

products which we would not detect (*i.e.*, N<sub>2</sub>, O<sub>2</sub>, or NO). The absorption of O<sub>3</sub> of 2537-Å. radiation is intense; the absorption coefficient (to base 10) is 0.176 mm.<sup>-1</sup> cm.<sup>-1</sup>. Thus only microns of O<sub>3</sub> could remove significant portions of the radiation, and the O<sub>3</sub> pressure would be kept small. An attractive feature of this possibility is that for every O(<sup>3</sup>P) atom removed by reaction f, another is prevented from forming because of the O<sub>3</sub> absorption at 2537 Å. Thus our reported rate constant for reaction f would be reduced by a factor of two to give excellent agreement with that of Kaufman and Kelso.

Table V is a compilation of the rate constant ratios determined in this study.

Table V. Rate Constant Ratios

Ratio	Value	Source
$k_b/k_c$	0.27	Eq. 1, Figure 3
$k_d/k_e$	6.5	Eq. 2
$k_f/(k_d + k_e)$	54 l./mole	Eq. 4, Figure 6
$k_i^2/k_h$	$\geq 0.0044$ l./mole sec.	Eq. 6, Figure 8
$k_k/(k_d + k_e)$	29	Eq. 7, Figure 9

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## Oxygen Exchange between Periodate and Water Studied by <sup>17</sup>O Nuclear Magnetic Resonance

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*Contribution from the Isotope Department, Weizmann Institute of Science, Rehovoth, Israel. Received April 17, 1965*

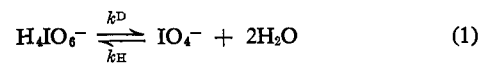
Oxygen exchange between periodate and water was studied by <sup>17</sup>O nuclear magnetic resonance (n.m.r.). In aqueous solutions of periodate, the water <sup>17</sup>O n.m.r. line is broadened and no signal due to the <sup>17</sup>O of periodate is observed. This is due to fast oxygen exchange between water and periodate. From the concentration and temperature dependence of the water <sup>17</sup>O line width, the kinetic parameters for the exchange reactions were determined. The pseudo-first-order rate constant of the exchange reaction,  $H_5IO_6 + H_2O^* \rightleftharpoons H_5IO_6O^* + H_2O$ , is  $4.5 \times 10^3$  sec.<sup>-1</sup> at 25° and its activation energy is 13.5 kcal. mole<sup>-1</sup>. The reaction is not catalyzed by hydrogen or chloride ions. For the oxygen-exchange rate of water with  $IO_4^-$ , an upper limit of  $1.2 \times 10^8$  sec.<sup>-1</sup> at 25° is found. The exchange with  $I_2O_8^{4-}$  ions is faster than  $2.8 \times 10^4$  sec.<sup>-1</sup> at the same temperature. The results are discussed in terms of hydration-hydrolysis equilibria and are compared with previous investigations of similar systems.

### Introduction

The study of the oxygen exchange between solvent water and oxy compounds is important for the understanding of their structure and kinetic behavior.<sup>1</sup> The rates of these reactions span a wide range; some are immeasurably slow, and others are too fast to be measured by conventional tracer techniques. Oxygen exchange of telluric, periodic, and xenic acids is extremely fast in comparison with other oxy compounds. Reuben, Samuel, Selig, and Shamir<sup>2</sup> showed that oxygen exchange between water and xenic acid [Xe(OH)<sub>6</sub>] is complete within 3 min.; when a concentrated aqueous solution of Xe(OH)<sub>6</sub> was mixed with water highly enriched with <sup>17</sup>O, the n.m.r. signal of <sup>17</sup>O

due to xenic acid was completely developed within the time necessary to make the first observation. By a similar procedure we were able to follow the increase in the intensity of the <sup>17</sup>O signal of telluric acid [Te(OH)<sub>6</sub>] dissolved in <sup>17</sup>O-enriched water. From this experiment, the half-life of the oxygen-exchange reaction was found to be ~10 min. at 25°.<sup>3</sup>

Anbar and Guttmann<sup>4</sup> have shown that the half-life of the oxygen exchange between periodate and water at pH 4 and 7 is less than 5 sec. and hence cannot be followed by the conventional tracer technique. More recently Kustin and Lieberman<sup>5</sup> using the temperature jump method studied the dehydration-hydration reactions



a process through which oxygen exchange between periodate and water takes place. The rate constants determined,  $k_D = 5.6 \times 10^3$  and  $k_H = 1.9 \times 10^2$  sec.<sup>-1</sup> in the pH range 3.4 to 5.0 at 20°, are consistent with the lower limit for the exchange rate given by Anbar and Guttmann.<sup>4</sup> Using the nuclear magnetic resonance (n.m.r.) line-broadening technique we have extended the study of oxygen exchange between periodate species and water.

It is well known that the n.m.r. line shape is sensitive to chemical exchange processes in which the resonating nuclei exchange their magnetic environment.<sup>6</sup> If the exchange rate is slow, the n.m.r. spectrum will appear as a superposition of the spectra due to the various species. At fast rates of exchange the spectrum will exhibit the time average of the discrete spectra. If the exchange rate is of the order of the width of the spectrum, measured in cycles per second, the n.m.r. line

(3) I. Pecht and Z. Luz, unpublished.

(4) M. Anbar and S. Guttmann, *J. Am. Chem. Soc.*, **83**, 781 (1961).

(5) K. Kustin and E. C. Lieberman, *J. Phys. Chem.*, **68**, 3869 (1964).

(6) For a recent review, see A. Loewenstein and T. M. Connor, *Ber. Bunsenges. Physik. Chem.*, **67**, 280 (1963).

(1) J. O. Edwards, "Inorganic Reaction Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1964, Chapter 8.

(2) J. Reuben, D. Samuel, H. Selig, and J. Shamir, *Proc. Chem. Soc.*, 270 (1963).

shape will depend on the exchange rate and can be used to study the reaction quantitatively. Proton-transfer reactions have been studied extensively by this technique.<sup>6</sup> In <sup>17</sup>O n.m.r. spectroscopy, this method has only a limited application since oxygen exchange reactions are usually too slow to affect the n.m.r. spectra. Exceptions are the hydration–dehydration reactions of some metal ions in aqueous solutions<sup>7,8</sup> and the exchange of oxygen between periodic acid and water which is described in the present paper.

## Experimental

**N.m.r. Measurements.** <sup>17</sup>O nuclear magnetic resonance spectra were recorded on a V-4200 Varian wide-line spectrometer operating at 8.13 Mc. sec.<sup>-1</sup>. The derivative of the absorption line was recorded using 20-c.p.s. field modulation. The modulation field and the radiofrequency power were kept low enough to avoid broadening due to overmodulation or saturation. Under these conditions the peak-to-peak separation,  $\Delta$ , of the derivative of the absorption line in cycles per second is related to the transverse relaxation time,  $T_2$ , by  $1/T_2 = \sqrt{3}\pi\Delta$ .

Line-width measurements at temperatures other than room temperature (25°) were made using a Varian variable temperature kit, Model V-4331-TWL. The sample temperature was measured by a thermocouple inserted in the air stream above the receiver coil. The accuracy in determining the temperature of the solution is estimated at  $\pm 2^\circ$ .

**Preparation of Solutions.** Stock solutions of periodic acid were prepared by dissolving Puriss grade H<sub>5</sub>IO<sub>6</sub> (Fluka) in water enriched with <sup>17</sup>O isotope. The concentrations of the solutions were calculated from the known weights of the water and periodic acid used. Solutions containing excess of strong acid were prepared by the addition of concentrated HClO<sub>4</sub> (10 M). The solutions containing lithium periodate were prepared by neutralizing periodic acid solutions with 4 M LiOH. The changes in the concentration of periodate due to dilution caused by the added acid or base were taken into account in the final calculation. In preliminary experiments we used NaOH as base. The results were identical with those obtained with LiOH except that it was impossible to prepare solutions of the disodium salts. Salts of periodic acid obtained upon titration of the second hydrogen are quite insoluble in water. It was, however, possible to prepare metastable solutions containing what seems to be<sup>9</sup> Li<sub>4</sub>I<sub>2</sub>O<sub>9</sub>, at appreciable concentrations. The procedure was to mix a solution of periodic acid with a solution of LiOH in excess of the amount necessary to neutralize 1 equiv. of the periodic acid. Upon mixing, a white precipitate appeared which soon dissolved, and the clear solutions, so obtained, were stable for approximately 15 min. After that time a white crystalline substance (presumably Li<sub>4</sub>I<sub>2</sub>O<sub>9</sub>) slowly precipitated. The precipitation was complete within about 1 hr. A gradual addition of LiOH to a solution of periodic acid gave a precipitate when the amount of base added was in excess of 1 equiv. of periodic acid.

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

(8) R. E. Connick and D. N. Fiat, *ibid.*, **39**, 1349 (1963).

(9) G. J. Buist and J. D. Lewis, *Chem. Commun.* (London), **1**, 66 (1965).

## Results

The <sup>17</sup>O n.m.r. spectra of aqueous periodic acid solutions show at room temperature only a single absorption line due to water. This line is broadened compared to the natural line width of <sup>17</sup>O in water. The observed values of the line width,  $1/T_2$ , in solutions containing different concentrations of H<sub>5</sub>IO<sub>6</sub> in water enriched to 4 atom % <sup>17</sup>O are shown in Table I. In the

**Table I.** Line Width of the <sup>17</sup>O Resonance in Aqueous Solutions of Periodic Acid in Water Enriched to 4 Atom % <sup>17</sup>O at 25°

[H <sub>5</sub> IO <sub>6</sub> ], <i>m</i>	$1/T_2$ , sec. <sup>-1</sup>	$1/mT_2'$ , <sup>b</sup> <i>m</i> <sup>-1</sup> sec. <sup>-1</sup>
0.00 <sup>a</sup>	180	...
0.53	440	490
0.90	660	530
1.39	850	480
2.03	1170	490

<sup>a</sup> Reference sample containing 0.1 M HClO<sub>4</sub>. <sup>b</sup>  $1/mT_2' = 1/m(1/T_2 - 1/T_2^0)$ .

last column of this table we give the broadening,  $1/mT_2'$ , caused by the periodic acid and normalized to unit concentration of H<sub>5</sub>IO<sub>6</sub>. This was calculated as the difference between the observed line width,  $1/T_2$ , and that of the reference water,  $1/T_2^0$ , divided by the molality,  $m$ , of the solution. Within the experimental accuracy, the broadening increases linearly with the concentration. The reference water was acidified with HClO<sub>4</sub> in order to eliminate the contribution to the line width due to proton exchange of water.<sup>10</sup> This effect is appreciable around pH 7 but is negligible below pH 5 and thus was unimportant in both the H<sub>5</sub>IO<sub>6</sub> solutions and the reference water sample.

The <sup>17</sup>O water peak in the periodic acid solutions was found to be slightly shifted relative to the <sup>17</sup>O in pure water. The shift is proportional to the concentration of periodic acid and is approximately 40 c.p.s. to lower field in a 1 *m* solution.

The effect of added acid (HClO<sub>4</sub>) and base (LiOH) on the observed n.m.r. line width was studied in solutions containing about 1 *m* H<sub>5</sub>IO<sub>6</sub>. The results for a 0.9 *m* H<sub>5</sub>IO<sub>6</sub> solution containing 4 atom % <sup>17</sup>O at 25° are shown in Figure 1. It is evident from the results that perchloric acid does not affect the line width appreciably, but neutralization of the periodic acid with LiOH strongly influences it. Neutralization of the first hydrogen results in the decrease of the line width  $1/T_2$ , almost to the value of the <sup>17</sup>O resonance in a reference solution of water containing only perchloric acid (*cf.* Table I). Further addition of LiOH results in a steep increase of the line width even beyond its value in the acidified solutions. However, as explained above, these solutions, containing LiOH in excess of 1 equiv., were unstable, slowly precipitating a white crystalline solid. Parallel to the precipitation the line width decreased down to approximately its value in the reference water solution. The <sup>17</sup>O line width in these solutions is therefore not accurately known (this range is shown in Figure 1 by a dashed curve).

To check on the possible catalytic effect of nucleophilic reagents on the oxygen-exchange rate,<sup>4,11</sup> the water <sup>17</sup>O line width in solutions containing 1.3 *m* H<sub>5</sub>IO<sub>6</sub> and various amounts of chloride ion was meas-

(10) S. Meiboom, *J. Chem. Phys.*, **34**, 375 (1961).

(11) M. Anbar and S. Guttman, *J. Am. Chem. Soc.*, **83**, 4741 (1961).

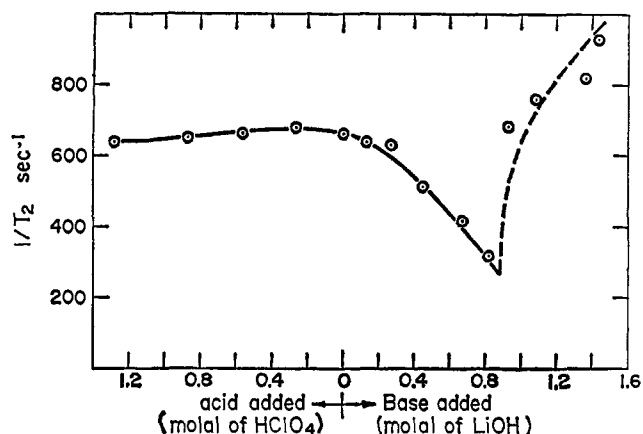


Figure 1.  $^{17}\text{O}$  transverse relaxation rate of water in a 0.9 *m* solution of periodic acid as a function of added  $\text{HClO}_4$  and  $\text{LiOH}$ .

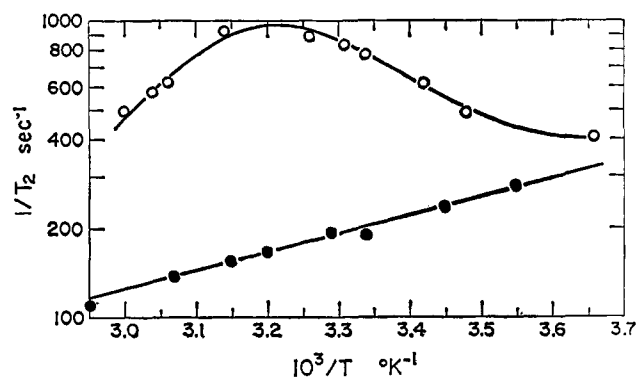


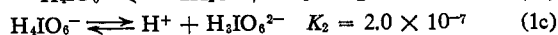
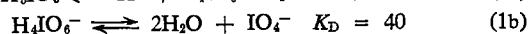
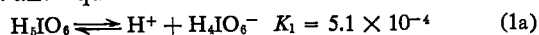
Figure 2.  $^{17}\text{O}$  transverse relaxation rate of water as a function of reciprocal absolute temperature. The open circles are for a solution containing 1.3 *m*  $\text{H}_5\text{IO}_6$  and 0.6 *M*  $\text{HClO}_4$ . The closed circles are for a solution of 0.1 *M*  $\text{HClO}_4$ .

ured. No broadening was observed up to 1.4 *m*  $\text{LiCl}$ .

The temperature dependence of the  $^{17}\text{O}$  line width was measured in a solution of 1.3 *m*  $\text{H}_5\text{IO}_6$  and 0.6 *m* perchloric acid between 5 and 60°. The perchloric acid served to keep the ratio of dissociated periodate to undissociated  $\text{H}_5\text{IO}_6$  molecules low. The results are shown in Figure 2. Also included in this figure are  $1/T_2$  values for the  $^{17}\text{O}$  line of a water reference solution containing 0.1 *M*  $\text{HClO}_4$ . In Figure 3 we have plotted  $1/T_2'$ , the difference between the  $^{17}\text{O}$  transverse relaxation rates in the periodic acid solution and the reference water solution calculated from the data in Figure 2. This gives the extra broadening of the water line due to periodic acid, as a function of reciprocal absolute temperature.

### Interpretation of the Results

Crouthamel, Hayes, and Martin<sup>12</sup> determined by a spectrophotometric method the species present in aqueous solutions of periodate. They showed that in the pH range 0–7 it is sufficient to consider the following species:  $\text{H}_5\text{IO}_6$ ,  $\text{H}_4\text{IO}_6^-$ ,  $\text{IO}_4^-$ , and  $\text{H}_3\text{IO}_6^{2-}$ . The equilibria and equilibrium constants at 25° are



The variations of the equilibrium constants (1) with temperature between 0 and 70° were also determined.<sup>12</sup>

(12) C. Crouthamel, A. Hayes, and D. Martin, *J. Am. Chem. Soc.*, **73**, 82 (1951).

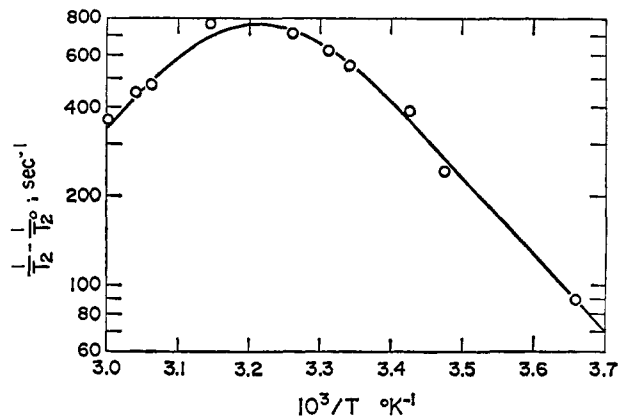


Figure 3. The contribution to the  $^{17}\text{O}$  relaxation due to periodic acid, calculated from the data of Figure 2.

It follows from equilibria 1 that in acidified solutions, undissociated  $\text{H}_5\text{IO}_6$  is the dominant species. Upon titration with base  $\text{H}_4\text{IO}_6^-$  and  $\text{IO}_4^-$  are formed, the latter being the dominant species. Beyond the first neutralization point,  $\text{H}_3\text{IO}_6^{2-}$  is formed. Recently Buist and Lewis<sup>9</sup> showed that the doubly charged periodate undergoes dimerization in aqueous solution. Using their equilibrium constant at 25° (660  $\text{mole}^{-1}$  l.) it follows that in solutions containing above 0.5 *m* periodate, in its doubly ionized form, more than 95% is dimerized. In the following discussion we shall use the equilibrium constants given by Crouthamel, *et al.*<sup>12</sup> These were obtained for solutions of lower concentrations than those used for the n.m.r. measurements and thus have to be modified. Unfortunately the effect of concentration on the *K* values is not known and we shall therefore use them as given, without modifications.

The dependence of the  $^{17}\text{O}$  line width on temperature (Figures 2 and 3) and on the amount of acid or base added (Figure 1) can be explained in terms of oxygen exchange between water and the various species of periodate. For the determination of the exchange rates from the experimental data we used eq. 2. This equation was derived by Swift and Connick<sup>7</sup> for a system in which a nucleus switches positions between two (or more) magnetic environments, one of them being much more populated than the other. In the present case the concentration of  $^{17}\text{O}$  in water is at least seven times larger than that of  $^{17}\text{O}$  in periodate and the n.m.r. signal consists essentially of a single Lorentzian peak, *i.e.*, that due to water. Assuming that the oxygen exchange occurs with a single species of periodate the observed line width of the water peak,  $1/T_2'$ , is given by<sup>7</sup>

$$1/T_2' = 1/T_2 - 1/T_2^0 = P \frac{1/T_{2s}(1/T_{2s} + 1/\tau) + \delta^2}{\tau(1/T_{2s} + 1/\tau)^2 + \delta^2\tau} \quad (2)$$

In this equation  $1/T_2^0$  is the  $^{17}\text{O}$  line width of water under conditions where no exchange broadening occurs and may be taken as  $1/T_2$  of water not containing periodate but otherwise at the same temperature and acidity (see Figure 2). *P* is the ratio of the concentrations of  $^{17}\text{O}$  nuclei in the periodate species that undergoes the exchange reaction and the  $^{17}\text{O}$  nuclei in water [for periodic acid,  $P = (6 \times \text{molality of } \text{H}_5\text{IO}_6) / 55.5]$ .  $\delta$  is the chemical shift between water and periodate, and  $\tau$  is the residence time of a  $^{17}\text{O}$  nucleus

in a periodate molecule between successive exchanges with water. In the analysis of the results it was assumed that the rate,  $1/\tau$ , follows an Arrhenius equation,  $1/\tau = A \exp(-\Delta E/RT)$ , where  $\Delta E$  is the activation energy of the exchange reaction.  $T_{2s}$  is the transverse relaxation time of  $^{17}\text{O}$  in periodate. This quantity could not be determined experimentally since a separate line for periodate could not be observed (see below). Fortunately, in our case,  $\tau$  is not sensitive to the value of  $T_{2s}$ . In fact, the exchange rate  $1/\tau$  at and below room temperature could be obtained from the approximate equation<sup>6,7</sup>

$$1/T_2' = 1/T_2 - 1/T_2^0 = P/\tau \quad (3)$$

which holds when  $\tau\delta \gg 1$ . That this condition is satisfied for periodic acid follows from the results of Figures 2 and 3.<sup>13</sup> The kinetic parameters could thus be determined with reasonable confidence without knowing  $T_{2s}$  and  $\delta$ . An analysis of eq. 2 shows that  $1/T_2$  will pass through a maximum when plotted vs. the rate of exchange if  $1/T_{2s} < \delta$ . In practice one plots  $1/T_2$  as a function of temperature (or rather reciprocal absolute temperature) and as shown in Figure 3 a maximum does in fact occur. It may therefore be concluded that the  $^{17}\text{O}$  n.m.r. width of periodic acid,  $1/T_{2s}$ , is smaller than the chemical shift.

In terms of oxygen exchange between periodate and water, the results of Figure 1 can be understood in the following way. In solutions of periodic acid the  $^{17}\text{O}$  water line is broadened owing to oxygen exchange between undissociated  $\text{H}_5\text{IO}_6$  molecules. As expected from eq. 2 the broadening,  $1/T_2'$ , increases linearly with the concentration of periodic acid (*cf.* Table I). Upon addition of perchloric acid the concentration of undissociated  $\text{H}_5\text{IO}_6$  molecules remains practically constant. Since the line width is not affected by the addition of  $\text{HClO}_4$ , or  $\text{LiCl}$ , it may be concluded that the reaction is not catalyzed by either  $\text{H}^+$  ions or nucleophilic reagents of strength comparable to  $\text{Cl}^-$ . According to equilibria 1 the addition of base ( $\text{LiOH}$ ) up to 1 equiv. is followed by a decrease in the concentration of  $\text{H}_5\text{IO}_6$  molecules and a corresponding increase in the  $\text{IO}_4^-$  concentration. (The concentration of  $\text{H}_4\text{IO}_6^-$  is relatively low over the whole range.) In this region  $1/T_2$  decreases with base concentration, and at 1 equiv. of  $\text{LiOH}$  the line width is approximately that of water and its frequency is not shifted relative to the water line in pure water. It may thus be concluded that oxygen exchange between  $\text{IO}_4^-$  and  $\text{H}_2\text{O}$  is too slow to affect the water  $^{17}\text{O}$  n.m.r. line. An upper limit for the pseudo-first-order rate constant of  $1.2 \times 10^3 \text{ sec.}^{-1}$  at  $25^\circ$  for this reaction can be estimated from the experimental  $1/T_2$  at about 1 equiv. of base (Figure 1). This is consistent with the result of Kustin and Lieberman.<sup>5</sup>

In the solutions containing  $\text{LiOH}$  in excess of 1 equiv., the n.m.r. peak broadens again indicating fast oxygen exchange. This can be associated with the formation of a new species, probably  $\text{I}_2\text{O}_9^{4-}$  (as suggested by Buist and Lewis<sup>9</sup>). As pointed out above these solutions were unstable and could therefore not

(13) Equation 3 is often referred to as the "exchange-broadening" approximation, since the line width increases with the rate of exchange and thus also with temperature. As the usual effect of temperature is to decrease the line width of liquids, exchange broadening can easily be recognized from the temperature dependence of the n.m.r. line.

be studied quantitatively. The experimental results of Figure 1 give only a lower limit of  $2.8 \times 10^4 \text{ sec.}^{-1}$  for the pseudo-first-order rate constant of the exchange reaction between the dimer species and water at  $25^\circ$ .

The temperature dependence of the  $^{17}\text{O}$  n.m.r. line width in a solution containing 1.3 *m*  $\text{H}_5\text{IO}_6$  and 0.6 *M*  $\text{HClO}_4$  was studied. The results (Figures 2 and 3) are typical for an exchange process and can be analyzed quantitatively by eq. 2 or 3. In this solution only undissociated  $\text{H}_5\text{IO}_6$  molecules contribute to the exchange, and their concentration as a function of temperature was calculated from the temperature dependence of  $K_1$  and  $K_d$  given by Crouthamel, *et al.*<sup>12</sup> From the results in Figure 3 the following kinetic parameters for this reaction were derived:  $1/\tau$  (at  $25^\circ$ ) =  $4.5 \times 10^3 \text{ sec.}^{-1}$  and  $\Delta E = 13.5 \text{ kcal./mole}^{-1}$ .

The chemical shift,  $\delta$ , of  $\text{H}_5\text{IO}_6$  can only be obtained from the experimental data of Figure 3 if  $T_{2s}$  is known. It was shown above that  $\delta > 1/T_{2s}$ . Thus for the two extreme cases,  $1/T_{2s} = 0$  and  $1/T_{2s} = \delta$ , the following limiting values for the chemical shift are obtained:  $\delta = 1800$  and  $900 \text{ c.p.s.}$ , respectively. The true value lies somewhere in between. Since the water line is shifted by the exchange with  $\text{H}_5\text{IO}_6$  to low field, it may be concluded that the  $^{17}\text{O}$  resonance of periodic acid has a downfield shift relative to water of 120 to 230 p.p.m. Similar values were obtained in other related compounds. For example, the shifts in telluric acid,<sup>8</sup> iodate,<sup>3</sup> selenate,<sup>14</sup> bromate,<sup>14</sup> and xenic acid<sup>2</sup> are, respectively,  $-120$ ,  $-200$ ,  $-200$ ,  $-297$ , and  $-278 \text{ p.p.m.}$

It follows from the above discussion that at low temperatures a separate  $^{17}\text{O}$  peak due to periodic acid should be observed. An attempt to detect this resonance in a solution containing 2 *m*  $\text{H}_5\text{IO}_6$  and 4 atom %  $^{17}\text{O}$  between 0 and  $5^\circ$  was unsuccessful. This failure may be due to the great width and therefore low intensity of the resonance line, which is made particularly difficult to detect when it is in the proximity of the intense water  $^{17}\text{O}$  peak. Similarly one would expect to observe a separate resonance for the  $\text{IO}_4^-$  ion in the solutions containing 1 equiv. of  $\text{LiOH}$ . Again such an experiment at room temperature was unsuccessful, probably for the same reasons as above. In these experiments various values of radiofrequency power and modulation fields were tried.

## Discussion

The n.m.r. results give the rate of the isotopic exchange of oxygen between periodate and water. For periodic acid the reaction is



and similar equations may be written for the other periodate species. The results do not, however, yield direct information about the mechanism through which the oxygen exchange proceeds.

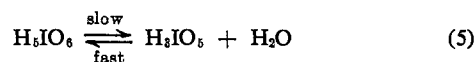
Several mechanisms have been proposed to explain the kinetics of oxygen exchange of oxy anions.<sup>1</sup> For oxy anions that are derived from small and highly charged central atoms the reaction is usually catalyzed by acids, and in some cases also by nucleophilic reagents such as chloride ions. Examples are  $\text{ClO}_3^-$ ,<sup>15</sup>

(14) B. N. Figgis, R. G. Kidd, and R. S. Nyholm, *Proc. Roy. Soc. (London)*, **A269**, 469 (1962).

(15) T. C. Hoering, F. T. Ishimori, and H. O. McDonald, *J. Am. Chem. Soc.*, **80**, 3876 (1958).

$\text{BrO}_3^-$ ,<sup>11</sup> and  $\text{NO}_3^-$ .<sup>11</sup> It has been suggested<sup>11,15,16</sup> that the oxygen exchange of these oxy anions proceeds *via* a bimolecular nucleophilic attack (of water or chloride ions) on the protonated species:  $\text{H}_2\text{ClO}_3^+$ ,  $\text{H}_2\text{BrO}_3^+$ , and  $\text{H}_2\text{NO}_3^+$ .

In oxy anions of larger central atom the rate of oxygen exchange is more likely controlled by the rate of elimination of water molecules from the oxy anions. Thus, the relatively fast oxygen exchange of iodate, which is assumed to exist in water mainly as  $\text{H}_2\text{IO}_4^-$ , has been suggested<sup>11</sup> to proceed *via* the rapid equilibrium,  $\text{H}_2\text{IO}_4^- \rightleftharpoons \text{IO}_3^- + \text{H}_2\text{O}$ . The high rate of oxygen exchange observed in periodic acid and the fact that the reaction is not catalyzed by chloride ions (an effective catalyst in the exchange of bromate and nitrate) indicate that this exchange also proceeds *via* a monomolecular dissociation reaction



This is similar to the mechanism for the dehydration of  $\text{H}_4\text{IO}_6^-$  given by Kustin and Lieberman,<sup>5</sup> who suggested that the dissociation of the water molecule is assisted by hydrogen bonding to the solvent water.

It is plausible to assume that the oxygen exchange of telluric and xenic acids also proceeds *via* a dissociative mechanism. The relatively fast oxygen exchange of these compounds, *via* a dissociative rate-determining step, may be understood by considering the nature of the central atom–oxygen bond. Tellurium, iodine, and

(16) T. C. Hoering, R. C. Butler, and H. O. McDonald, *J. Am. Chem. Soc.*, **78**, 4829 (1956).

xenon occupy the fifth row of the periodic table and are the largest nonmetallic elements that form oxy compounds. Owing to their large radii, these elements may form compounds of high coordination number, and it is in these compounds that the oxygen exchange was found to be fastest. Interatomic-distance data for the I–O bond in oxygen–iodine compounds have been quoted and discussed by Pauling.<sup>17</sup> The I–O bond in the octahedral ( $\text{IO}_6$ ) configuration was shown to have a small amount of double bond character. It is, however, much less than in the I–O bond of the tetrahedral iodine compounds or in X–O bonds of the other nonmetallic oxy compounds with low coordination number. The high lability of the I–O bond in periodate may thus be associated with the relatively weak double bond character of the octahedrally coordinated iodine. Similar arguments hold for tellurate and xenate. On these grounds it may be expected that oxygen exchange of perxenic acid [ $\text{Xe}(\text{OH})_6$ ] with water will be even faster than for xenic acid.

Generally, the rate of exchange in a series of isoelectronic oxy compounds decreases as the charge of the central atom increases.<sup>1</sup> It is interesting to note that the contrary is observed on comparing the rates of oxygen exchange of periodic acid and its isoelectronic neighbor in this series,  $\text{Te}(\text{OH})_6$ ; apparently the rule does not apply to oxy compounds of large central atoms in their high coordination state where the nature of the X–O bond is altered to a great extent.

(17) L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1948, Chapter 7.

## A New Boron Hydride, $\text{B}_8\text{H}_{18}$ <sup>1</sup>

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*A new unstable hydride of boron has been prepared by treatment of tetramethylammonium triborohydride-8 with polyphosphoric acid. A number of physical and chemical properties are reported for the compound. Two possible structures are suggested with some preference for a model based on linkage of two  $\text{B}_4\text{H}_9$  units through a B–B bond.*

The reaction to triborohydride ion with polyphosphoric acid has previously been shown to yield a number of boron hydrides; in particular, it constitutes a useful preparative method for tetraborane-10 and hexaborane-12.<sup>2</sup> This reaction has now been shown to yield octaborane-18 as a trace product.

Unlike the recently discovered octaborane-12,<sup>3,4</sup> the existence of which had been indicated by mass

(1) Studies of Boranes. XVII; for paper XVI of this series, see R. Schaeffer, Q. Johnson, and G. Smith, *Inorg. Chem.*, **4**, 917 (1965).

(2) D. F. Gaines and R. Schaeffer, *ibid.*, **3**, 438 (1964).

(3) R. E. Enrione, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **86**, 1451 (1964).

(4) R. E. Enrione, F. P. Boer, and W. N. Lipscomb, *Inorg. Chem.*, **3**, 1659 (1964).

spectrographic studies,<sup>5,6</sup> there are no previous reports of an octaborane having as high a hydrogen content as octaborane-18. An octaborane thought to be octaborane-14 and its n.m.r. spectrum were reported to be among the products of the discharge reaction of diborane.<sup>7</sup> It has recently been suggested that the substance isolated in 1933 by Burg and Schlesinger was probably  $\text{B}_9\text{H}_{15}$  rather than an octaborane as originally suggested.<sup>8,9</sup>

### Experimental

*Preparation and Isolation of Octaborane-18.* The reaction of tetramethylammonium triborohydride with polyphosphoric acid was carried out in exactly the

(5) I. Shapiro and B. Keilin, *J. Am. Chem. Soc.*, **76**, 3864 (1954).

(6) I. Shapiro, C. O. Wilson, J. F. Ditter, and W. J. Lehman, "Advances in Chemistry Series, No. 32, R. F. Gould, Ed., American Chemical Society, Washington, D. C., 1961, p. 127.

(7) J. F. Ditter, H. B. Landesman, and R. E. Williams, National Engineering Science Co., Pasadena, Calif., Technical Report AF04 (611)5156, 1961.

(8) A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **55**, 4009 (1933).

(9) A. B. Burg and R. Kratzer, *Inorg. Chem.*, **1**, 725 (1962).