83. Kinetics of Oxygen Exchange in the System BrO_3^- - H_2O (D_2O)

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Summary. The kinetics of oxygen exchange between water (H_2O, D_2O) and ^{18}O-labelled bromate ion has been investigated over the range of $1.7 \leq pH \leq 14.3$ and $20 \leq °C \leq 95$. At 60° and ionic strength $I \simeq 1.0$ M ($NaNO_3$), the experimental results were consistent with the rate laws (R in mol l^{-1} s^{-1}):

$$R = [BrO_3^-]\{1.59 \cdot 10^{-6} + 8.1 \cdot 10^{-7}[OH^-] + 0.122[H^+]^2\} \text{ in } H_2O \text{ and}$$

$$R = [BrO_3^-]\{4.69 \cdot 10^{-7} + 4.1 \cdot 10^{-7}[OD^-] + 0.378[D^+]^2\} \text{ in } D_2O.$$

From the temperature dependence of the rate constants the activation parameters $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta C^{\neq}$ were derived.

In the acid-catalysed region the form of the rate law and the direction of the solvent isotope effect were the same as previously found, but the numerical values of $\Delta H^{\neq}$ and k_{2H}/k_{2D} differ considerably. For the spontaneous and the OH^--catalysed exchange reactions bimolecular displacement mechanisms are proposed.

1. Introduction. – The isotopic exchange of oxygen between bromate ions and water according to the reaction

$$Br^{18}O_3^- + 3H_2{}^{16}O \rightleftarrows Br^{16}O_3^- + 3H_2{}^{18}O \qquad (A)$$

has been investigated extensively in the range pH ≤ 2.5 [1] [2], but apparently no attempt has been made to extend the exchange experiments to neutral or alkaline solutions. According to the rate laws and activation energies found by *Hoering et al.* [1] and *Anbar et al.* [2], the exchange reaction (A) at pH ≥ 7 and at 100°C would be expected to have a half-time of exchange $> 10^7$ years and to be nearly twice as fast in D_2O as in H_2O. In contradiction to this extremely low extrapolated rate, ^{18}O-tagged potassium bromate (a convenient reagent for preparing ^{18}O-enriched O_2), can be prepared simply by refluxing potassium bromate with ^{18}O-enriched water for six to ten days [3]. Preliminary experiments by *Marsel* [4] indicated that in neutral solutions at about 100° the half-time of reaction (A) is about 10 hours in H_2O and 24 hours in D_2O. Obviously the rate and activation energies valid in acid solutions allow prediction of neither the order of magnitude of the reaction rate nor the direction of the solvent isotope effect in neutral or alkaline solutions. Therefore we decided to reinvestigate the kinetics of the ^{18}O exchange in the system BrO_3^-–H_2O (D_2O), using as wide a range of H^+-ion concentrations and temperatures as possible.

2. Experimental. – 2.1. *Materials.* High purity H_2O, D_2O (99.99% D, 0.4% ^{18}O) and H_2^*O (7% ^{18}O) were obtained from the water destillation and isotope separation facilities of the E.I.R. Würenlingen. KBr^*O_3 (6% ^{18}O) was prepared by refluxing a saturated solution of $KBrO_3$ in H_2^*O for 140 h. After crystallization by cooling, the KBr^*O_3 was dried at 180° and was stored in a vacuum desiccator. All chemicals used were reagent grade.

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2.2. *Procedures.* The proper amounts of KBr^*O_3, HNO_3 or NaOH were dissolved in H_2O or D_2O and the solution was adjusted to an ionic strength $I \simeq 1.0$M with $NaNO_3$. The exchange of oxygen between nitrate ion and solvent is very slow under the conditions of these experiments [2]. The test solutions were placed in glass ampoules, glass stoppered flasks (short half-times) or small teflon containers (alkaline solutions) and kept in thermostats at 20, 40, 60, 80 or 95°. The densities of the solutions at the reaction temperatures and the BrO_3^-, HNO_3 or NaOH contents were determined for each run. Thus the concentrations of the reacting species at the reaction temperatures could be expressed in moles/l. Samples were drawn at four to six different time intervals, t ($0.2 \leq t/t_{1/2} \leq 5$), with hypodermic syringes and were injected into ice-cooled test tubes containing $AgNO_3$ and enough HNO_3 to maintain a slightly acid solution. The reaction mixtures were vigorously stirred to speed up the $AgBr^*O_3$ precipitation. Consequently reaction (A) was quenched within a few seconds. The $AgBr^*O_3$ precipitate was centrifuged and was washed first with water, then ethanol and finally acetone. After drying under vacuum, the $AgBr^*O_3$ was thermally decomposed to give oxygen gas, which was isotopically analysed with a cycloidal mass spectrometer CEC 21-620 A. The mass spectra of the isotopic oxygen molecules were scanned at least four times to reduce the errors in peak height measurement to less than 0.3%. Since the decomposition was practically complete, it is assumed that the oxygen produced by pyrolysis of $AgBr^*O_3$ had the same isotopic composition as the parent bromate.

2.3. *Calculation of results.* The mole fractions, x, of ^{18}O in the gaseous oxygen samples submitted to mass spectrometric analysis were calculated from the peak heights at m/e 32 ($^{16}O_2^+$), 33 ($^{16}O^{17}O^+$), 34 ($^{16}O^{18}O^+$ and $^{17}O_2^+$), 35 ($^{17}O^{18}O^+$) and 36 ($^{18}O_2^+$) according to the following equations:

$$x = \frac{(34)/2 + (35)/2 + (36)}{(32) + (33) + (34) + (35) + (36)}, \qquad (1) \qquad\qquad x = \frac{(34)}{2(32) + (33) + (34)}. \qquad (2)$$

In eq. (1) the contribution of $^{17}O_2^+$ to m/e 34 was neglected. Eq. (1) does not imply any restrictions concerning the distribution of oxygen isotopes in the molecules, whereas eq. (2) assumes statistical distribution. ^{18}O abundances, x, calculated by eq. (1) and eq. (2), were the same within experimental error. The rate R of reaction (A) leading to the isotopic exchange [5] was calculated by

$$R = \frac{3[BrO_3^-] \cdot [H_2O]}{3[BrO_3^-] + [H_2O]} \cdot \frac{1}{t} \cdot \ln \frac{x_0 - x_\infty}{x_t - x_\infty}, \qquad (3)$$

where

R = rate of oxygen transfer between H_2O (D_2O) and BrO_3^- in mol O $l^{-1} \cdot s^{-1}$,
$[BrO_3^-]$ = total concentration of bromate in mol/l,
$[H_2O]$ = total concentration of exchangeable oxygen in the solvent in mol/l,
t = time in s,
x_0, x_t, x_∞ = mole fraction of ^{18}O in bromate at times: $t = 0$, t = time of sampling, $t = \infty$ (at exchange equilibrium).

In principle eq. (3) is valid only if there is no equilibrium isotopic fractionation between H_2O and BrO_3^-, that is the mole fraction of ^{18}O is the same in both H_2O and BrO_3^- at equilibrium. In our system only a slight enrichment of ^{18}O in H_2O (D_2O) with respect to BrO_3^- was found, the fractionation factors α being smaller than 1.03 between 20° and 100° [6]. A calculation following the general treatment given by *Bunton et al.* [7] shows that in these cases the relative error introduced in R by assuming no fractionation ($\alpha = 1.000$) is of the order of 10^{-3}. This error is negligible in comparison with the experimental errors.

3. Results.

3.1. *Survey of data.* All experimental data are compiled in Tables 1 (H_2O) and 2 (D_2O). Each result is the average of 4–6 measurements, which differed only in times, t, of reaction. The values of $R/[BrO_3^-]$ usually agreed within 1–2% and, in agreement with eq. (3), showed no variation with t. Within a small region around pH $\simeq$ 3, at 60°C (and probably other temperatures) bromate relatively rapidly decomposes to bromine and oxygen. Under these conditions (run No. 13 and 33) reliable results could be obtained only with short exchange times $t \leq 0.2\,t_{1/2}$. We have

Table 1. *Rate of oxygen exchange in the system* BrO_3^-–H_2O
$[BrO_3^-]$, $[H_2O]$, $[H^+]$, $[OH^-]$, I in mol · l^{-1}, $R/[BrO_3^-]$ in s^{-1}

Run No.	T^0 K	$[BrO_3^-] \cdot 10^2$	$[H_2O]$	$[H^+]$	$[OH^-]$	I	$R/[BrO_3^-]$
1	293.2	3.814	53.4	$9.44 \cdot 10^{-2}$	–	1.02	$2.014 \cdot 10^{-5}$
2	313.2	5.043	53.1	$1.88 \cdot 10^{-2}$	–	1.04	$6.537 \cdot 10^{-6}$
3	333.2	4.833	52.8	$<10^{-5}$	$<10^{-5}$	1.01	$1.592 \cdot 10^{-6}$
4	333.2	4.780	52.8	–	$1.12 \cdot 10^{-2}$	1.02	$1.597 \cdot 10^{-6}$
5	333.2	8.701	53.0	–	$9.52 \cdot 10^{-2}$	1.04	$1.645 \cdot 10^{-6}$
6	333.2	1.899	52.8	–	$9.60 \cdot 10^{-2}$	1.06	$1.641 \cdot 10^{-6}$
7	333.2	19.43	53.0	–	$9.64 \cdot 10^{-2}$	1.07	$1.647 \cdot 10^{-6}$
8	333.2	4.907	53.0	–	$9.76 \cdot 10^{-2}$	1.08	$1.657 \cdot 10^{-6}$
9	333.2	0.983	53.2	–	$9.76 \cdot 10^{-2}$	1.08	$1.694 \cdot 10^{-6}$
10	333.2	10.19	54.2	–	$4.81 \cdot 10^{-1}$	1.07	$1.983 \cdot 10^{-6}$
11	333.2	19.88	55.2	–	$9.36 \cdot 10^{-1}$	1.13	$2.457 \cdot 10^{-6}$
12	333.2	4.900	53.1	$8.73 \cdot 10^{-4}$	–	1.02	$1.714 \cdot 10^{-6}$
13	333.2	5.109	52.6	$2.75 \cdot 10^{-3}$	–	1.07	$2.566 \cdot 10^{-6}$
14	333.2	4.792	52.9	$9.21 \cdot 10^{-3}$	–	1.02	$1.167 \cdot 10^{-5}$
15	333.2	5.034	52.8	$1.86 \cdot 10^{-2}$	–	1.03	$4.538 \cdot 10^{-5}$
16	333.2	4.661	51.2	$<10^{-5}$	$<10^{-5}$	1.90	$1.374 \cdot 10^{-6}$
17	333.2	18.99	53.4	–	$8.57 \cdot 10^{-1}$	1.90	$2.158 \cdot 10^{-6}$
18	333.2	19.63	55.9	–	1.74	1.94	$3.303 \cdot 10^{-6}$
19	333.2	5.131	50.9	$1.79 \cdot 10^{-2}$	–	1.93	$5.450 \cdot 10^{-5}$
20	353.2	4.815	52.2	$<10^{-5}$	$<10^{-5}$	0.99	$1.103 \cdot 10^{-5}$
21	353.2	9.403	53.8	–	$4.61 \cdot 10^{-1}$	1.01	$1.388 \cdot 10^{-5}$
22	353.2	4.455	52.1	$1.85 \cdot 10^{-2}$	–	1.02	$2.810 \cdot 10^{-4}$
23	368.2	4.848	52.0	$<10^{-5}$	$<10^{-5}$	0.99	$3.983 \cdot 10^{-5}$
24	368.2	9.698	53.2	–	$4.17 \cdot 10^{-1}$	0.96	$4.917 \cdot 10^{-5}$
25	368.2	4.387	51.9	$1.81 \cdot 10^{-2}$	–	1.01	$9.816 \cdot 10^{-4}$

Table 2. *Rate of oxygen exchange in the system* BrO_3^-–D_2O
$[BrO_3^-]$, $[D_2O]$, $[D^+]$, $[OD^-]$, I in mol · l^{-1}, $R/[BrO_3^-]$ in s^{-1}

Run No.	T^0 K	$[BrO_3^-] \cdot 10^2$	$[D_2O]$	$[D^+]$	$[OD^-]$	I	$R/[BrO_3^-]$
26	293.2	4.888	53.2	$4.83 \cdot 10^{-2}$	–	1.02	$1.767 \cdot 10^{-5}$
27	313.2	4.585	53.2	$9.74 \cdot 10^{-3}$	–	1.04	$5.570 \cdot 10^{-6}$
28	333.2	4.944	52.7	$<10^{-5}$	$<10^{-5}$	1.03	$4.685 \cdot 10^{-7}$
29	333.2	4.915	52.5	–	$8.50 \cdot 10^{-2}$	1.11	$4.932 \cdot 10^{-7}$
30	333.2	9.708	53.5	–	$4.76 \cdot 10^{-1}$	1.06	$6.655 \cdot 10^{-7}$
31	333.2	18.83	55.0	–	$9.20 \cdot 10^{-1}$	1.11	$8.989 \cdot 10^{-7}$
32	333.2	4.914	52.6	$5.68 \cdot 10^{-5}$	–	1.02	$4.615 \cdot 10^{-7}$
33	333.2	4.751	52.7	$9.37 \cdot 10^{-4}$	–	1.00	$7.196 \cdot 10^{-7}$
34	333.2	4.937	52.5	$2.69 \cdot 10^{-3}$	–	1.09	$3.106 \cdot 10^{-6}$
35	333.2	4.708	52.7	$9.64 \cdot 10^{-3}$	–	1.01	$3.679 \cdot 10^{-5}$
36	333.2	4.828	51.1	$<10^{-5}$	$<10^{-5}$	1.91	$4.065 \cdot 10^{-7}$
37	333.2	18.98	53.3	–	$8.66 \cdot 10^{-1}$	1.91	$7.770 \cdot 10^{-7}$
38	333.2	19.81	55.8	–	1.75	1.95	$1.331 \cdot 10^{-6}$
39	333.2	4.997	51.0	$9.28 \cdot 10^{-3}$	–	1.92	$4.560 \cdot 10^{-5}$
40	353.2	4.816	52.2	$<10^{-5}$	$<10^{-5}$	1.00	$3.345 \cdot 10^{-6}$
41	353.2	9.302	53.4	–	$4.94 \cdot 10^{-1}$	1.04	$4.914 \cdot 10^{-6}$
42	353.2	4.796	52.2	$9.41 \cdot 10^{-3}$	–	1.00	$2.099 \cdot 10^{-4}$
43	368.2	4.842	51.8	$<10^{-5}$	$<10^{-5}$	0.99	$1.301 \cdot 10^{-5}$
44	368.2	10.33	53.3	–	$5.37 \cdot 10^{-1}$	1.09	$1.934 \cdot 10^{-5}$
45	368.2	4.584	51.6	$9.34 \cdot 10^{-3}$	–	1.00	$7.373 \cdot 10^{-4}$

no explanation for bromate decomposition at pH $\simeq$ 3 and for its stability at both higher and lower pH values.

3.2. *Dependence of* R *on concentrations at 60 °C.* The kinetic order of R with respect to the bromate concentration was determined at essentially constant ionic strength

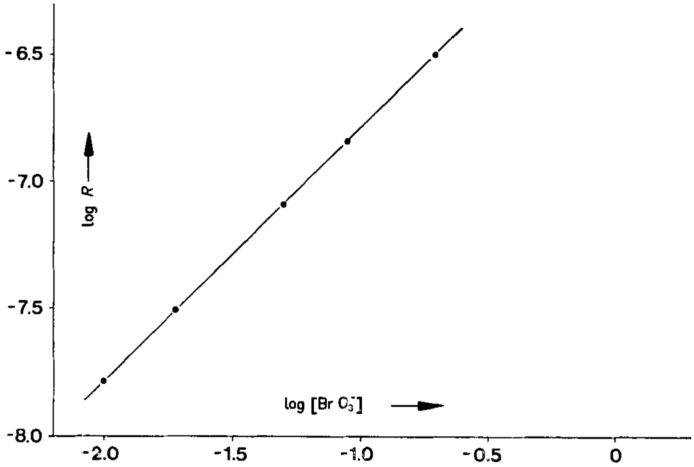

Fig. 1. *Dependence of* log R *on* log $[BrO_3^-]$
(H_2O, 60 °C, $[OH^-] \simeq 0.1$ M, $I \simeq 1$ M)

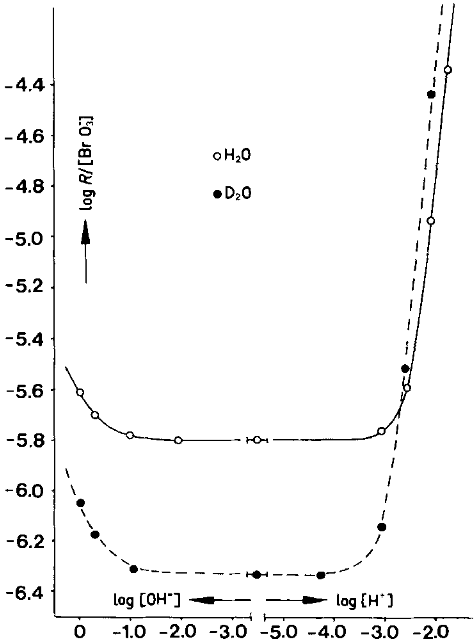

Fig. 2. *Dependence of* log $R/[BrO_3^-]$ *on* log $[H^+]$ *and* log $[OH^-]$ (60 °C, $I \simeq 1$ M)
The experimental points were taken from Tables 1 and 2, the curves were calculated using eq. (4a) and the rate constants of Table 3

and OH^- concentration (runs No. 5–9). Plots of $\log R$ *versus* $\log[BrO_3^-]$ fell on a straight line of slope 1.00 (Fig. 1). Thus, the exchange is first order in bromate.

Therefore the bromate-independent reaction rate $R/[BrO_3^-]$ was chosen as the main variable and was followed over a wide range of pH in H_2O and D_2O (runs No. 3–15 and No. 28–35). In Fig. 2 $\log R/[BrO_3^-]$ is plotted against $\log[H^+]$ ($\log[D^+]$) and $\log[OH^-]$ ($\log[OD^-]$), respectively. From Fig. 2 it can be concluded that the regions of acid- and base-catalysed exchange are clearly separated by a relatively broad region of uncatalysed exchange with a constant rate. This situation suggests a rate law of the general form

$$R/[BrO_3^-] = k_0 + k_1[OH^-]^n + k_2[H^+]^m. \qquad (4)$$

The rate constants k_1 as well as the exponent n were determined by plotting $\log(R/[BrO_3^-] - k_0)$ *versus* $\log[OH^-]$ (see Fig. 3) in the alkaline region, where the last term of eq. (4) is negligible. As $R/[BrO_3^-] - k_0$ is the difference of two relatively large numbers, k_1 is subject to larger fractional errors than k_0. The experimental data lie on straight lines of slopes close to 1.0, indicating a first order dependence, $n = 1$, of R on $[OH^-]$ ($[OD^-]$). The numerical values of k_0 and k_1 obtained from these plots are summarized in Table 3.

Table 3. *Rate constants and solvent isotope effects*[a]) *at* $I \simeq 1$ M ($NaNO_3$)
k_0 in s^{-1}, k_1 in $l \cdot s^{-1} \cdot mol^{-1}$, k_2 in $l^2 \cdot s^{-1} \cdot mol^{-2}$; k_{0H}, k_{1H}, k_{2H} in H_2O; k_{0D}, k_{1D}, k_{2D} in D_2O

Rate constant	95°C	80°C	60°C	40°C	20°C
k_{0H}	$3.98 \cdot 10^{-5}$	$1.10 \cdot 10^{-5}$	$1.59 \cdot 10^{-6}$	–	–
k_{0D}	$1.30 \cdot 10^{-5}$	$3.35 \cdot 10^{-6}$	$4.69 \cdot 10^{-7}$	–	–
k_{0H}/k_{0D}	3.06	3.30	3.40	–	–
k_{1H}	$2.2 \cdot 10^{-5}$	$6.2 \cdot 10^{-6}$	$8.1 \cdot 10^{-7}$	–	–
k_{1D}	$1.2 \cdot 10^{-5}$	$3.2 \cdot 10^{-6}$	$4.1 \cdot 10^{-7}$	–	–
k_{1H}/k_{1D}	1.8	1.9	2.0	–	–
k_{2H}	2.87	0.785	0.122	$1.80 \cdot 10^{-2}$	$2.26 \cdot 10^{-3}$
k_{2D}	8.19	2.37	0.378	$5.82 \cdot 10^{-2}$	$7.57 \cdot 10^{-3}$
k_{2H}/k_{2D}	0.350	0.331	0.323	0.309	0.299

[a]) The rate constant k_{2H} obtained by *Hoering et al.* [1] in H_2O at 30°C agrees, within the limits of error stated, with the value obtained using our experimental data and eq. (5). Their solvent isotope effect $k_{2H}/k_{2D} = 0.581$ at 30°C is in rather poor agreement with the value of 0.304 obtained from our data.

The values measured by *Marsel* [4] for k_{0H} at 100°C are consistent with our values using eq. (5), his isotope effect $k_{0H}/k_{0D} = 2.62$ being slightly lower.

A similar method was used for the determination of k_2 and m. Since the term with k_1 in eq. (4) can be neglected in acid solutions $\log(R/[BrO_3^-] - k_0) = \log k_2 + m \log[H^+]$. According to Fig. 4 $\log(R/[BrO_3^-] - k_0)$ is a linear function of $\log[H^+]$ with a slope of 2.0. Thus the exchange is second order with respect to the hydrogen ion concentration, in agreement with the results of *Hoering et al.* [1] and *Anbar et al.* [2]. Numerical values of k_2 are given in Table 3. These evaluations of the experimental data in H_2O and D_2O lead to the following rate law:

$$R/[BrO_3^-] = k_0 + k_1[OH^-] + k_2[H^+]^2. \qquad (4a)$$

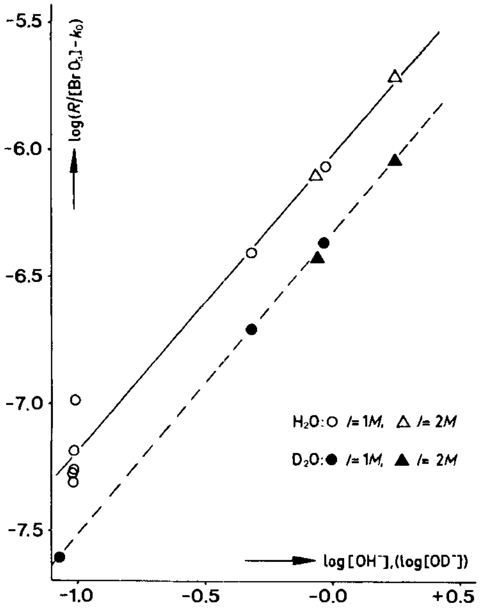

Fig. 3. *Dependence of* $\log(R/[\mathrm{BrO_3^-}]-k_0)$ *on* $\log[\mathrm{OH^-}]$ (60°C)

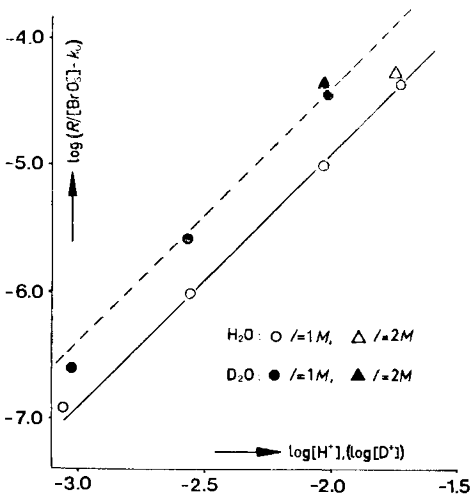

Fig. 4. *Dependence of* $\log(R/[\mathrm{BrO_3^-}]-k_0)$ *on* $\log[\mathrm{H^+}]$ (60°C)

Preliminary experiments performed at higher ionic strength (runs No. 16–19 and 36–39) showed that k_1 remains constant within the limits of error, whereas k_0 decreases and k_2 increases with increasing ionic strength, the effects, however, being quite small. Therefore no corrections due to minor variations of ionic strengths were applied.

3.3. *Temperature dependence of rate constants and solvent isotope effect.* If eq. (4a) is valid between 20 and 95°C, k_0, k_1 and k_2 could be evaluated for different temperatures from a series of corresponding exchange measurements. Because of the low reaction rates in neutral or alkaline solutions, k_0 and k_1 were not measured directly below 60°C. Extrapolated values of k_0 were used for the calculation of k_2 from eq. (4a) at 20 and 40°C. Since k_0 furnishes only a minor contribution to the overall rate at pH ≤ 2 the error due to this extrapolation can be neglected. In Table 3 the rate constants for different temperatures and the corresponding solvent isotope effects are listed. In accord with the transition state theory [8] $\log(k/T)$ was plotted *versus* $1/T$ in Fig. 5. These plots are linear for both neutral and alkaline solutions, whereas they are slightly curved in the case of acid solutions. The latter behaviour can be accounted for by introducing a non-zero heat capacity $\Delta C^{\ddagger}$ of activation, which in turn leads to the following equation:

$$\mathcal{R}\ln(k/T) = -\Delta H^{\ddagger}/T + \Delta S^{\ddagger} + \Delta C^{\ddagger}(298.2/T - 1 + \ln(T/298.2)) + \mathcal{R}\ln(\mathcal{R}/Nh). \quad (5)$$

The activation parameters compiled in Table 4 were derived from the experimental data by a least-squares treatment using eq. (5) [9].

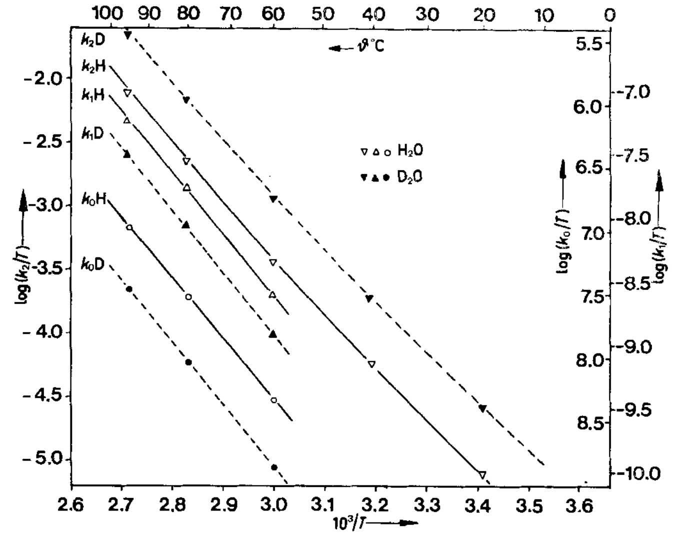

Fig. 5. *Dependence of* $\log(k/T)$ *on* $1/T$

The straight lines and curves were calculated using eq. (5) and the activation parameters of Table 4, the experimental points were taken from Tables 1 and 2

Table 4. *Activation parameters for the oxygen exchange between* BrO_3^-–H_2O (D_2O) *in neutral* (k_0), *alkaline* (k_1) *and acid* (k_2) *solutions*[a]

Rate constant	$\Delta H^{\neq}$ kcal/mol	$\Delta S^{\neq}$ eu	$\Delta C^{\neq}$ cal/mol deg
k_{0H}	21.7 ± 0.1	-20.0 ± 0.5	–
k_{0D}	22.4 ± 0.2	-20.4 ± 0.7	–
k_{1H}	22.5 ± 0.6	-19 ± 2	–
k_{1D}	22.7 ± 0.9	-20 ± 3	–
k_{2H}	$17.8 \pm 0.2_5$[b] [c]	-9.8 ± 0.8[b]	66 ± 8
k_{2D}	17.5 ± 0.3[b]	-8.4 ± 0.9[b]	62 ± 9

[a] The errors given are 2σ (σ is the standard deviation).

[b] These values refer to 298.2°K.

[c] *Hoering et al.* [1] and *Anbar et al.* [2] give a value of $\Delta H_2^{\neq} = 13.6$ and 14.0 kcal/mol, respectively.

4. Discussion. – 4.1. *Oxygen exchange in neutral and alkaline solutions.* The spontaneous exchange with water (rate constant k_0) and the OH^--catalysed exchange (rate constant k_1) probably both proceed through similar displacement mechanisms such as

$$H_2O + Br^*O_3^- \rightarrow [H_2O\ldots.Br^*O_3]^- \rightarrow BrO_3^- + H_2{}^*O \qquad (B)$$

and

$$HO^- + Br^*O_3^- \rightarrow [HO\ldots.Br^*O_3]^{2-} \rightarrow BrO_3^- + {}^*OH^-. \qquad (C)$$

Reaction (B) implies that the concentration of the solvent water enters the first term of eq. (4a); this implication, however, cannot be tested experimentally. Taking $k_0 = k_{H_2O}[H_2O]^p$ the entropy of activation, $\Delta S^{\neq}$, becomes more negative by a term $R \ln [H_2O]^p$, while the activation enthalpy, $\Delta H^{\neq}$, remains constant. From the pronounced solvent isotope effect of k_{0H}/k_{0D} (see Table 3), it is evident that the two O–H bonds in the activated complex are weaker than in the H_2O molecule (see *e.g.* [10]). Since the activation entropies, $\Delta S_0^{\ddagger}$, for H_2O and D_2O are very similar (see Table 4), eq. (5) leads to the following approximation:

$$k_{0H}/k_{0D} = \exp[-(\Delta H_{0H}^{\ddagger} - \Delta H_{0D}^{\ddagger})/RT]. \tag{6}$$

With the experimental values of k_{0H}/k_{0D} (see Table 3) one obtains an essentially temperature-independent difference of the activation enthalpies of

$$\Delta H_{0H}^{\ddagger} - \Delta H_{0D}^{\ddagger} = -820 \text{ cal/mol}.$$

Since the thermal excitation of the vibrational energy of the water molecules can be neglected in the prevailing temperature range, the value of 820 cal/mol closely represents the energy by which the difference of the zero point energies between the H- and the D-species is higher in the water molecule than in the transition state.

Using k_{1H}/k_{1D} (see Table 3) and a relation similar to eq. (6) for the OH^--catalysed reaction (C), a difference of the isotopic activation enthalpies of

$$\Delta H_{1H}^{\ddagger} - \Delta H_{1D}^{\ddagger} = -450 \text{ cal/mol}$$

is obtained.

According to the discussion above, this value represents the decrease in isotopic zero point energy difference of hydroxyl ions passing over to the transition state. Since the value of $\Delta H_{1H}^{\ddagger} - \Delta H_{1D}^{\ddagger}$ is about half of the value of $\Delta H_{0H}^{\ddagger} - \Delta H_{0D}^{\ddagger}$ it may be assumed, that in the transition states belonging to (C) and (B) one and two O–H bonds are involved, respectively. Thus both reactions appear to be bimolecular displacements. It can also be concluded that the O–H bond energy in H_2O and OH^- is reduced by about 30% in the respective transition states.

4.2. *Acid-catalysed oxygen exchange.* The acid-catalysed reaction (rate constant k_2) has already been discussed [1] [2]. The exchange probably proceeds through two successive steps: the fast equilibrium formation of the doubly protonated ion $H_2BrO_3^+$

$$BrO_3^- + 2H^+ \overset{K}{\rightleftarrows} H_2BrO_3^+, \tag{D}$$

with

$$K = [H_2BrO_3^+][BrO_3^-]^{-1}[H^+]^{-2}, \tag{7}$$

and the slow oxygen exchange by some kind of bimolecular water displacement in $H_2BrO_3^+$

$$H_2Br^*O_3^+ + H_2O \overset{k}{\rightarrow} H_2{}^*O + H_2BrO_3^+. \tag{E}$$

The rate of oxygen exchange R according to (E) thus would be

$$R = k[H_2BrO_3^+][H_2O] = k \cdot K[H_2O][BrO_3^-][H^+]^2, \tag{8}$$

which leads to

$$k_2 = k \cdot K[H_2O].$$

It should be mentioned that *Sykes et al.* [11] observed also an $[H^+]^2$ but no $[H^+]$ term for the bromate oxidation of the mercury (I) dimer. This suggests that BrO_2^+

ions play an important role in the redox reactions of bromate as well as in the oxygen exchange reaction. On the other hand the results of *Wright et al.* [12] were not consistent with the formation of the intermediate BrO_2^+ ion. The true nature of the probably occurring intermediate thus remains unknown, but it can be inferred from the experimental evidence, that the exchange proceeds *via* some kind of hydrated BrO_2^+.

The observed inverse isotope effect k_{2H}/k_{2D} is an overall effect to which the rate constant k and the equilibrium constant K may contribute. It is very likely that the latter predominates in this respect, as inverse isotope effects of this magnitude are found in many reactions with similar acid-base preequilibria [13]. As indicated by the inverse isotope effect, hydrogen is less strongly bound in the hydrated proton than in the protonated bromate. Now, as the heavier atom prefers the stronger bond, the equilibrium concentration of $H_2BrO_3^+$ in H_2O will be lower than the concentration of $D_2BrO_3^+$ in D_2O.

No clear interpretation can be given for the slight non-linearity of the function $\log(k_2/T) = f(1/T)$ (see Fig. 5). However, such non-linearities might be quite normal for experiments covering such large temperature ranges.

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