Oxygen Exchange between Iodate and Water: Catalysis by Hydrogen and Hydroxide Ions

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The ^{18}O-exchange reaction between iodate ions and water has been investigated using a rapid chemical-quenching technique. Over the range $2.1 < pH < 12.5$ the exchange occurs by hydrogen- and hydroxide-ion catalysed paths according to the rate law (i). At 5 °C and $I = 1.0$ mol dm^{-3} (Li[ClO$_4$]) the rate constants are $k_0 < 0.01$ s^{-1},

$$R/[IO_3^-] = k_0 + k_1[H^+] + k_2[H^+]^2 + k_3[OH^-] \qquad \text{(i)}$$

$k_1 = (3.20 \pm 0.11) \times 10^3$ dm^3 mol^{-1} s^{-1}, $k_2 = (1.38 \pm 0.24) \times 10^5$ dm^6 mol^{-2} s^{-1}, and $k_3 = (2.49 \pm 0.16) \times 10^2$ dm^3 mol^{-1} s^{-1} respectively. Activation parameters from data at 5—25 °C are $\Delta H_1^\ddagger = 61.5 \pm 3.8$ kJ mol^{-1}, $\Delta S_1^\ddagger = 43.1 \pm 13.0$ J K^{-1} mol^{-1}, $\Delta H_3^\ddagger = 47.4 \pm 1.7$ kJ mol^{-1}, and $\Delta S_3^\ddagger = -28.3 \pm 5.9$ J K^{-1} mol^{-1}. The following values for the kinetic solvent deuterium-isotope effect were obtained (5 °C) : $k_1^H/k_1^D = 2.1$, $k_2^H/k_2^D = 0.49$, and $k_3^H/k_3^D = 1.7$. The normal isotope effect suggests proton transfer as the rate-determining steps corresponding to k_1 and k_3, whereas the inverse isotope effect on k_2 can be explained by a rapid acid–base pre-equilibrium. These results provide further evidence for associative substitution mechanisms with iodine(V).

THE simple oxygen-exchange reaction between iodate ions and solvent water, (1), is known to play an important

$$H_2{}^*O + [IO_3]^- \rightleftharpoons H_2O + [IO_2{}^*O]^- \qquad (1)$$

role in the mechanisms of redox and substitution reactions involving iodine(V). It is, for example, generally agreed that the rates of redox processes for oxo-anions are correlated with the rates of exchange.[1] However, a meaningful comparison is possible only if the full rate law of reaction (1) is evaluated, since exchange occurs frequently by different paths.[2] Recently, rapid complex formation between iodate ions and substitution-inert aquametal ions has been discovered.[3] These reactions, (2), are stoicheiometrically very similar to the exchange

$$[M(OH_2)_6]^{3+} + [IO_3]^- \rightleftharpoons [M(OH_2)_5(IO_3)]^{2+} + H_2O \qquad (2)$$

process, differing only in that the water molecule is already co-ordinated to a metal. The high rates of (2) indicate that substitution takes place at I^V, while the metal–oxygen bonds remain intact. Clearly, precise information about the rates of reaction (1) are relevant to any mechanistic discussion of the complex formation (2). Oxygen exchange in the system $[IO_3]^-$–H_2O has been investigated quantitatively by Anbar and Guttmann[4] using a conventional oxygen-18 tracer technique. The rates observed at $4.5 < pH < 10.5$ have been fitted to the rate equation (3). Moreover, general acid and

$$\text{Rate}/[IO_3^-] = k_a[H^+] + k_b[OH^-] \qquad (3)$$

general base catalysis have been assumed. Considering the fast exchange rates reported,[4] it seemed somewhat risky to rely on the conventional approach, and in fact preliminary experiments[5] showed that it is rather difficult to obtain reproducible results with this technique. With an oxygen-17 n.m.r. method Dwek *et al.*[6] found an additional rate term proportional to $[H^+]^2$ predominating at hydrogen concentrations above 0.1 mol dm^{-3}. Even with this method it was not possible to determine the activation parameters. For a detailed kinetic investigation of reaction (1) it seemed most promising to combine oxygen-18 labelling with rapid chemical quenching, since instruments for the latter technique are now commercially available. In this work we have attempted to determine the rate law, the activation parameters, and the solvent isotope effect of the iodate–water exchange reaction (1). Catalysts other than H^+ and $[OH]^-$ have been carefully excluded.

EXPERIMENTAL

Materials.—Lithium iodate and lithium perchlorate were prepared from lithium carbonate and iodic acid and perchloric acid respectively. Stock solutions were either carefully freed from protolytic impurities as described earlier,[7] or recrystallised samples were used. High-purity oxygen-18 labelled water (5% ^{18}O, 0.5% ^{17}O, 0.15% D) and D_2O (99.97% D, 6.55% ^{18}O) were obtained from the isotope separation facilities of the E.I.R. Water with normal isotopic composition was double distilled using an all-quartz apparatus.

Procedure.—Solutions of the general composition S_1 $\{[IO_3^-]_T = a,\ [H^+]_T = h,\ [Li^+] = (1.0 - h),\ [ClO_4^-] = (1.0 - a)$ mol dm$^{-3}\}$ or S_2 $\{[IO_3^-]_T = a,\ [OH^-] = b,\ [Li^+] = 1.0,\ [ClO_4^-] = (1.0 - a - b)$ mol dm$^{-3}\}$ were mixed rapidly with equal volumes of labelled water (5% ^{18}O) containing solution S_3 ($[Li^+] = [ClO_4^-] = 1.0$ mol dm^{-3}). Atmospheric carbon dioxide was excluded by passing pure nitrogen through S_1, S_2, and S_3. After preselected time intervals the exchange reactions were quenched by rapid addition of 0.1 mol dm^{-3} Ag[NO$_3$]. For individual runs *ca.* 10 mg of Ag[I*O$_3$] were collected for mass-spectrometric analysis. Alkaline reactant solutions ($S_2 + S_3$) required a slightly acid Ag[NO$_3$] reagent so as to avoid coprecipitation of Ag_2O.

The mixing and quenching procedure was carried out using a Durrum D-132 Multi-Mixing-System. With this equipment reaction time intervals can be continuously varied from 2×10^{-2} to 11 s. The Ag[I*O$_3$] precipitate was centrifuged and washed carefully with water, ethanol, and acetone. After drying *in vacuo*, the Ag[I*O$_3$] was pyrolysed

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[4] M. Anbar and S. Guttmann, *J. Amer. Chem. Soc.*, 1961, **83**, 781.

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[7] H. Gamsjäger, W. Kraft, and P. Schindler, *Helv. Chim. Acta*, 1970, **53**, 290.

to give oxygen gas which was isotopically analysed with a cycloidal CEC 21-620 A mass spectrometer. The mass spectra of the isotopic oxygen molecules were scanned three times in order to reduce the errors in peak-height measurements to less than 0.5%. Since the pyrolytic decomposition was complete, isotope fractionation was negligible, and the isotopic compositions of the oxygen produced and of the parent $Ag[I^*O_3]$ were assumed to be identical. Exchange rates were measured at 4—6 different time intervals.

Calculation of Results.—Actual hydrogen-, hydroxide-, and iodate-ion concentrations were calculated from the analytical compositions of solutions S_1, S_2, and S_3 and the appropriate pK values of iodic acid.[8] The mole fractions, x, of ^{18}O in the gaseous samples submitted to mass-spectrometric analysis were calculated [9] from peak heights at m/e 32—36. The rate of reaction (1) leading to isotopic exchange was calculated from the McKay [10] expression (4a)

$$R = \frac{3[IO_3^-]_T[H_2O]}{3[IO_3^-]_T + [H_2O]} \cdot \frac{1}{t} \ln \frac{x_\infty - x_0}{x_\infty - x_t} \qquad (4a)$$

where R is the rate of oxygen transfer between H_2O and $[IO_3]^-$ in mol dm^{-3} s^{-1}, t is the time in s, and x_0, x_t, and x_∞ are the mole fractions of ^{18}O in iodate at times $t = 0$, t = time of quenching, and $t = \infty$ (at exchange equilibrium). Since under the conditions studied $[IO_3^-]_T$ was small compared to $[H_2O]$, equation (4a) reduces to (4b). The equilibrium

$$R/[IO_3^-]_T = k_{obs.} = \frac{3}{t} \cdot \ln \frac{x_\infty - x_0}{x_\infty - x_t} \qquad (4b)$$

fractionation factor, α, of $^{18}O/^{16}O$ in the system $[IO_3]^-$–H_2O was calculated previously [11] and found to be smaller than 1.03 between 0 and 100 °C; consequently equation (4b) was applied without further correction. Regression analysis of all the data was performed on an HP 2000 A time-sharing-system computer. Errors in rate constants and activation parameters are standard deviations.

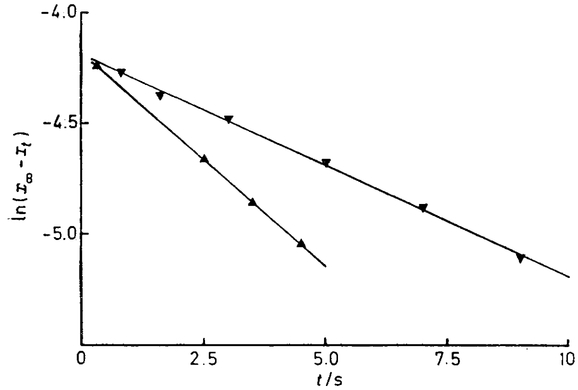

FIGURE 1 McKay plots for the oxygen exchange in the system $[IO_3]^-$–D_2O, at 5 °C and I = 1.0 mol dm^{-3} (Li[ClO$_4$]). $[OD^-]$ = 1.97 × 10^{-3} (▼) or 4.00 × 10^{-3} mol dm^{-3} (▲)

RESULTS

Plots of ln $(x_\infty - x_t)$ against time were linear up to 85% completion of exchange. After two half-lives, larger scattering was observed; therefore only data measured at $t < 2t_{\frac{1}{2}}$ have been included in the calculation of rates. Typical McKay plots are shown in Figure 1. Relative exchange rates, $k_{obs.}$ (4b), obtained at 5 °C, are summarised in Table 1. Within experimental error, $k_{obs.}$ was independent of $[IO_3^-]_T$ and was followed over as wide a range of pH as possible, the limit being given by the reaction times accessible. Plots of $k_{obs.}$ against $[H^+]$, shown in Figure 2 (Table 1), exhibited a slight but significant curvature. At higher $[H^+]$ two exchange paths, involving rate terms proportional to $[H^+]$ and $[H^+]^2$ respectively, could be distinguished. In the alkaline range $k_{obs.}$ was a linear function of $[OH^-]$. Data from runs 12—18 of Table 1 fell on a straight line with an intercept not significantly different from zero. Attempts to measure the rate of spontaneous exchange [5] directly in a range where H^+ and $[OH]^-$ catalysis is negligible led only to a rough estimate of the lower limit, $k_{obs.}$ being less than 10^{-2} s^{-1} at 5 °C. The difficulty in obtaining reproducible rates in unbuffered solutions arises from ubiquitous traces of protolytic impurities, which invariably cause general acid or base catalysis of reaction (1). All the data measured at 5 °C and I = 1.0 mol dm^{-3} (Li[ClO$_4$]) (Table 1) are consistent with the three-term rate equation (5), with $k_1 = (3.20 \pm 0.11) \times 10^3$

$$R/[IO_3^-]_T = k_1[H^+] + k_2[H^+]^2 + k_3[OH^-] \qquad (5)$$

TABLE 1

Relative rates of exchange, $k_{obs.}$, in the system $[IO_3]^-$–H_2O at 5 °C and I = 1 mol dm^{-3} (Li[ClO$_4$])

Run	$10^2[IO_3^-]_T$	$10^3[H^+]$	$10^3[OH^-]$	$k_{obs.}$
		mol dm^{-3}		s^{-1}
1	8.00	0.0001		<0.01
2	8.00	0.51		1.53
3	3.00	1.00		2.80
4	8.00	1.00		2.97
5	24.0	1.00		3.20
6	8.00	2.00		6.44
7	8.00	2.81		9.32
8	8.00	3.98		14.9
9	8.00	5.02		20.4
10	8.00	5.63		21.2
11	8.00	7.95		33.7
12	8.00		1.51	0.37
13	3.00		3.00	0.80
14	8.00		3.00	0.82
15	24.0		3.00	0.89
16	8.00		6.15	1.55
17	8.00		9.00	2.23
18	8.00		12.0	2.74

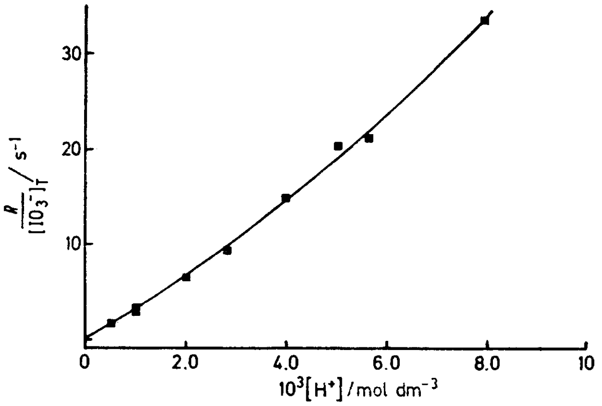

FIGURE 2 Hydrogen-ion dependence of the rate constant $k_{obs.}$ = $R/[IO_3^-]_T$ in water at 5 °C and I = 1.0 mol dm^{-3} (Li[ClO$_4$])

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[11] S. C. Agarwal, P. Baertschi, and H. Gamsjäger, *Helv. Chim. Acta*, 1972, **55**, 2178.

$dm^3 mol^{-1} s^{-1}$, $k_2 = (1.38 \pm 0.24) \times 10^5$ $dm^6 mol^{-2} s^{-1}$, and $k_3 = (2.49 \pm 0.16) \times 10^2$ $dm^3 mol^{-1} s^{-1}$.

In a series of experiments (Table 2) water was replaced by D_2O as solvent. The quotient $k_{calc.}^H/k_{obs.}^D$, where $k_{calc.}^H$ was calculated from equation (5), was a function of $[H^+]$ in the acid range, whereas $k_{calc.}^H/k_{obs.}^D$ was, within the limits of experimental error, independent of $[OH^-]$ in the alkaline range. Numerical evaluation of these results (Table 2) indicates normal and inverse kinetic solvent isotope effects on the rate terms with first- and second-order dependences on $[H^+]$ respectively, while a normal isotope effect was found for the $[OH]^-$-catalysed reaction path. The values at 5 °C are $k_1^H/k_1^D = 2.1$, $k_2^H/k_2^D = 0.49$, and $k_3^H/k_3^D = 1.7$.

The exchange rates were also studied at constant hydrogen- and hydroxide-ion concentrations over the range 5—25° C (Table 3). In order to avoid complications due to fast rates, $[H^+]$ was kept below 1.0×10^{-3} mol dm^{-3}, so that the contribution of the k_2 term to the overall rate was almost negligible. Linear Eyring plots of the rate constants k_1 and k_3 were obtained and the activation parameters computed by regression analysis are $\Delta H_1^\ddagger = 61.5 \pm 3.8$ kJ mol^{-1}, $\Delta S_1^\ddagger = 43.1 \pm 13.0$ J $K^{-1} mol^{-1}$, $\Delta H_3^\ddagger = 47.4 \pm 1.7$ kJ mol^{-1}, and $\Delta S_3^\ddagger = -28.3 \pm 5.9$ J $K^{-1} mol^{-1}$.

TABLE 2

Values of $k_{obs.}$ in the system $[IO_3]^-$–D_2O at 5 °C, $I = 1$ mol dm^{-3} ($Li[ClO_4]$), and $[IO_3^-]_T = 0.080$ mol dm^{-3}

Run	$10^3[D^+]$	$10^3[OD^-]$	$k_{obs.}$	$k_{calc.}^H/$ $k_{obs.}^D$
	mol dm^{-3}		s^{-1}	
19	1.00		1.45	2.30
20	5.02		15.3	1.28
21	10.0		43.4	1.06
22		1.97	0.30	1.64
23		4.00	0.57	1.75
24		9.56	1.44	1.65

TABLE 3

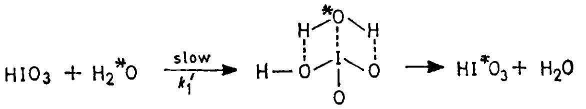
Temperature dependence of $k_{obs.}$ in the system $[IO_3]^-$–H_2O with $I = 1$ mol dm^{-3} ($Li[ClO_4]$) and $[IO_3^-]_T = 0.080$ mol dm^{-3}

Run	$10^3[H^+]$	$10^3[OH^-]$	$k_{obs.}$	T
	mol dm^{-3}		s^{-1}	K
25	1.00		4.87	283.15
26	1.00		8.32	289.55
27	1.00		13.4	292.85
28	1.00		16.3	297.05
29		1.51	0.58	283.35
30		1.51	0.76	287.95
31		1.51	1.11	293.45
32		1.51	1.67	298.55

DISCUSSION

The iodate–water exchange differs from similar processes involving bromate [12,13] or chlorate [14] in that the overall rate equation (5) contains a term first order in the hydrogen-ion concentration. The corresponding activated complex consists of HIO_3 and an unknown number of water molecules. For this exchange path the mechanism in equations (6) and (7) is proposed. The activated complex in reaction (7) is quite similar to that invoked by Sykes and his co-workers [3] for the complexing of iodate with inert aquametal ions (2) assuming associative activation.

$$[IO_3]^- + [H_3O]^+ \underset{K_1}{\overset{fast}{\rightleftharpoons}} HIO_3 + H_2O \qquad (6)$$



(7)

The two-step mechanism leads to a rate equation (8a)

$$R/[IO_3^-]_T = k_{obs.} = k_1'K_1[H_2O][H^+]/(1 + [H^+]K_1) \qquad (8a)$$

which reduces for the prevailing conditions, where $[H^+]K_1 \ll 1$, to (8b). The experimental rate constant k_1

$$R/[IO_3^-]_T = k_{obs.} = k_1'K_1[H_2O][H^+] \qquad (8b)$$

can be identified with $k_1'K_1[H_2O]$. The constant K_1 has been determined previously [8] under essentially the same conditions as used in this work. With the values log K_1-(H_2O) = 0.24 and log $K_1(D_2O) = 0.57$ at 5 °C, and allowing for the influence of the equilibrium constants on the overall kinetic isotope effect, we obtain $k_1'(H_2O)/k_1'(D_2O) = 4.4$. It should be noticed that slightly different standard states have been used in this work and in ref. 8, but this does not alter the essentially qualitative character of the argument. An isotope effect of this magnitude is consistent with proton transfer as the rate-determining step,[15] as implied by the associative mechanism (7). The alternative possibility compatible with the experimental rate equation, dissociative loss of an $[OH]^-$ group, seems rather unlikely since in this case an inverse solvent isotope effect would be expected.[16] Considering the difference in the ionic medium and the pH range studied, the rate constant extrapolated to 25 °C, $k_1 = 1.90 \times 10^4$ $dm^3 mol^{-1} s^{-1}$, agrees remarkably well with the value 3.24×10^4 $dm^3 mol^{-1} s^{-1}$ given by Anbar and Guttmann.[4] Comparison of the $[H^+]$-dependent exchange path and the related complex formation [3] (2) is now possible except that the ionic medium has been made up to 1.0 mol dm^{-3} with $Li[ClO_4]$ and $Na[ClO_4]$ respectively, but this has only a minor influence on the results. The composite rate constants for complex formation [3] exceed k_1 by a factor of *ca.* 5 which is also evidence against a dissociative mechanism; thus the activated complex in (7) gains plausibility. The $[H^+]^2$-dependent path observed at $[H^+] > 5 \times 10^{-3}$ mol dm^{-3} seems to be a common feature of halogenate(V) oxygen-exchange reactions.[6,12-14] In each case [12-14] inverse kinetic solvent isotope effects due to acid–base pre-equilibria were detected. The reactions of bromate [17] and iodate [18] with iodide show a similar $[H^+]^2$ dependence suggesting $[H_2XO_3]^+$ to be the reactant species.

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Since the value obtained by Luz and his co-workers [6] and our value for k_2 are related to different temperatures and ionic media, a straightforward comparison is not possible, nevertheless it is tempting to estimate the activation enthalpy $\Delta H_2^\ddagger$ from k_2 at 5 and 25 °C. The resulting figure $\Delta H_2^\ddagger = 80.0$ kJ mol^{-1}, however crude, is not unreasonable and compares well with $\Delta H_2^\ddagger = 74.5$ kJ mol^{-1} for the $[H^+]^2$-catalysed bromate–water exchange.[13] Similar mechanisms seem to be operative in the $[H^+]^2$-dependent oxygen-exchange reactions of the systems $[BrO_3]^-$–H_2O and $[IO_3]^-$–H_2O.

An $[OH]^-$-catalysed exchange path has been found previously with iodate [4] and bromate.[13] Again our rate constant at 25 °C, 1.0 mol dm^{-3} Li[ClO$_4$], and in water as solvent, $k_3 = 1.05 \times 10^3$ dm^3 mol^{-1} s^{-1}, agrees better than expected with the value 1.35×10^3 dm^3 mol^{-1} s^{-1} reported earlier.[4] The normal kinetic solvent isotope effects on k_3 in the iodate and bromate systems are numerically comparable suggesting similar mechanisms. Thus, the $[OH^-]$-dependent exchange is tentatively described as an associative reaction between iodate and $[OH]^-$, with proton transfer as the rate-determining step.

A spontaneous exchange path involving only $[IO_3]^-$ and water could not be demonstrated unambiguously, but if existing the rate constant k_0 (5 °C) should fall within the range 10^{-2}—10^{-4} s^{-1}. The upper limit results from experiments as discussed above, while the lower limit was derived from minimising equation (5), taking the ionic product of water [19] at 5 °C and $I = 1.0$ mol dm^{-3} (Li[ClO$_4$]) to be $10^{-14.46}$. Now, following the treatment of Kurz,[20] the virtual acidity constant $K_a^\ddagger$ of the activated complex (7) can be calculated using equation (9).

$$\mathrm{p}K_a^\ddagger = \log (k_1/k_0) \qquad (9)$$

Although the result, $5.5 < \mathrm{p}K_a^\ddagger < 7.5$, is rather speculative, the corresponding hydrated species are indeed expected to be weaker Brønsted acids than HIO_3.[21]

Not enough information is available to discuss systematically activation parameters of halogenate(v)–water exchange reactions. In the present case at least, the overall activation parameters $\Delta H_1^\ddagger$ and $\Delta S_1^\ddagger$ are separable into the enthalpy and entropy of reactions (6) and (7). With ΔH_6 and ΔS_6 obtained previously,[8] the calculation results in $\Delta H_7^\ddagger = 55.2$ kJ mol^{-1} and $\Delta S_7^\ddagger = 15.8$ J K^{-1} mol^{-1}. No discrimination [22] between associative and dissociative mechanisms is feasible with $\Delta S^\ddagger$ in the range ±42 J K^{-1} mol^{-1}. Moreover, the true value of $\Delta S^\ddagger$ depends on the experimentally unknown number of water molecules entering the transition state.[13] While $[OH^-]$ and $[H^+]^2$ catalysis has been encountered with other halogenate(v)–H_2O exchange reactions, the $[H^+]$-dependent path only occurs in the system $[IO_3]^-$–H_2O. Although much more information is desirable, it already seems justified to assign an associative mechanism with proton transfer as the rate-determining step to this reaction path.

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