\tau_{Cr}$  vs.  $-\log [H^+]$  for a 0.0600  $M$   $Cr(NO_3)_3$  solution at 283°K.

which contained added  $HClO_4$  in place of  $HNO_3$ . The concentration of  $Cr^{3+}$  was 0.0600  $M$  and the three concentrations of  $HClO_4$  employed were 1.10, 1.29, and 1.80  $M$ . The relaxation times as a function of temperature were uniformly within a few per cent of those given in Figure 1.

These results revealed conclusively that the variation of  $T_2$  values in Figure 1 with added nitric acid is due to the variation of  $\tau_{Cr}$  with  $[H^+]$ .

At temperatures near 0° the three plots of Figure 1 are nearly linear and to a good approximation  $PT_2$  is given by  $\tau_{Cr}$ . The variation of  $\tau_{Cr}$  at 283°K with  $\log [H^+]$  over a relatively large range of acid concentrations is given in Figure 2.

Three distinct regions are discernible in this plot. In the range of  $\log [H^+]$  between  $-1$  and  $-2$  the principal reaction leading to the transfer of protons from the  $Cr(H_2O)_6^{3+}$  ion to the bulk is clearly reaction 1 since the pseudo-first-order rate constant for this reaction is pH independent. The increase in the rate of exchange in passing from  $\log [H^+] = -2$  to  $\log [H^+] = -3$  is undoubtedly due to the formation of acid dissociation products and is the anticipated result. This effect could possibly be used to obtain information concerning the acid dissociation products of  $Cr(H_2O)_6^{3+}$ , but it is of little interest in the present investigation.

The third region near  $\log [H^+] = 0$  possesses a slope opposite in sign to that anticipated for acid dissociation

and is clearly the result of a proton-transfer mechanism which has not previously been considered for hydrated cations.

The quantitative relationship between  $\tau_{Cr}$  and  $[H^+]$  in this third region is shown in Figure 3 for four different temperatures. The relationship is linear and  $\tau_{Cr}$  may be formulated as

$$1/\tau_{Cr} = k_1 + k_2[H^+] \quad (3)$$

where  $k_1$  is the rate constant for reaction 1 and  $k_2$  is the rate constant for the acid-catalyzed reaction. Values for  $k_1$  and  $k_2$  and the activation parameters were easily calculated from the data in Figure 3 and are given in Table I. The uncertainties in the values of the rate constants are indicated by the significant figures given.

TABLE I  
VALUES OF  $k_1$  AND  $k_2$  AS FUNCTIONS OF TEMPERATURE AND VALUES OF  $\Delta H^*$  AND  $\Delta S^*$  OBTAINED FROM THEM FOR  $Cr(H_2O)_6^{3+}$  IN AQUEOUS SOLUTION

$T, ^\circ K$	$10^{-4}k_1$		$10^{-4}k_2$		$\Delta H^*,$ kcal	$\Delta S^*,$ eu
	sec <sup>-1</sup>	sec <sup>-1</sup>	sec <sup>-1</sup>	sec <sup>-1</sup>		
283	3.2			4.6		
286.5	4.2			5.0		
292.5	5.8	$7 \pm 1$	$-12 \pm 3$	5.0	$0.5 \pm 0.5$	$-36 \pm 2$
304	8.7			5.0		

A mechanism was proposed to account for the  $k_2$  term in eq 3, and this mechanism is presented and discussed in the following section.

The question immediately arose concerning other

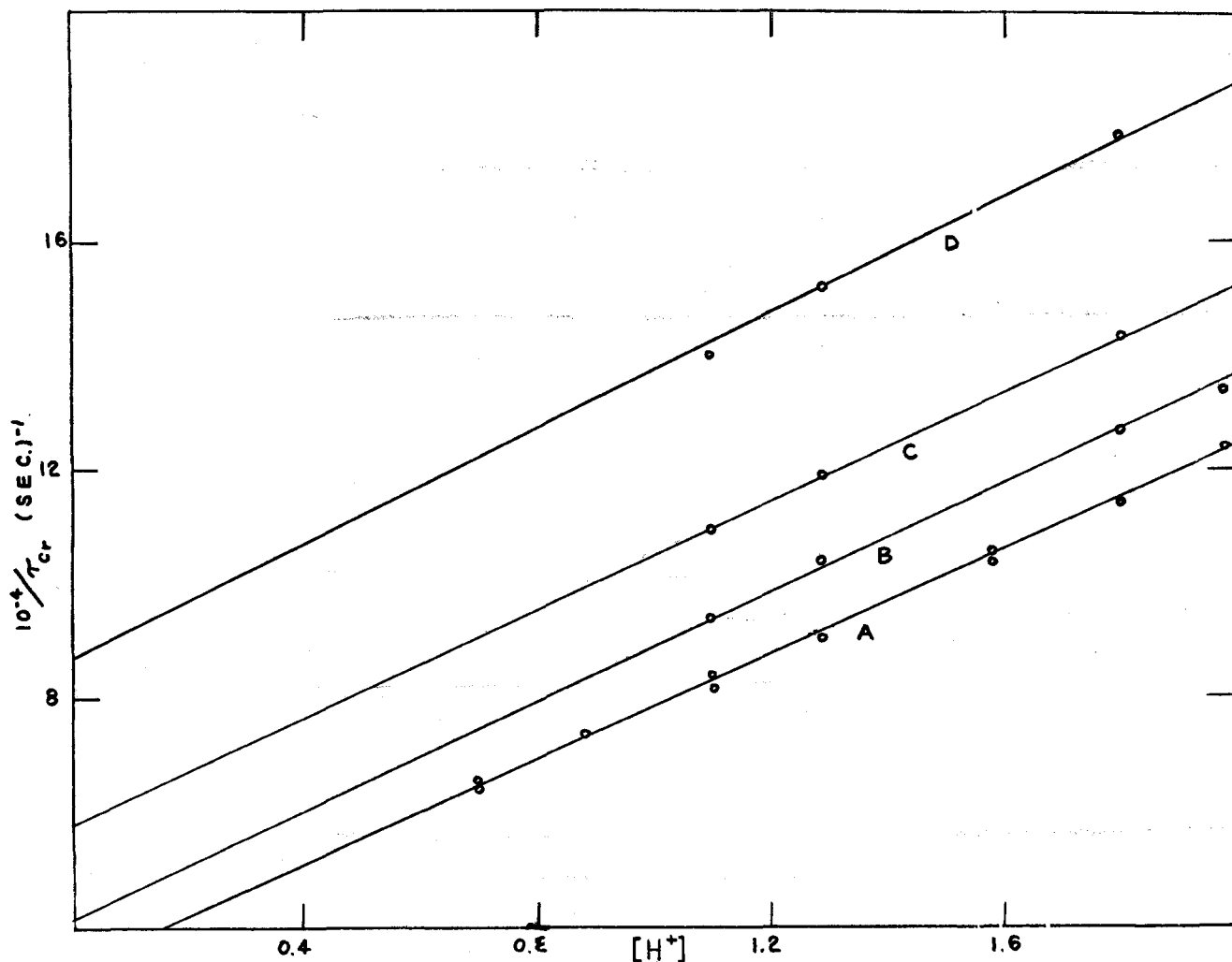


Figure 3.—Graphs of  $\tau_{Cr}$  vs.  $[H^+]$  for a 0.0600  $M$   $Cr(NO_3)_3$  solution at the following four temperatures: A, 283.0°K; B, 286.5°K; C, 292.5°K; D, 304.0°K.

metal ions which might display the same sort of acid-catalyzed proton exchange as  $Cr(H_2O)_6^{3+}$  and the conditions under which the operation of the acid-catalyzed reaction can be observed in proton relaxation. Concerning this latter question two conditions were clear: (1) A chemical-exchange-controlled region must be observable in the relaxation of protons by the ion in question. (2) The value of  $k_1$  must be small enough in relation to  $k_2$  to permit the observation of a line-broadening contribution from the  $k_2$  reaction. The large value<sup>2,6</sup> of  $k_1$  is clearly the reason that no  $k_2$  step is observable for manganous ion in aqueous solution.

One ion for which these conditions appeared to be fulfilled is  $Ni(H_2O)_6^{2+}$ . Hausser and Laukien<sup>4</sup> have studied the relaxation of protons by nickelous ion in aqueous solution, and Swift and Connick<sup>5</sup> have studied the relaxation of  $^{17}O$  by the same ion.

The plot of  $\log T_2$  vs. reciprocal absolute temperature given by Hausser and Laukien for the relaxation of protons by  $Ni(H_2O)_6^{2+}$  shows a region of temperature near 0° in which the proton relaxation appears to approach chemical-exchange control. This is shown by

the rather sharp bend in the relaxation time as a function of temperature in this region.

Values of  $PT_2$  taken from this plot in the region near 0° are quite close to the values of  $\tau_{Ni}$ , the average lifetime of a water molecule in the first coordination sphere of a hydrated  $Ni^{2+}$ , obtained by Swift and Connick. It appeared from the results of this comparison that chemical-exchange control is indeed observable in the relaxation of protons by  $Ni(H_2O)_6^{2+}$  in aqueous solution and that the exchange observed is the exchange of whole water molecules.

Proton relaxation times as a function of temperature for several  $Ni(NO_3)_2$  solutions at various acid concentrations were obtained in this laboratory. The data of Hausser and Laukien<sup>4</sup> were reproduced for all solutions in which the pH was greater than 2. At pH values < 2 the bendover in the data ascribed to chemical-exchange control became less pronounced, and it was not observable at acid concentrations above about 0.4  $M$ . This behavior of the relaxation time as a function of the concentration of  $H^+$  appeared to be completely analogous to that shown for chromic ion in Figure 1.

At temperatures above the bendover region the proton relaxation produced by  $Ni^{2+}$  is controlled by the

(6) R. A. Bernheim, T. H. Brown, H. S. Gutowsky, and D. E. Woessner, *J. Chem. Phys.*, **30**, 950 (1959).

rate of relaxation of protons in the first coordination sphere of the paramagnetic ion. Swift and Connick<sup>5</sup> have considered the limiting cases possible in the spin-spin relaxation of nuclei by paramagnetic species, and these limiting cases are presented in their eq 9.

The small slope of  $\log T_2$  vs. reciprocal absolute temperature at temperatures above the bendover region clearly indicated that the appropriate limiting case<sup>6</sup> for this region is characterized by the inequalities

$$1/\tau_{Ni}^2 \gg 1/T_{2Ni}^2 \gg \Delta\omega_{Ni}^2 \quad (4)$$

where  $\tau_{Ni}$  is the average lifetime of a proton in the first coordination sphere of a hydrated nickelous ion in solution,  $T_{2Ni}$  is the proton relaxation time in the first coordination sphere, and  $\Delta\omega_{Ni}$  is the separation ( $\text{sec}^{-1}$ ) between the operating frequency of the spectrometer for the recording of the proton signal and the resonance frequency of the protons in the first coordination sphere of the paramagnetic ion.

In the light of these conclusions it may be stated that the proton relaxation produced by  $Ni^{2+}$  in aqueous solution is given to a good approximation at all temperatures studied<sup>4</sup> by the form of eq 2.

As was the case with chromic ion, the dependence of the proton-relaxation rate on the concentration of added nitric acid was investigated further in order to determine if the dependence was due to changes in  $T_{2Ni}$ ,  $\tau_{Ni}$ , or both.

This question was quickly settled since it was found that at temperatures above  $30^\circ$ , where  $PT_2$  is very nearly equal to  $T_{2Ni}$ , the proton relaxation rate is independent of the concentration of added nitric acid within experimental uncertainty. This result revealed that as with chromic ion the dependence of the proton relaxation rate on the concentration of added nitric acid is due to changes produced in the proton-exchange rate.

The separate effects produced by variation of  $[H^+]$  and  $[NO_3^-]$  were investigated in the same manner as with chromic ion, and the results showed conclusively that the primary effect is produced by the variation of the hydrogen ion concentration and not by changes in the nitrate ion concentration.

Figure 4 shows plots of  $P/\tau_{Ni}$  as a function of  $[H^+]$  for three different temperatures. Values of  $P/\tau_{Ni}$  were calculated from the  $Ni^{2+}$  analog of eq 2 together with the values of  $T_{2Ni}$  obtained from the proton relaxation times in highly acidic solutions. It is quite clear from Figure 4 that  $1/\tau_{Ni}$  is of the same form as  $1/\tau_{Cr}$  in eq 3. Values of  $k_1$ ,  $k_2$ , and the activation parameters were easily calculated from the data of Figure 4 and are given in Table II. Experimental uncertainties in the values given for the rate constants are indicated by the number of significant figures given.

It is of importance to note that the values of  $k_1$  and the activation parameters obtained from  $k_1$  are in reasonably good agreement with the values obtained by Swift and Connick<sup>5</sup> from  $^{17}O$  resonance data. This result confirmed the previous assumption that the bendover in the proton relaxation data<sup>4</sup> is due to the onset of chemical-exchange control.

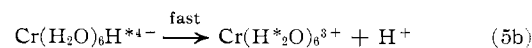
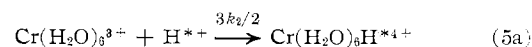
TABLE II  
VALUES OF  $k_1$  AND  $k_2$  AS FUNCTIONS OF TEMPERATURE AND  
VALUES OF  $\Delta H^*$  AND  $\Delta S^*$  OBTAINED FROM THEM FOR  
 $Ni(H_2O)_6^{2+}$  IN AQUEOUS SOLUTION

$T$ , °K	$10^{-4}k_1$ , sec <sup>-1</sup>	$\Delta H^*$ , kcal	$\Delta S^*$ , eu	$10^{-4}k_2$ , M <sup>-1</sup> sec <sup>-1</sup>	$\Delta H^*$ , kcal	$\Delta S^*$ , eu
264.5	0.9			1.3		
274.5	1.7	$11 \pm 2$	$1 \pm 6$	1.3	$0.5 \pm 0.5$	$-30 \pm 2$
279.0	2.8			1.3		

### Discussion

There can be little doubt that an acid-dependent step is present in the proton exchange involving both  $Cr(H_2O)_6^{3+}$  and  $Ni(H_2O)_6^{2+}$ . From a comparison of the activation parameters for the  $k_2$  step given in Tables I and II it is highly likely that the mechanism of this acid-dependent step is essentially the same for both ions.

On the bases of the linear dependence on  $[H^+]$ , the value near zero for  $\Delta H^*$ , and the large negative value for  $\Delta S^*$  for the  $k_2$  step, the following mechanism is proposed.



One of the water molecules in the  $Cr(H_2O)_6^{3+}$  ion is protonated, forming a coordinated  $H_3O^+$ , in which the three protons are equivalent. In the rapid deprotonation step which follows there is a probability of two-thirds that the proton transferred is not the proton originally accepted by the ion. The rate-determining step is proposed to be reaction 5a, leading to the observed rate law.

Reaction 5a may in turn be separated into two reactions. The first is the formation of a hydrogen bond between the donor  $H_3O^+$  ion and a lone pair of electrons on the acceptor primary hydration sphere water molecule. The formation of such a hydrogen bond involves considerable rearrangement of the structure of the secondary hydration sphere of the chromic ion and would account for the rather large negative  $\Delta S^*$  observed for the  $k_2$  process.

The enthalpy of activation for this mechanism may be considered to be composed of three separate enthalpy terms. These are the enthalpy for an  $H_3O^+$  ion entering the second hydration sphere of a chromic ion, the enthalpy of the hydrogen bond formation, and the enthalpy of the actual proton transfer. It is not unreasonable to propose that all three of these terms are rather small and that the total enthalpy is near zero.

It is of considerable interest to compare the values of the activation parameters for the  $k_2$  reaction given in Table I with those calculated for the reaction which is the reverse of reaction 1. Both this reaction and reaction 5a involve the protonation of a positively-charged chromic species, and some similarities in the activation parameters might be expected.

Values of the activation parameters for the reverse of reaction 1 are easily obtained from the data given in Table I together with the over-all enthalpy and entropy

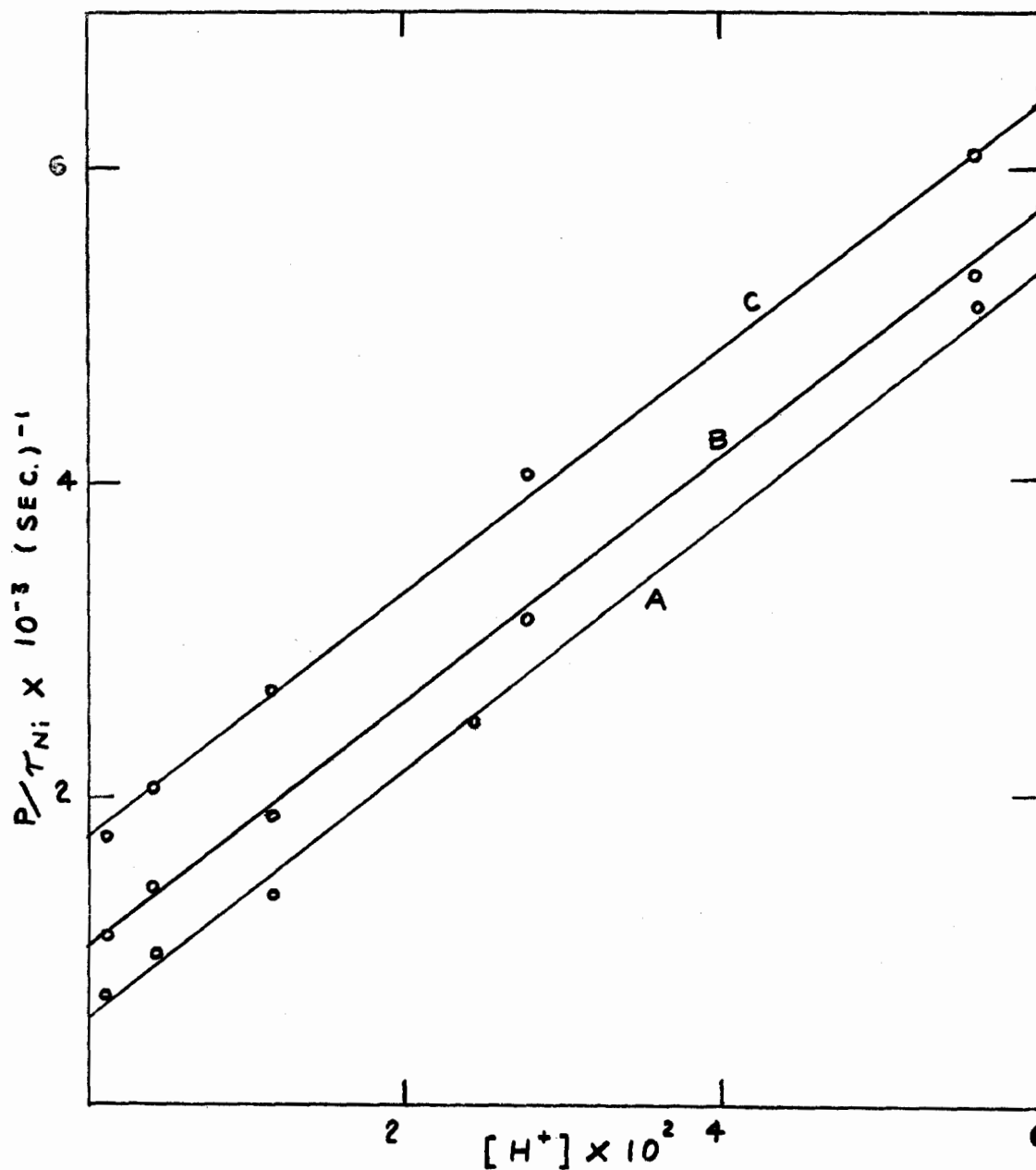


Figure 4.— $P/\tau_{Ni}$  as a function of  $[H^+]$  for a 0.564  $M$   $Ni(NO_3)_2$  solution at the following three temperatures: A, 264.5°K; B, 274.5°K; C, 279.0°K.

for reaction 1 given by Postmus and King.<sup>7</sup> The calculated  $\Delta H^*$  is  $-2.4$  kcal and  $\Delta S^*$  is  $-26.1$  eu. The small absolute value of the enthalpy and large negative value of the entropy are in agreement with the values given in Table I and would appear to lend support to reactions 5a and 5b as the proper interpretation of the  $k_2$  step.<sup>8</sup>

(7) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208 (1955).

Equations 5a and 5b have been written for  $Cr^{3+}$ . They are proposed to apply equally as well to  $Ni^{2+}$  and, quite likely, to any hydrated ion for which  $k_1$  is sufficiently small.

**Acknowledgment.**—We wish to acknowledge the financial support of the National Science Foundation in the form of grant No. GP-3198.

(8) We are indebted to one of the referees for pointing out the data in ref 7 and the interesting comparison which may be derived from them.