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The Isotopic Exchange of Oxygen between Iodate Ions and Water

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The isotopic exchange of oxygen between iodate ions and water has been studied in the pH range 4.5–10.5. The reaction was found both acid and base catalyzed. The rate of exchange $R = \text{mole l.}^{-1} \text{sec.}^{-1}$ may be expressed by $R = 3.24 \cdot 10^4 (H^+)(IO_3^-) + 1.35 \cdot 10^3 (OH^-)(IO_3^-)$ at 25° . The suggested mechanism of exchange is *via* the reactions: $H_2IO_4^- \rightleftharpoons IO_3^- + H_2O$ and $OH^- + HIO_4^- \rightleftharpoons OH^- + HIO_4^-$. General acid and general base catalysis was observed. The general base catalysis is expressed by the equation $HIO_4^- + B \rightleftharpoons BIO_3^- + OH^-$. The formation of complexes of the type BIO_3^- is postulated where $B = \text{ammonia, pyridine, cyanide, borate, urea, acetate and fluoride}$.

The oxygen exchange reactions between various oxy-anions and water have been studied extensively.¹ Oxy-anion containing halogens were shown to exchange their oxygen atoms with water by processes involving the free acids² or *via* cationic species^{3,4} like $H_2BrO_3^+$ or $H_2ClO_3^+$. In the latter cases it was found that the rate of isotopic exchange between non-protonated oxy-anions and water is negligible. An exception to this generalization is demonstrated by the iodate ion that could not be separated from aqueous solution, even in the alkaline region, without attaining isotopic equilibrium with the solvent.^{3,5} In a careful kinetic investigation it became possible to separate iodate from solution before it had reached isotopic equilibrium with the solvent and to follow the kinetics of this exchange. As this kinetic study was carried out in the neutral pH region, it is unlikely that the species involved in the isotopic exchange of iodate is the conjugate acid of HIO_3 , thus a different mechanism than that indicated for the chlorate and bromate exchange reactions had to be suggested.

Experimental

$LiIO_3$ was recrystallized from water and dried in a vacuum oven at 60° . The salt was then dissolved in H_2O^{18} to form a 1 molar solution. An isotopic equilibrium with the solvent was attained within 1 hr. at room temperature. Aliquots of this solution (0.01–0.25 ml.) were taken by a micro pipet and injected into a small beaker containing 5 ml. of freshly redistilled H_2O^{16} . During injection the water was stirred vigorously by a magnetic stirrer. The pH of the water was adjusted by adding minute quantities of $NaOH$ or $HClO_4$ $m/100$ and was determined after the addition of the $LiIO_3^{18}$ by a Metrohm combined micro electrode Type 125 U with a Metrohm potentiometer type E 148C. After a predetermined interval (1 sec.–30 min.) 5 ml. of 0.5 molar $Ba(ClO_4)_2$ solution in 80% ethanol was poured rapidly into the reaction mixture which was again vigorously stirred. Under these conditions the reaction was quenched within one second by precipitation of $Ba(IO_3)_2$ from the alcoholic solution. In most series the pH of each reaction mixture was individually determined. In fast runs where most of the points were taken within one minute the pH could not be determined for each reaction mixture separately. In these cases several identical reaction mixtures were prepared for pH determination. Each series at a certain pH value consisted of some 12–15 individual points. In spite of the fact

that each reaction mixture was prepared and quenched separately, the kinetic results gave rate constants with a reproducibility of $\pm 5\%$. In a number of series various compounds were introduced into the reaction mixture; the procedure of starting and quenching the exchange were the same as for pure water.

After precipitation the reaction mixture was introduced into a test tube, the $Ba(IO_3)_2$ was separated by centrifuge, washed at 96% ethanol and dried in a vacuum oven. The dry $Ba(IO_3)_2$ was introduced into a Pyrex glass tube of 7 mm. diameter with a standard ground joint and a break off tip. The tube was then evacuated to less than $2 \cdot 10^{-3}$ mm. sealed off and heated in an oven at 400° for 30 minutes. The tube was then opened on the vacuum line of the mass spectrometer and the isotopic ratio of $O_2^{16,18}/O^{16,18}$ was determined. The mass spectrometer used was a CEC Model 402 isotope ratio instrument.

The calculation of the rates of exchange from the mass spectrometric data is described elsewhere.⁶

Determination of the IO_4^- – H_2O Exchange.—One ml. of H_2O^{18} (87% O^{18}) was injected into a vigorously stirred periodate solution (5 ml.). This solution was buffer free and its pH was adjusted as above and determined. Within 5 seconds 2 ml. of saturated KNO_3 solution was injected and KIO_4 precipitated. The precipitate was separated by centrifuge, washed with ethanol, dried and pyrolyzed at 250° in a sealed glass tube as described above.

Results

The results of IO_3^- – H_2O oxygen exchange in non-buffered solutions in the pH range 4.5–10.65 are presented in Table I. The rate constants

TABLE I
THE EFFECT OF pH ON IO_3^- – H_2O EXCHANGE IN NON-BUFFERED SOLUTIONS

pH	$k' = \frac{0.693}{t_{1/2}}$ (l. mole ⁻¹ sec. ⁻¹) $\times 10^{-2}$	$k_{OH^-} = k'/(OH^-)$ (l. mole ⁻¹ sec. ⁻¹) $\times 10^{-2}$
4.5	1.5×10^{-1}	4.78
5.0	8.8×10^{-2}	8.8
6.1	9.2×10^{-3}	11.5
6.4	5.1×10^{-3}	12.7
7.0	1.1×10^{-3}	11.0
7.5	3.2×10^{-4}	10.0
8.3	5.2×10^{-4}	2.6
8.6	2.6×10^{-3}	6.5
9.2	9.6×10^{-3}	6.0
9.3	5.5×10^{-3}	2.75
9.6	1.65×10^{-2}	4.1
10.1	5.8×10^{-2}	4.6
10.65	2.3×10^{-1}	5.15

$k' = 0.693/t_{1/2}$ are plotted against pH in Fig. 1. It may be seen from these data that the rate of exchange is both acid and base catalyzed, and it passes through a minimum at about pH 7.7. The rate of exchange in the pH range investigated follows a first order dependence both in the H_2O^+

(6) A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951.

(1) H. Taube, *Ann. Rev. Nuclear Science*, **6**, 277 (1956); D. R. Stranks and R. G. Wilkins, *Chem. Revs.*, **57**, 743 (1957); D. Samuel and F. Steckel, "Bibliography of the Stable Isotopes of Oxygen," Pergamon Press, New York, N. Y., 1959.

(2) M. Anbar and H. Taube, *THIS JOURNAL*, **80**, 1073 (1958).

(3) T. C. Hoering, R. C. Butler and H. O. McDonald, *ibid.*, **78**, 4829 (1956).

(4) T. C. Hoering, F. T. Ishimori and H. O. McDonald, *ibid.*, **80**, 3876 (1958).

(5) J. Halperin and H. Taube, *ibid.*, **74**, 375 (1952); A. E. Brodsky and N. A. Vysotskaya, *Zhur. Fiz. Khim.*, **32**, 1521 (1958).

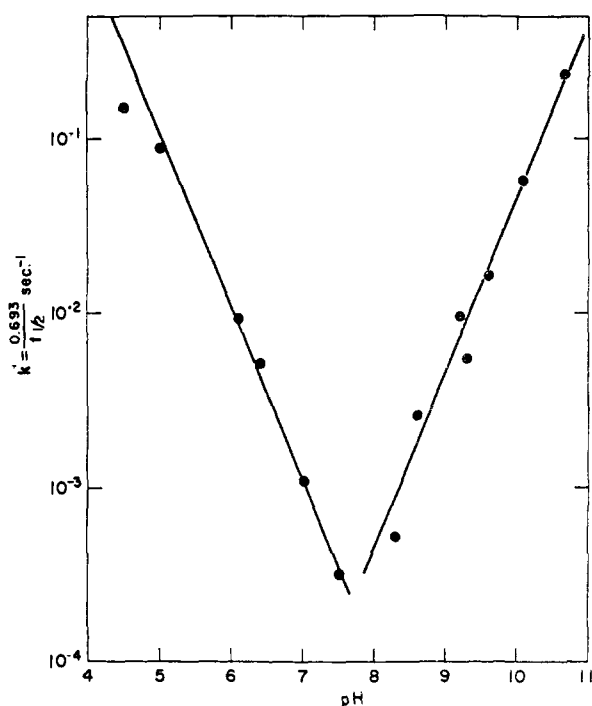


Fig. 1.—The rate of iodate and water oxygen exchange in non-buffered solutions as a function of pH .

and OH^- concentrations. It should be noted, however, that the rate constants in the acid region deviate from the first order law and become less acid dependent below pH 5.

In Table II we may see that there is no effect of iodate concentration on the rate of exchange within experimental error.

TABLE II
EFFECT OF IO_3^- CONCENTRATION

(IO_3^-) mole l. ⁻¹	$k'/(H^+)$ in acid region $\times 10^{-3}$	$k'/(OH^-)$ in alkaline region $\times 10^{-3}$
0.005	14.0	3.3
.015	10.6	4.5
.05	14.8	5.3
.2	12.5	5.0

The rate of exchange was found to be considerably increased in presence of various ions and organic bases. This catalysis is probably the reason why the iodate-water oxygen exchange was considered too fast to be measured. In Table III a typical series of results is presented showing the catalytic effect of ammonia. From the catalytic rate constants $k_c = k' - k_0'$, (k_0' is interpolated for the measured pH from Fig. 1) and from the pK of $NH_3 = 4.75$, it is possible to derive by the least mean squares method two separate specific rate constants for NH_4^+ and NH_3 .

The catalytic specific rate constants for a number of compounds is given in Table IV, each was derived from similar data to those appearing in Table III. In order to obtain specific rate constants from k' these have to be multiplied by a factor of 3 according to the equation

$$R = \frac{3(IO_3^-)(H_2O)}{3(IO_3^-) + H_2O} k' \sim 3k'(IO_3^-) = k(IO_3^-)$$

These specific rate constants were arbitrarily clas-

TABLE III
THE EFFECT OF AMMONIA ON THE RATE OF IO_3^- - H_2O EXCHANGE

pH	(IO_3^-) (mole l. ⁻¹)	(NH_4^+) (mole l. ⁻¹)	$k' \times 10^3$ (sec. ⁻¹)	$k_0' \times 10^3$ (sec. ⁻¹)	$\frac{k' - k_0'}{(NH_4^+)(OH^-)}$ (mole ⁻² l. ² sec. ⁻¹) $\times 10^{-3}$
6.2	0.02	0.04	19.8	6.6	41.5
6.8	.02	.04	17.8	1.8	6.3
6.8	.02	.20	121.0	1.8	9.5
7.1	.02	.06	67.3	1.2	8.8
7.35	.02	.02	26.6	0.5	5.8
7.4	.005	.04	55.4	.45	5.5
7.5	.2	.02	31.4	.35	4.9
7.6	.05	.04	86.7	.3	5.4
7.7	.02	.02	43.4	.3	4.3
8.0	.02	.02	99.0	.6	4.9

TABLE IV
CATALYTIC COEFFICIENTS AT 25° OF VARIOUS COMPOUNDS
IN THE IO_3^- - H_2O EXCHANGE RATE EXPRESSION

Compound (base)	k_{base} (mole ⁻¹ l. sec. ⁻¹)	Compound (acid)	k_{acid} (mole ⁻¹ l. sec. ⁻¹)
OH^-	1350	H_2O	10^{-4}
NH_3	270	NH_4^+	0.9
Pyridine	60
CN^-	45	HCN	0.9
$H_2BO_3^-$	7.5	H_3BO_3	0.6
Urea	5.4
Acetate	2.2	Acetic acid	12.3
F^-	0.09
H_2O	10^{-4}	H_3O^+	3.24×10^4
I^-	10^{-3}
IO_3^-	10^{-3}

sified as acid and base catalysts. From Table IV it may be seen that there is a general base catalysis of exchange. The "basic" catalytic coefficients follow the sequence of increasing base strength of the catalysts; the general acid coefficients follow the sequence of rising acidity.

It is hard, however, to obtain a quantitative correlation between the catalytic specific rate constants and the pK 's of these compounds.

The Rate of Oxygen Exchange between Periodate Ions and Water.—Under the experimental conditions described above, the periodate separated within 5 seconds was found completely equilibrated with the solvent, both at pH 4 and at pH 7. The lower limit of the specific rate of this exchange in non-buffered solutions is therefore 3×10^9 sec.⁻¹.

Discussion

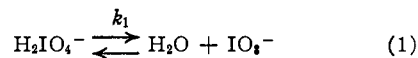
The isotopic oxygen exchange between iodate ions and water, in the pH range 4.5–10.65, is both general acid and general base catalyzed.⁷ Specific acid and base catalysis may, however, also contribute to the exchange reaction. It seems probable that in the neutral pH region there exists a species which does not exchange its oxygen atoms with water at an appreciable rate. Interaction of this species with both acids and bases may induce isotopic exchange with the solvent. A specific acid catalysis may also be postulated, this would mean that the involved species is in equilibrium with

(7) R. P. Bell, "The Proton in Chemistry," Chapter 9, Cornell Univ. Press, New York, N. Y., 1959.

its conjugate acid and that the latter undergoes a rather fast exchange with the solvent; the deviation from first order in H_3O^+ at $\text{pH} \sim 5$ strongly suggests such an equilibrium.

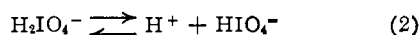
The behavior of iodate ions in solution indicate that it exists mainly in hydrated forms.⁸ The simplest hydrated ion will be the monohydrate H_2IO_4^- . The existence of H_2IO_4^- was also suggested by Taube⁵ to account for the fast isotope exchange with the solvent.⁹

The equilibrium reaction of this ion with IO_3^-



may be a route for oxygen exchange with the solvent. It is assumed that k_{-1} , the rate of hydration of iodate is a very fast reaction, thus the equilibrium constant of reaction 1 is much smaller than unity.

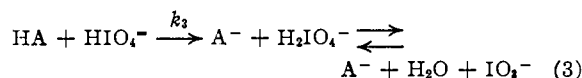
When H_2IO_4^- undergoes dissociation in more alkaline solutions



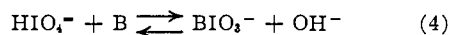
the HIO_4^- formed cannot undergo a spontaneous and reversible dehydration like H_2IO_4^- . The decrease in H_2IO_4^- concentration with rising alkalinity would then be followed by a decrease in the rate of oxygen exchange. The dissociation constant for reaction 2 is unknown, still a roughly estimated value¹⁰ of K_2 10^{-6} can be obtained from the dissociation constant of iodic acid.¹¹ The deviation from the first order law below $\text{pH} 5$ (see Fig. 1) enables one to derive the approximate value of $K_2 = 2 \times 10^{-5}$. Taking the latter value for K_2 , a rate constant for $k_1 = 6.5 \times 10^{-1} \text{ sec.}^{-1}$ may be calculated from $k_{\text{H}_2\text{O}}$ of Table IV.

$$R = 6.5 \times 10^{-1} / \text{H}_2\text{IO}_4^-$$

The general acid catalysis of acetic and other acids may be interpreted as a direct interaction of these acids with HIO_4^-



The general base reaction must be due to a substitution of an OH^- ion in HIO_4^- followed by the formation of a complex.



A reversible reaction of this type may account for the general base catalysis of the exchange. A

(8) N. V. Sidgwick, "The Chemical Elements and their Compounds," Oxford, Press, New York, N. Y., 1960, p. 1229.

(9) In principle it should be possible to determine by methods of isotopic dilution analysis whether iodate really exists in aqueous solution mainly the H_2IO_4^- form, only that the accuracy required on mass spectrometric assay should exceed 0.1%.

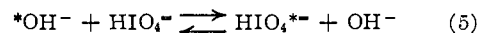
(10) J. E. Ricci, *THIS JOURNAL*, **70**, 109 (1948); J. C. McGonnan, *Chem. and Ind. (London)*, 632 (1948).

(11) S. Nadich and J. E. Ricci, *THIS JOURNAL*, **61**, 3268 (1939). H. v. Halban and J. Brull, *Helv. Chim. Acta*, **27**, 1719 (1949).

general base catalysis in isotopic exchange reactions of oxyanions has been observed also in the case of bromate and nitrate ions.¹² The over-all rate expression for the exchange reaction is therefore

$$R = k_1(\text{H}_2\text{IO}_4^-) + k_a(\text{HA})(\text{HIO}_4^-) + k_b(\text{B})(\text{HIO}_4^-)$$

In the special case of $\text{B} = \text{OH}^-$ we observe a typical bimolecular nucleophilic substitution



The effect of OH^- on the rate of exchange is of double nature, first it decreases the concentration of H_2IO_4^- by reaction 2, and thus it decreases the rate of exchange, but at higher OH^- concentrations reaction 5 becomes predominant and the rate of exchange increases with pH , this accounts for the V shape of Fig. 1.

In the case of other bases the existence of complexes like $\text{NH}_3 \cdot \text{IO}_3^-$, $\text{pyridine} \cdot \text{IO}_3^-$, $\text{CN} \cdot \text{IO}_3^-$, $\text{H}_2\text{BO}_3 \cdot \text{IO}_3^-$, $\text{F} \cdot \text{IO}_3^-$ has to be assumed. It is not only that these bases enter the activated complex, but we have to assume the existence of intermediates of the type BIO_3^- in order to account for the oxygen exchange *via* reaction 4. The ability of iodates to form complexes with amines and various nitrogen bases like pyridine has been experimentally demonstrated.¹³ The fact that iodate catalyses the nucleophilic substitution of Cl^- on ammino complexes of chromium¹⁴ may be due to a complex formation with the amines, making the central atom more vulnerable to a nucleophilic attack. There is no independent evidence for the cyaniodate complex; however, this complex may be considered as another nitrogen base complex. There is also no independent evidence for the borate-iodate complex, but complexes of iodates with phosphates, arsenates, molybdates and tungstates have been studied, as well as borate complexes of tungstates,¹⁵ thus the formation borate-iodate complexes seems rather likely. As for the fluoride iodate complex, this has been recently characterized.¹⁶

The experiments with periodate showed this ion to exchange with water in non-buffered solutions at a rate too fast to enable separation before isotopic equilibrium is completed. This means that periodate exchanges with water at least one thousand times faster than iodate. This fast exchange is probably due to the existence of a variety of polyhydrated and polymeric species in fast equilibrium.

(12) M. Anbar and S. Guttmann, to be published.

(13) A. E. Kretov, *J. Russ. Phys. Chem. Soc.*, **60**, 1427 (1928); *C. A.*, **23**, 2117 (1929). R. Cernatescu and M. P. Poni, *Ann. Acad. Rep. Populare Romane, Ser. Mat. Fiz. Khim.*, **3**, Men. 6 (1950); *C. A.*, **46**, 504b (1952).

(14) M. Ikuta, H. C. Acadie, W. M. Smith, *Can. J. Chem.*, **34**, 1361 (1956).

(15) W. Hüchel, "Structural Chemistry of Inorganic Compounds," Elsevier Publishing Co., Houston, Texas, 1950, pp. 182-184.

(16) A. Ray and G. Mitra, *J. Indian Chem. Soc.*, **35**, 211 (1958).