208. Kinetic Salt Effect in the ^{18}O-Exchange Reaction between Bromate and Water

by **H. Gamsjäger** and **P. Baertschi**

Institut für anorganische, analytische und physikalische Chemie der Universität Bern
und Eidgenössisches Institut für Reaktorforschung, 5303 Würenlingen

(27. VI. 72)

Summary. The kinetic salt effect in the ^{18}O-exchange reaction between bromate ion and water has been investigated at 60° in a range of ionic strength from $0.02\,\text{M} < I < 1.9\,\text{M}$ using $NaNO_3$ or $NaClO_4$ as inert salts. From the experimental data the following relation was deduced for the uncatalysed reaction path

$$\log k_0 = -5.736 - 0.061 \cdot I$$

In the H^+-catalysed reaction path the *Brønsted-Davies* equation was obeyed up to $I \simeq 0.1\,\text{M}$

$$\log k_2 = -0.70 - 1.1\,[I^{1/2}/(1 + I^{1/2}) - 0.3\,I]$$

At $I > 0.8\,\text{M}$ the sign of $\Delta \log k_2/\Delta I^{1/2}$ was positive. The theoretical interpretation of these results is consistent with the mechanistic evidence obtained previously from the rate law and the solvent isotope effects.

1. Introduction. – In a previous paper [1] the ^{18}O-exchange reaction between bromate and water has been investigated at essentially constant ionic strength $I \simeq 1.0\,\text{M}$ ($NaNO_3$). From this work the rate law is known to have the form

$$R\,/\,[BrO_3^-] = k_0 + k_1[OH^-] + k_2[H^+]^2 \tag{1}$$

where the concentrations are in M (mol/l) and R is in M s^{-1}. Preliminary experiments indicated that k_0 decreases, k_1 remains constant and k_2 increases as the ionic strength is changed from 1.0 to 1.9 M ($NaNO_3$) [1]. Application of the *Debye-Hückel* theory¹) to these results would suggest that the rate controlling steps involve association between unlike charged ions in the spontaneous reaction path (k_0), ion molecule interaction in the OH^--catalysed reaction path (k_1), and association between like charged ions in the H^+-catalysed reaction path (k_2). Such conclusions are clearly incompatible with the mechanistic interpretation of the BrO_3^- – H_2O isotopic exchange reaction obtained from the rate law and the solvent isotope effects [1]. A similar behaviour has been observed in the acid-catalysed ^{18}O-exchange reaction between $S_2O_3^{2-}$ and H_2O [3]. The mechanism postulated for this reaction predicts $\delta \log k_2/\delta I^{1/2}$ to be negative, but actually k_2 at $I = 1.3\,\text{M}$ is slightly higher than at $I \leqslant 0.046\,\text{M}$ [3].

Apparently no investigation of kinetic salt effects in oxygen exchange reactions between oxyanions and water covering the whole range up to an ionic strength of 1 or 2 M has been made so far.

In the present work the variation of the rate constants k_0 and k_2 (see Eq. 1) with the ionic strength ($0.02\,\text{M} < I < 2\,\text{M}$) for the BrO_3^- – H_2O isotopic exchange has been

---

¹) See e.g. [2].

studied. The OH^--catalysed path (k_1) shows up only at relatively high OH^- concentrations, hence measurements of k_1 at low ionic strength are not reliable enough to estimate the sign of the salt effect on k_1.

2. Results and discussion. – The methods of measuring and calculating the rates of exchange have been described earlier [1]. $NaNO_3$ or $NaClO_4$ was used as the supporting electrolyte. All experimental results are reported in Table 1 (neutral solutions), Table 2 (acid solutions) and Table 3 (alkaline solutions). Runs 1 to 26 were carried out at 60°, runs 27–30 at 80°.

2.1. *Dependence of the spontaneous exchange reaction on the ionic strength.* – In neutral solutions $\log R/[BrO_3^-] = \log k_0$ was found to be a linear function of I; the slope was small but certainly nonzero. This is expected for a reaction of an ion with a neutral molecule in solutions of higher ionic concentrations[2]. For comparison with the specific rate constant k_2 of the acid-catalysed path in Fig. 1 $\log k_0$ was plotted versus $I^{1/2}$. The upper curve was calculated by regression analysis and corresponds to the equation

$$\log k_0 = \log k_0^0 - b\,I, \qquad \text{where } \log k_0^0 = -5.736, \text{ and } b = 0.061. \tag{2}$$

If $NaNO_3$ was replaced by $NaClO_4$ as inert electrolyte the rate changes barely exceeded the experimental errors.

2.2. *Dependence of the H^+-catalysed exchange reaction on the ionic strength.* – From the experiments in acid solutions $\log k_2 = \log \{(R/[BrO_3^-] - k_0)/[H^+]^2\}$ was calculated and plotted against $I^{1/2}$.

As may be seen from Fig. 1, $\log k_2$ at low ionic strengths decreases, whereas at higher ionic strengths $\log k_2$ increases with increasing I. In the range $0.1\,\text{M} < I < 0.9\,\text{M}$ the experimental values show a broad minimum with almost constant $\log k_2$. The data up to $I \simeq 0.1$ M could be fitted (lower curve in Fig. 1) by the equation

$$\log k_2 = \log k_2^0 - 2\,\alpha\,[I^{1/2}/(1 + I^{1/2}) - 0.3\,I], \tag{3}$$

where

k_2, k_2^0 = rate constants at ionic strength I and at infinite dilution, respectively, $\log k_2^0 = -0.70$.

α = *Debye-Hückel* coefficient; for numerical values at different temperatures see. [5].

Eq. (3) is consistent with the assumption that the *Davies* approximation [6] can be applied for calculating activity coefficients of ions reacting in the exchange mechanism.

Since generally the *Davies* equation is valid at $I \leqslant 0.2$ M only, it is not surprising that the experimental data deviate from the curve at higher I. On the other hand the typical form of the curve showing a minimum around $I \simeq 0.4$ M is retained by the observed $\log k_2$ values. Thus even the sign of $\Delta \log k_2/\Delta I^{1/2}$ changes at higher ionic

---

[2] See e.g. [4].

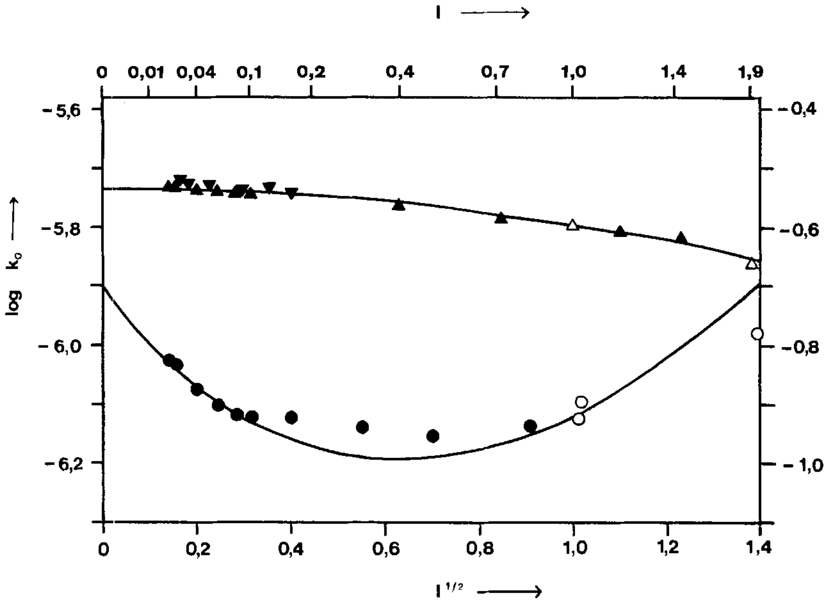


Fig. 1. *Dependence of* $\log k_0$ *and* $\log k_2$ *on* $I^{1/2}$ *(60°)*

△ ▲ neutral solutions, $NaNO_3$ added; ▼ $NaClO_4$ added; ○ ● acid solutions, $NaNO_3$ added
Filled symbols are from this work, open symbols from [1].
The curves have been calculated by the equations
$\log k_0 = -5.736 - 0.061\, I$ (upper curve)
$\log k_2 = -0.70 - 1.1\, [I^{1/2}/(1 + I^{1/2}) - 0.3\, I]$ (lower curve)

strength, whereas independence on I is implied by the *Brønsted-Bjerrum-Christiansen* Equation (4)

$$\log k = \log k^0 + 2 z_A z_B\, I^{1/2}, \tag{4}$$

where

z_A, z_B = charge of the species A and B reacting in the rate controlling step.

In the H^+-catalysed range of oxyanion-water exchange reactions there is strong evidence of rapid acid base equilibria prior to the rate controlling steps [7]. The preequilibria postulated in the $BrO_3^- - H_2O$ [1, 8], $ReO_4^- - H_2O$ [9] and $S_2O_3^{2-} - H_2O$ [3] exchange mechanisms are given as examples

$$2\,H^+ + BrO_3^- \rightleftarrows H_2BrO_3^+ \tag{A}$$

$$2\,H^+ + ReO_4^- \rightleftarrows H_2ReO_4^+ \tag{B}$$

$$H^+ + S_2O_3^{2-} \rightleftarrows HS_2O_3^- \tag{C}$$

Since the equilibrium constants K of the reactions (A), (B) and (C) will vary with I, primary and secondary salt effects must simultaneously be present. Probably the latter dominate, since in the slow steps either reactions with neutral H_2O or S_{N1}-processes occur. Then with the *Davies* Equation [6], for reaction (A) and (B) the K's and consequently the specific rate constants k_2 become the same functions of I as in Eq. (3). For reaction (C) the I containing term in parenthesis must be multiplied by 4α.

Table 1. *Rate of oxygen exchange in the system $BrO_3^- - H_2O$*
$[BrO_3^-]$, $[H_2O]$, I in M, $R/[BrO_3^-]$ in s^{-1}; neutral solutions; 60°

Run No.	Added Salt	$10^2 \cdot [BrO_3^-]$	$[H_2O]$	I	$10^6 \cdot R/[BrO_3^-]$	$\log k_0$
1	$NaNO_3$	0.988	54.6	0.0192	1.853	−5.732
2	$NaNO_3$	1.476	54.6	0.0240	1.844	−5.734
3	$NaNO_3$	2.459	54.6	0.0394	1.832	−5.737
4	$NaNO_3$	2.460	54.5	0.0591	1.815	−5.741
5	$NaNO_3$	2.459	54.4	0.0788	1.802	−5.744
6	$NaNO_3$	2.457	54.3	0.0985	1.795	−5.746
7	$NaNO_3$	9.853	54.4	0.3941	1.728	−5.763
8	$NaNO_3$	2.457	52.6	0.7142	1.642	−5.785
9	$NaNO_3$	2.457	52.0	1.207	1.561	−5.807
10	$NaNO_3$	2.457	51.8	1.513	1.519	−5.818
11	$NaClO_4$	1.000	55.1	0.0281	1.909	−5.719
12	$NaClO_4$	1.496	55.2	0.0331	1.885	−5.725
13	$NaClO_4$	2.494	55.2	0.0521	1.857	−5.731
14	$NaClO_4$	2.493	55.1	0.0883	1.825	−5.739
15	$NaClO_4$	2.493	55.0	0.1245	1.822	−5.735
16	$NaClO_4$	2.493	54.9	0.1607	1.809	−5.743

Table 2. *Rate of oxygen exchange in the system $BrO_3^- - H_2O$*
$[BrO_3^-]$, $[H_2O]$, $[H^+]$, I in M, $R/[BrO_3^-]$ in s^{-1}; acid solutions; $NaNO_3$ added; 60°

Run No.	$10^2\,[BrO_3^-]$	$[H_2O]$	$10^2\,[H^+]$	I	$10^5\,R/[BrO_3^-]$	$\log k_2$
17	0.987	54.7	1.035	0.0202	1.784	−0.826
18	1.478	54.7	1.034	0.0251	1.746	−0.835
19	2.463	54.6	1.034	0.0399	1.621	−0.878
20	2.460	54.6	1.033	0.0596	1.513	−0.904
21	2.465	54.6	1.035	0.0816	1.475	−0.919
22	2.459	54.6	1.032	0.0990	1.456	−0.922
23	2.467	54.4	1.036	0.1601	1.462	−0.923
24	2.468	54.1	1.036	0.3029	1.402	−0.942
25	2.466	53.8	1.035	0.4701	1.369	−0.955
26	2.466	53.1	1.035	0.8202	1.402	−0.937

Table 3. *Rate of oxygen exchange in the system $BrO_3^- - H_2O$*
$[BrO_3^-]$, $[H_2O]$, $[H^+]$, I in M, $R/[BrO_3^-]$ in s^{-1}; alkaline solutions; $NaNO_3$ added; 80°

Run No.	$10^2\,[BrO_3^-]$	$[H_2O]+[OH^-]$	$[OH^-]$	I	$10^5\,R/[BrO_3^-]$	$10^5\,k_0$3)	$\log k_1$
27	4.906	54.4	0.0981	0.147	1.31	1.24	-5.1_5
28	4.921	54.7	0.197	0.246	1.31	1.22	-5.3_4
29	4.935	54.8	0.296	0.345	1.33	1.21	-5.3_9
30	4.917	54.8	0.393	0.442	1.38	1.19	-5.3_2

3) Extrapolated from k_0 at I = 0.99 M [1], assuming that Eq. (2) is valid with b = 0.061 at 80°.

As may be seen from Fig. 2 the data obtained in the ReO_4^- – H_2O (LiCl) system at 25° fit closely Eq. (3). For the system $S_2O_3^{2-}$ – H_2O (NaCl) at 80° the data are perhaps not accurate enough to justify a detailed treatment [3], but certainly they do not contradict the mechanism postulated.

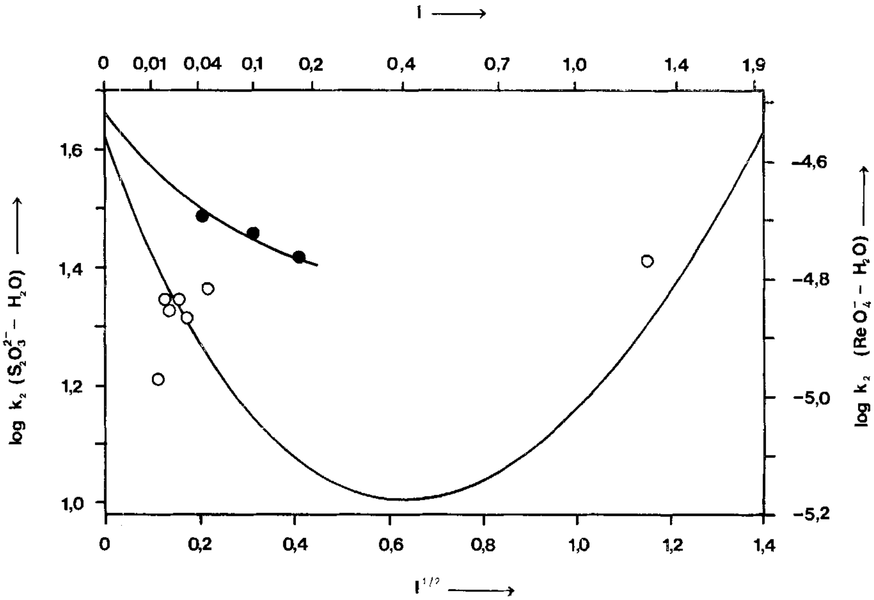


Fig. 2. *Dependence of log k_2 on $I^{1/2}$*

● ReO_4^- – H_2O exchange, 25° [9]; ○ $S_2O_3^{2-}$ – H_2O exchange, 80° [3]

The curves have been calculated using the *Davies* Equation [6] and the appropriate *Debye-Hückel* coefficient [5].

2.3. *Dependence of the OH^--catalysed reaction path on the ionic strength.* – A few measurements were performed at 80°, see Table 3, run 27–30. As expected, at low I only a small fraction of the total exchange proceeded via OH^--catalysis. At best log k_1 could be estimated with an accuracy of $\pm$ 0.1, which accuracy is not sufficient for conclusions concerning kinetic salt effects.

We thank our students Miss *S. Haddad* and Mr. *P. Grossenbacher* for carefully performing the experiments. We are also indebted to Mr. *O. Antonsen*, Mr. *F. Rudin* (E.I.R. Würenlingen), PD Dr. *U. P. Schlunegger* (Bern) for help with the mass spectrometric measurements and to Dr. *A. Held* (Bern) for correcting the English of the text.

The financial support of the *Swiss National Foundation* is gratefully acknowledged (project No. 2.404.70).

BIBLIOGRAPHY

[1] *H. Gamsjäger, A. Grütter & P. Baertschi*, Helv. *55*, 781 (1972).
[2] *E. S. Gould*, Mechanismus und Struktur in der organischen Chemie, Verlag Chemie GmbH, Weinheim/Bergstrasse, 1964, p. 222–225.
[3] *W. A. Pryor & U. Tonellato*, J. Amer. chem. Soc. *89*, 3379, 6392 (1967).

[4] *A. A. Frost & R. G. Pearson*, Kinetics and Mechanism, John Wiley & Sons, Inc., 2nd ed., New York 1961, p. 150–157.

[5] *R. A. Robinson & R. H. Stokes*, Electrolyte Solutions, Butterworths 2nd ed., London 1959, p. 468.

[6] *C. W. Davies*, Ion Association, Butterworths, London 1962, p. 41, 136–149.

[7] *E. Chaffee & J. O. Edwards*, Progr. Inorg. Chem. *13*, 205 (1970).

[8] *T. C. Hoering, R. C. Butler & H. O. McDonald*, J. Amer. chem. Soc. *78*, 4829 (1956).

[9] *R. K. Murmann*, J. phys. Chem. *71*, 974 (1967).

---

209. The Crystal and Molecular Structure of 3,5,7-Triphenyl-4*H*-1,2-Diazepine Picrate

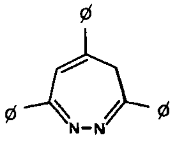
by **R. Gerdil**

Département de chimie organique de l'Université,
30, Quai de l'Ecole-de-Médecine, 1211 Genève

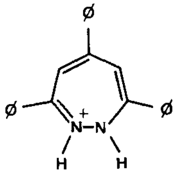
(16. VI. 72)

Summary. The crystal structure of 3,5,7-triphenyl-4*H*-1,2-diazepine (monoclinic, a = 8.132, b = 13.180, c = 24.204 Å, β = 104.15°, space group $P2_1/c$, Z = 4) has been determined by X-ray analysis. The 1,2-diazepine ring adopts a boat conformation with a methylene group at the prow. The phenoxide group of the picrate moiety is bonded to one of the diazepine nitrogen atoms through an hydrogen bond.

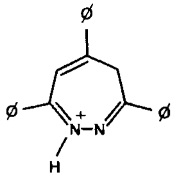
The N-unsubstituted configuration **1** was assigned to 3,5,7-triphenyl-1,2-diazepine which was formed by the condensation of 2,4,6-triarylthiapyrylium salts with hydrazine [1]. The protonation of **1** was formerly thought to produce the 'planar' cation **2**. However a recent NMR. investigation [2] has demonstrated the presence of a methylene group in the protonated form of **1** thus suggesting the more credible 'non-planar' structure **3**.



1



2



3

It was therefore interesting to study the crystal structure of an available crystalline derivative of the protonated form of **1** (picrate salt) to ascertain the position of the extra proton and to find out how the formal positive charge would influence the conformation of the diazepine ring.

Several valid indications about the conformation of the neutral ring are offered by recent crystal structure determinations [3] of substituted 1,2-diazepines.

Experimental Part. – The X-ray data were collected by Dr. *E. Klingsberg* at the crystallographic centre of the *Lederle* Laboratories[1]), and kindly submitted to us for the present structure analysis.

---

[1]) A division of the American Cyanamid Company, Pearl River, New York, USA.