Barrer[1] have speculated that nitrite and nitrate ions result from the reaction of NO_2 with residual intracrystalline water to produce HNO_2 and HNO_3. Although such a reaction may be the source of protons and nitrite ions, it does not appear to be the major source of nitrate ions, since (a) the disproportionation reaction on decationated zeolites produced SiOH groups, but very few nitrate or nitrite ions, and (b) very few SiOH groups were produced when 0.2 molecule per cage of NO_2 was adsorbed on CaY. At this NO_2 level the nitrate ion concentration was comparable to that from the disproportionation reaction.

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Oxygen-17 Nuclear Magnetic Resonance and Oxygen Exchange in Aqueous Solutions of Iodate

R. A. Dwek, Z. Luz,*[1] S. Peller, and M. Shporer

Contribution from the Isotope Department,
The Weizmann Institute of Science, Rehovot, Israel.
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Abstract: Oxygen-17 nmr measurements on aqueous solutions of $LiIO_3$ are reported. The iodate resonance, having a line width $1/T_2 = 995 \pm 20$ sec^{-1}, lies 206.4 ± 1 ppm downfield from the solvent $H_2{}^{17}O$ line. Relative intensity, as well as shift, measurements indicate that the iodate is present as IO_3^- in the solution. Addition of acid results in line broadening of both the iodate and water resonances due to oxygen exchange with the solvent water. Analysis of the results indicates that in addition to the first-order acid-catalyzed exchange reaction studied previously there is a second-order oxygen-exchange reaction (with respect to acid) which predominates when $[H^+]$ is above 0.1 M. This reaction involves presumably the double-protonated iodate, and its rate law is rate = $k[IO_3^-][H^+]^2$, with $k = 1.5 \pm 0.5 \times 10^6$ sec^{-1} M^{-2}.

A number of experimental findings have suggested that the iodate ions in aqueous solution are strongly hydrated. For example, the ionic mobility of iodate is significantly lower than the value expected from comparison with the ionic mobilities of chlorate and bromate.[2] Also, the acid-catalyzed isotopic oxygen-exchange rate of iodate is much higher than that of chlorate and bromate and, contrary to the latter, is also general-base catalyzed.[3] These observations brought Anbar and Guttmann to propose that the iodate ion in solutions exists mainly in the hydrated form $H_2IO_4^-$ through the equilibrium

$$IO_3^- + H_2O \rightleftharpoons H_2IO_4^- \qquad (1)$$

Oxygen-17 nmr (omr) seems to be an ideal tool[4] to study this problem, since the resonance signal of the iodate can be directly observed.[5] In this paper we report the results of such a study and show that the *dominant iodate species in aqueous solutions is* IO_3^-. It is also shown that at high acid concentration oxygen exchange between water and iodate becomes sufficiently fast to affect the omr line width of both the water and IO_3^- resonances. The kinetics of this reaction is studied and it is found that in addition to the reaction studied by Anbar and Guttmann[3] there is an additional reaction, second order with respect to acid, which dominates the exchange rate at high acid concentrations.

Experimental Section

$LiIO_3$ and $HClO_4$ were obtained as the purest available grades from Alfa Inorganic Chemicals and Fluka Chemicals, respectively. The $LiIO_3$ was dried in a vacuum oven at 60° for 10 hr. Water enriched with ^{17}O was obtained from the Institute's enrichment plant and distilled before use. Omr measurements were carried out on a Varian DP-60 nmr spectrometer operating at 8.13 MHz. For the relative intensity as well as for the shift measurements, the absorption mode was recorded using the side band of a 2-kHz field modulation. For the kinetic measurements, both the absorption mode and the derivative of the absorption mode were used. Appropriate corrections were applied to account for broadening due to saturation and modulation effects.

Acidified aqueous solutions were prepared by adding, using a micropipet, small amounts of either a 2.50 or 12.5 M $HClO_4$ solution to the $LiIO_3$ solutions.

Results and Discussion

(a) Description of Omr Spectrum and Identification of the Iodate Species. The omr spectrum of a neutral solution of $LiIO_3$ consists[5] of two resonances, the bulk water line and the line due to iodate, lying at -206.4 ± 1 ppm (relative to solvent water) with width of 317 ± 5 Hz. The iodate signal can be observed immediately after preparation of the solution. Its shift was found to be independent of temperature and $LiIO_3$ concentration. In order to identify the iodate species, *i.e.*, whether it is IO_3^- or $H_2IO_4^-$, two experiments were performed. One consisted of direct intensity measurements of the water and the iodate signals and the other involved measurements of the difference in the chemical shift of the solvent water line under conditions of slow and fast exchange, respectively.

(i) Intensity Measurements. These measurements were performed using the high-frequency side-band

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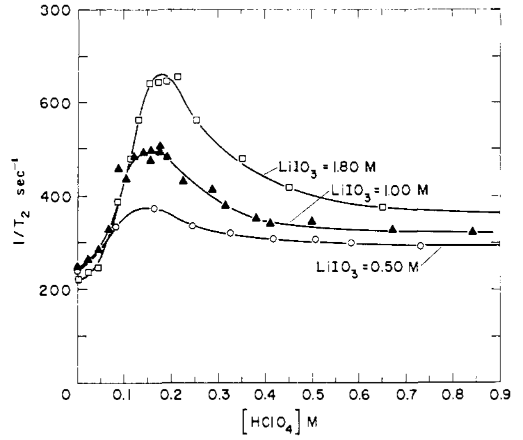

Figure 1. The observed $1/T_2$ of the water ^{17}O signal in $LiIO_3$ solutions as function of added $HClO_4$ (temperature 25 ± 2°).

absorption mode on a neutral solution of $LiIO_3$ (1.6 *M*) in water having the oxygen isotopic composition 45.91 atom % ^{16}O, 11.50 atom % ^{17}O, 42.49 atom % ^{18}O, and normalized to the natural abundance of hydrogen. The exact mole ratio [iodate]/[water] was 32.9 and the expected relative intensity of the iodate-to-water signal was thus 11.0 if the iodate were present as IO_3^- and 8.0 if it were $H_2IO_4^-$. The experimental relative intensity was taken as the product of the height times the width of the corresponding absorption signals. Since the two resonances were recorded at different gains, proper calibrations of the spectrometer were made. Each spectrum was run at least six times and the final result for the relative intensity was 10.3 ± 1.5.

(ii) Shift Measurements. As will be shown below, addition of $HClO_4$ catalyzes oxygen exchange between water and iodate. If the acid concentration is high enough, this exchange becomes sufficiently fast to average out completely the resonances of the water and the iodate. The combined resonance is then shifted to low field relative to the water line, in solution where no exchange takes place, by an amount

$$\Delta = \delta\frac{n[\text{iodate}]}{[\text{water}] + n[\text{iodate}]}$$

where δ is the chemical shift between iodate and water and n is either 3 or 4, depending on whether the iodate species is IO_3^- or $H_2IO_4^-$. In practice, the iodate solution described above for the intensity measurements was divided into two equal parts. Concentrated $HClO_4$ was added gravimetrically to one of the parts to make it ~0.5 *M* in $HClO_4$, which is sufficient to cause complete averaging of the water and iodate lines (*vida infra*). Taking into account the amount of water present in the concentrated $HClO_4$ and the fact that $HClO_4$ causes a slight low-field shift of the bulk water line (~4 Hz for 0.5 *M* $HClO_4$),[6] Δ is calculated to be 140 and 185 Hz for IO_3^- and $H_2IO_4^-$, respectively. Experimentally, Δ was determined as follows. Low-frequency (300–500 Hz) modulation was applied and one of the side bands, together with the main resonance of the water in either the neutral or the acidified solution, was recorded. Then, without stopping the field sweep, the solutions were changed fast enough to record the other side band. This procedure was repeated many times with several variations, sweeping alternately to high field and low field, and changing the order of the solutions. The difference between the side bands and the central band gave a direct measure of Δ. The result was $\Delta = 135 \pm 10$ Hz.

We believe that both the relative intensity and the shift measurements indicate unequivocally that the iodate is predominantly present in the solution as IO_3^-, and our kinetic results described below are treated accordingly.

(b) Effect on the Omr of Addition of Acid and Kinetic Measurements. The addition of small amounts of acid to iodate solutions resulted in the line broadening of both the iodate and water omr signals. Detailed line-broadening measurements could only be made on the water signal, since the iodate signal was washed out completely when the acid concentration exceeded about 0.05 *M*. The dependence of the water $1/T_2$ on $HClO_4$ concentration for three solutions containing different amounts of $LiIO_3$ is shown in Figure 1. As may be seen in each case, the line first broadens and then narrows again after passing through a maximum. The maximum increase in the line width is roughly proportional to the iodate concentration and occurs at about the same acid concentration in all three solutions. Addition of HCl had the same effect, and it was found to be reversible by addition of equivalent amounts of base (NaOH).

This behavior is no doubt due to oxygen exchange between iodate and water and can be interpreted quantitatively to give the kinetics and rate of the reaction. However, although the general behavior shown in Figure 1 was always obtained, the exact line width results were not completely reproducible, particularly at acid concentrations above about 0.3 *M*. In this range, the line-width results appeared to depend on the freshness of the solutions, the width being broader in the older solutions. This effect is most probably due to polymerization reactions, which are known to occur in solutions of iodic acid.[2,7] The quantitative results reported below are for fresh solutions measured on the day of preparation.

Since the fraction of oxygen in iodate is small compared with that in water, we may use Swift and Connick's[8] equation for the interpretation of the line-broadening effect

$$\frac{1}{P}\left(\frac{1}{T_2} - \frac{1}{T_2^0}\right) = \frac{1/T_{2M}(1/T_{2M} + 1/\tau) + \delta^2}{\tau(1/\tau + 1/T_{2M})^2 + \tau\delta^2} \qquad (2)$$

where $1/T_2^0$ and $1/T_{2M}$ are the line widths of water and iodate in the absence of exchange, τ is the mean lifetime of the oxygen in iodate, and P is the fraction of oxygen in iodate. For the derivation of $1/\tau$, the observed line widths were compared with a theoretical plot of $(1/T_2 - 1/T_2^0)/P$ *vs.* $1/\tau$ calculated from eq 2 using $\delta = 10{,}500$ rads sec^{-1} and $1/T_{2M} = 995$ sec^{-1}. In the analysis, P was taken as 3[iodate]/[water] and $1/T_2^0$ was taken in each series as the value of $1/T_2$ at the point where $[HClO_4] = 0$. As indicated above, quantitative interpretation was made only up to 0.3 *M* acid. In a few cases the rate was also determined from the broadening of the iodate resonance. The results were in

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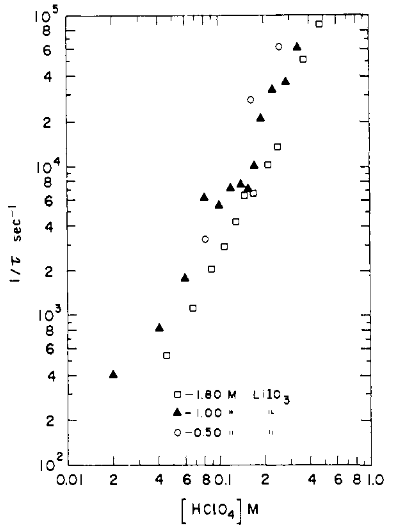

Figure 2. Observed specific rate of oxygen exchange of IO_3^- as function of acid concentration derived from the results of Figure 1. The results were calculated fom eq 2.

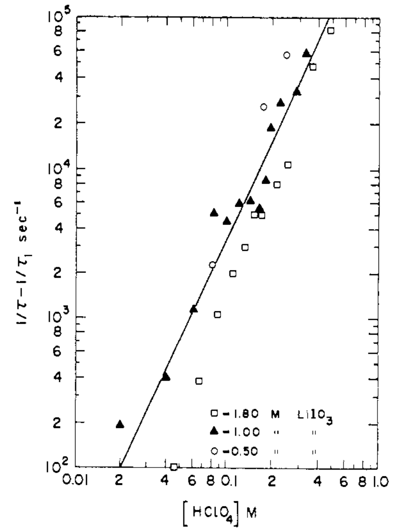

Figure 3. Net specific rate of oxygen exchange after subtracting the contribution of the first-order reaction as explained in the text. The slope of the line is 2.18.

agreement with those obtained from the corresponding water signals. The results for $1/\tau$ are plotted in Figure 2 *vs.* acid concentration on a log–log plot. It is obvious that the main contribution to the broadening cannot come from the first-order acid-catalyzed oxygen-exchange reaction studied by Anbar and Guttmann;[3] the observed rate is much too high and the order of the reaction is larger than one. The contribution of the first-order reaction to $1/\tau$ is given by

$$1/\tau' = 3.23/3 \times 10^4[\mathrm{HClO_4}]\ \mathrm{sec}^{-1} \qquad (3)$$

where 3.23×10^4 is the rate constant for the first-order reaction in M^{-1} sec^{-1}. Subtracting this contribution from $1/\tau$ and plotting log $(1/\tau - 1/\tau_1)$ as function of log [$HClO_4$] gives the results shown in Figure 3.

Although there is a considerable scatter of the individual points, the overall picture is quite satisfactory, considering the fact that the rates extend over almost three orders of magnitude. The order of the reaction with respect to acid is obtained from the slope of the log–log plot in Figure 3 and found to be 2. (The slope of the line drawn in the figure is 2.18.) Within our experimental accuracy, the reaction is first order with respect to IO_3^-, although it appears that the rate constant decreases at high iodate concentration. Formally this reaction may be written as

$$IO_3^- + 2H_3O^+ \overset{k}{\rightleftharpoons} IO_3^-(H_3O^+)_2 \qquad (4)$$

Its rate constant is related to $1/\tau$ by

$$1/\tau - 1/\tau_1 = (k/3)[H_3O^+]^2 \qquad (5)$$

The exact value of k is subject to considerable error, but from the results for the solutions containing 1.0 and 1.8 M $LiIO_3$ its value is estimated to be $= 1.5 \pm 0.5 \times 10^6\ M^{-2}$ sec^{-1}.

The first-order acid-catalyzed reaction proceeds most likely *via* the hydration equilibrium

$$IO_3^- + H_3O^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_3IO_4 \qquad (6)$$

with $k_{-1} \gg k_1$, while the second-order reaction involves a second protonation of the iodate. However, the identity of this doubly protonated species is not clear; it might, *e.g.*, be $H_6IO_5^+$ or $H_4IO_4^+$. It would be interesting to complement these results by independent kinetic and other measurements of the hydration of iodate.

The effect of temperature was studied on a 1.8 M solution of $LiIO_3$ containing 0.1 M $HClO_4$. At this point (*cf.* Figure 1) increasing the rate should increase the line width significantly. In practice, however, almost no change in the line width was obtained. Upon heating the solution from 28 to 70°, there was an increase in $1/T_2$ of about 40 sec^{-1}, which corresponds (taking into account the effect of temperature on $1/T_2^0$) to an increase in k of only about 40%. It is possible that the small temperature dependence of the nmr line width results from the compensation effect of the dissociation of H_3IO_4 (reverse of reaction 6) with increasing temperature. This will result in a decrease of the effective rate of oxygen exchange.

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