

TABLE I

Cation concn., f K^+	$[MnO_4^-]$, f	$[MnO_4^-]$, f	Temp., °C.	$10^{-3} k$, $f^{-1} \text{ sec.}^{-1}$
1.00	0.34	0.007-0.14	30 ± 0.6	14.3 ± 0.7
1.00	.15	.007- .14	30 ± .6	14.3 ± .7
0.57	.15	.012- .10	30 ± .3	10.2 ± .4
.57	.15	.020- .20	29.6 ± .6	9.8 ± .4
.57	.15	.020- .20	20.0 ± .5	5.6 ± .6
.57	.15	.020- .20	12.1 ± .4	3.6 ± .5
Na ⁺				
1.13	.31	.150- .35	30.7 ± .6	9.9 ± 1.0
1.13	.31	.150- .35	6.3 ± .4	3.0 ± 0.5

measurement, as corrected by a conversion factor obtained through use of a frequency counter. The H_z field was measured by probe current which was calibrated by fitting it to a normalized and corrected derivative saturation curve. Uncertainties indicated in the graphs are based on the average of the several determinations.

Results and Discussion

At each positive ion concentration, graphs of $1/t_2$ against the manganate ion concentration are straight lines within experimental error. Rate constants calculated from slopes of these lines are listed in Table I. Figure 1 is a plot of $1/t_2$ against the manganate ion concentration for two different permanganate ion concentrations in 1*f* total potassium ion solutions showing that the two curves are superimposed, so the present observations agree with the rate dependence on the reactants found by the tracer technique for the sodium hydroxide system. They are consistent

with the assumption that the reaction is first order with respect to the manganate and permanganate ion concentrations, respectively. An activation energy of the reaction in 0.6*f* potassium hydroxide is 8.3 kcal./mole. This was calculated from an Arrhenius plot (Fig. 2). The 30, 20 and 12° points represent n.m.r. experiments while the 0° point is from the tracer data. These data are consistent also with salt effects found by Shepard and Wahl.¹ Using the tracer data the extrapolated rate constant in 1*f* potassium hydroxide at 0°, assuming the linear salt effect, is $3550f^{-1} \text{ sec.}^{-1}$. Assuming an activation energy of 8.3 kcal./formula and using the n.m.r. data at 30°, the calculated rate constant is $3100f^{-1} \text{ sec.}^{-1}$ at 0°. Using the 10.5 kcal./mole activation energy found in the tracer experiments and the n.m.r. data at 30°, the calculated rate constant for this reaction at 0° in 1*f* sodium ion concentration is $1500f^{-1} \text{ sec.}^{-1}$ compared to $1700f^{-1} \text{ sec.}^{-1}$ found in the tracer experiments. The two methods are in good agreement, and the observed discrepancies may be attributed to differences in sodium or potassium manganate purity or the method of analysis used.

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[CONTRIBUTION FROM THE ISOTOPE DEPARTMENT, WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL]

The Catalytic Effect of Chloride Ions on the Isotopic Oxygen Exchange of Nitric and Bromic Acids with Water

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The kinetics of the isotopic exchange of oxygen between nitric acid and water were investigated in the concentration range 1 to 7 *M* HNO₃, in the presence of chloride ions, at 60 and 100°. The rate of exchange was found to obey the rate law $R = [HNO_3]_f [H_2O^+] (k_1 + k_2 [Cl^-])$ where $[HNO_3]_f$ is the concentration of undissociated nitric acid; $k_1 = 4.8 \times 10^{-3} \text{ l. mole}^{-1} \text{ min.}^{-1}$, $k_2 = 3.2 \times 10^{-1} \text{ l.}^2 \text{ mole}^{-2} \text{ min.}^{-1}$ at 100°. The energies of activation of the two processes are comparable, 22.1 and 21.8 kcal./mole, respectively. The isotopic exchange of oxygen between bromate ions and water in acid solutions which was investigated between $pH = 1.0$ to 2.25, in the temperature range 0–60°, showed a similar behavior $R = [BrO_3^-] [H_2O^+]^2 (k_1 + k_2 [Cl^-])$; $k_1 = 5.6 \times 10^{-1} \text{ l.}^2 \text{ mole}^{-2} \text{ min.}^{-1}$; $k_2 = 3.6 \times 10^1 \text{ l.}^3 \text{ mole}^{-3} \text{ min.}^{-1}$ at 30°; $E_1 = 14.6 \text{ kcal./mole}$, $E_2 = 13.9 \text{ kcal./mole}$. A bimolecular nucleophilic attack of chloride ions and of water molecules on the conjugate acids $H_2NO_3^+$ and $H_2BrO_3^+$ is suggested.

The isotopic exchange of oxygen between nitric acid and water has been investigated extensively in concentrated nitric acid solutions¹ at 0°. It was suggested that the rate determining step of the exchange reaction is the rate of dehydration of $H_2NO_3^+$ and the formation of the NO_2^+ ions.² The kinetic study of the exchange reactions of bromate³ and chlorate⁴ ions showed a second order dependence on hydronium ion concentration and an increased rate of exchange in D₂O solutions; these results

implied the participation of $H_2BrO_3^+$ and $H_2ClO_3^+$ as intermediates. Hoering suggests that the rate-determining step in the bromate and chlorate reactions is a nucleophilic attack of a water molecule on the conjugate acids. This assumption is based on the analogy with reactions of the halic acids with halide ions as demonstrated by the empirical equations proposed by Edwards.⁵ There is however, no experimental proof that the rate determining step in the oxygen exchange reaction is really a bimolecular nucleophilic attack (Sn2) and not a monomolecular process. The same ambiguity was previously encountered in similar isotopic exchange reactions such as the exchange of nitrite ions with water⁶ or the uncatalyzed path in the

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(2) C. A. Bunton and E. A. Halevi, *ibid.*, 4917 (1952).

(3) T. C. Hoering, R. C. Butler and H. O. McDonald, *J. Am. Chem. Soc.*, **78**, 4829 (1956).

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

(5) J. O. Edwards, *ibid.*, **76**, 1540 (1954).

iodate-water exchange.⁷ It was found, however, that both nitrous acid^{8,9} and iodate⁷ oxygen exchange reactions are catalyzed by various ions in solution; phosphate, acetate and nitrite ions were found to catalyze the nitrite-water oxygen exchange, and nitrite ions catalyzed the nitric acid-water oxygen exchange.¹⁰ In the case of the nitrous acid oxygen exchange it was hard to separate the noncatalyzed "water reaction" from the effects of buffers or nitrite ions on the exchange rate. The nitrite-catalyzed nitric acid-water oxygen exchange has been observed in a range of acidity different from that where the uncatalyzed exchange was investigated; thus it is impossible to draw any conclusions from the catalytic reaction on the mechanism of the uncatalyzed exchange. The effect of nitrite ions on the nitric acid-water oxygen exchange has been considered as a specific phenomenon in nitrogen chemistry, namely, the formation of the mixed anhydride N_2O_4 by the action of NO^+ on NO_3^- . It was the purpose of this study to investigate the effect of a simple nucleophilic reagent, which does not contain oxygen on the rate of exchange of bromate and nitrate ions; chloride ion was chosen as a reagent that fulfills these requirements. In the case of nitric acid it became necessary to compare the catalyzed with the noncatalyzed path under comparable conditions, thus this exchange reaction was investigated in a range of lower acidities than that studied by Bunton.^{1,2}

Experimental

Materials.— H_2O^{18} was obtained from the oxygen distillation plant of the Weizmann Institute. Nitrite free nitric acid was prepared by distillation from urea under reduced pressure. A constant boiling fraction was separated and it was tested for nitrite by the method described by Bunton.¹ The stock solution of concentrated HNO_3 was kept in a dark glass-stoppered bottle at -10° . $NaBrO_3^{18}$ in H_2O^{18} was prepared by exchange of $NaBrO_3^{16}$ with H_2O^{18} . $Ba(BrO_3)_2$ was precipitated, and an excess of it was subsequently shaken with Na_2SO_4 in H_2O^{18} . $BaSO_4$ and the excess $Ba(BrO_3)_2$ were then removed by filtration. H_2O_2 was Merck "Superoxol" stabilizer-free reagent. All other reagents were of analytical grade and were used without further purification.

Procedure. 1. Exchange of Nitric Acid.—Measured amounts of concentrated HNO_3 were diluted at 0° with H_2O^{18} to the desired concentrations, which were confirmed by acidimetric titrations. Sodium chloride, sodium nitrate or perchloric acid was introduced when required. Next a small amount (0.05 ml.) of 10% H_2O_2 was added to 10 ml. of solution in order to oxidize any nitrite or N_2O_4 accidentally formed. Aliquots were analyzed to confirm the absence of nitrite, and any reaction mixture that showed a positive nitrite test was discarded. It has been shown¹¹ that hydrogen peroxide does not catalyze the HNO_3 - H_2O oxygen exchange. Although an oxygen exchange between HNO_3 and H_2O_2 takes place, the latter exchange hardly affected the isotopic composition of HNO_3 . This exchange reaction is therefore negligible.

The reaction mixtures were kept in a thermostat at 60, 70 and at $100 \pm 0.1^\circ$; aliquots of 0.5 ml. were taken at inter-

vals and introduced into 5 ml. of 0.4 M $Ba(ClO_4)_2$ solution in 50% ethanol. $Ba(NO_3)_2$, which precipitated, was centrifuged, washed with 95% ethanol and dried in a vacuum oven at 70° . The dry $Ba(NO_3)_2$ was then mixed with re-sublimed ammonium chloride 1:3 w./w. and placed in a glass tube with a break-off tip and a seal-off constriction. The tube was then evacuated and sealed off; then it was heated at 400° in a thermostated oven for 45 minutes. The heated ampoule contained nitrous oxide, water and some nitrogen; these were separated by freezing in liquid nitrogen, pumping off the permanent gas and subsequently distilling off the N_2O at -70° . The nitrous oxide was introduced into the mass spectrometer (a CEC model 41-201 isotope ratio type instrument) and the mass ratio 46/44 was determined. On several occasions the separate mass abundances 44-48 were recorded to test for NO_2 contamination.

2. Exchange of Bromate.—The reaction mixtures were prepared either by dissolving $NaBrO_3$ in H_2O^{18} or by preparing $NaBrO_3^{18}$ in H_2O^{18} as described above. The pH was adjusted by $HClO_4$ or $NaOH$ and the ionic strength was kept constant by adding $NaClO_4$. The pH was determined by a glass electrode with a Metrohm type 148C potentiometer. At intervals samples of 0.5 ml. were taken, precipitated by $Ba(ClO_4)_2$ in alcoholic solution and treated as described above. The dried $Ba(BrO_3)_2$ was placed in a glass tube with a break-off tip, which was sealed off after evacuation. The $Ba(BrO_3)_2$ was decomposed to oxygen by heating in a thermostated oven at 350° for 30 minutes. The gas was then submitted to mass spectrometric analysis. It has been shown¹² that the oxygen evolved on decomposition of bromate is completely "scrambled," i.e., the isotopic abundance of the species of masses 32-36 is statistically equilibrated, thus it was possible to analyze the isotopic ratio of mass 34/32 without further corrections.

3. Calculation of Results.—The half lives of the exchange reactions ($t_{1/2}$) were derived graphically from the experimental points (8-12 points per run) by plotting the logarithm of $A_\infty - A_t$ vs. time, where A is the isotopic concentration of O^{18} . The rates of exchange were then calculated by the formula

$$R = \frac{3(XO_3^-)(H_2O)}{3(XO_3^-) + (H_2O)} \times \frac{0.693}{t_{1/2}}$$

where (XO_3^-) is the stoichiometrical concentration of nitrate or bromate in the reaction mixture disregarding its chemical form.

Results and Discussion

A. The Exchange of Nitric Acid with Water.—The rate of the isotopic exchange of oxygen between nitric acid and water was followed at 70° and at 100° . The results of the experiments are presented in Tables I and II, respectively. These

TABLE I
ISOTOPIC EXCHANGE OF OXYGEN BETWEEN NITRIC ACID AND WATER 70°

(HNO_3) _{total} mole l. ⁻¹	(H_2O^{18}) mole l. ⁻¹	(HNO_3) _t mole l. ⁻¹	R_t mole l. ⁻¹ min. ⁻¹ $\times 10^4$	($R/(H_2O^{18})_t$) mole ⁻¹ l. min. ⁻¹ $\times 10^4$
1.00	0.974	0.026	0.10	3.8
2.00	1.85	.15	1.09	3.9
4.00	3.20	.80	9.3	3.8
4.54	3.52	1.02	10.1	2.8
5.95	4.08	1.87	25.8	3.4
6.76	4.30	2.46	39.7	3.8

data show an approximately third order dependence of the rate of exchange (R) on the stoichiometric concentration of nitric acid. It is hard to

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TABLE II
ISOTOPIC EXCHANGE OF OXYGEN BETWEEN NITRIC ACID
AND WATER AT 100°

	(NO ₃ ⁻) _{total} mole l. ⁻¹	(H ₃ O ⁺), mole l. ⁻¹	(HN- O ₃) _f , mole l. ⁻¹	(Cl- O ₄ ⁻), mole l. ⁻¹	R × 10 ³ , mole l. ⁻¹ min. ⁻¹	R/(H ₃ O ⁺) (HNO ₃) _f × 10 ³ , mole l. ⁻¹ min. ⁻¹
2.1	1.0	0.96	0.04	..	0.102	2.7
2.2	1.0	.96	.04	1.0	.135	3.5
2.3	2.0	.92	.08	..	.19	2.6
2.4	2.0	1.80	.20	..	1.71	4.8
2.5	2.0	1.80	.20	1.0	1.98	5.5
2.6	4.0	1.60	.40	..	3.42	5.3
2.7	4.0	1.60	.40	..	3.19	5.0
2.8	3.0	2.50	.50	..	4.0	3.2
2.9	3.0	2.50	.50	..	3.13	2.5
2.10	2.0	3.02	.98	2.0	25.0	8.4
2.11	2.0	3.02	.98	2.0	18.0	6.1
2.12	4.0	3.00	1.00	..	12.0	4.0
2.13	7.4	3.92	3.48	..	113	8.3

suggest a plausible mechanism for the exchange reaction based on such a dependence. An attempt to correlate log R with the acidity function H_0 in nitric acid solutions¹³ shows approximately a 1.5 power dependence; this, however, has little meaning in terms of a reaction mechanism. Moreover, in both cases it was impossible to fit quantitatively the catalytic effects of nitrate ions and of perchloric acid. The rate of exchange R was correlated with the concentration of undissociated nitric acid (HNO₃)_f. The values used were taken or interpolated from those of Hood and Reilly¹⁴ for 70°; the values for 100° have been graphically extrapolated from the same data. The low accuracy of the kinetic data justified this crude extrapolation. The suggested rate law $R = k(\text{HNO}_3)_f \times (\text{H}_3\text{O}^+)$ yields specific rate constants which remain unchanged through a 400 fold change in R at 70° and a similar one thousand fold change at 100°. The values of (HNO₃)_f for solutions to which NaNO₃ (2.3, 2.6, 2.7) or HClO₄ (2.11, 2.12) were added were calculated from the values of the degree of dissociation at the respective acidities. It may be seen in Table II that the specific rate constants for these solutions are in good agreement with those of the uncatalyzed experiments.

The specific rate constants k found were $3.6 \pm 0.4 \times 10^{-4}$ l. mole⁻¹ min.⁻¹ at 70°, and $k = 4.8 \pm 2.0 \times 10^{-3}$ l. mole⁻¹ min.⁻¹ at 100°. From these values an activation energy of 22.1 kcal./mole for the exchange process is derived.

The suggested mechanism includes an undissociated HNO₃ molecule and a H₃O⁺ ion. The rate determining step may be the interaction of H₃O⁺ with HNO₃ forming H₂NO₃⁺; this may subsequently undergo exchange with the solvent either by a Sn1 or a Sn2 mechanism. Such a mechanism, which is in fact a proton transfer process, should have a much lower activation energy than that experimentally found and should proceed at a much higher rate. Alternative mechanisms are Sn1 dissociation of H₂NO₃⁺ to form NO₂⁺ or a nucleophilic attack of water on H₂NO₃⁺;

the decision between these two mechanisms will be discussed in the following section.

B. The Catalytic Effect of Chloride Ions on the Nitric Acid Exchange.—It has been found that the rate of oxygen exchange between nitric acid and water is catalyzed by chloride ions. The exchange has been followed under identical conditions to those described above and the results of exchange at 100° are summarized in Table III. Although a certain positive salt effect has been observed (*cf.* 2.1–2.2, 2.4–2.5) (this may be a secondary salt effect increasing the H₂NO₃⁺ concentration), the specific catalytic effect of chloride ions is clearly demonstrated. The chloride catalysis obeys the rate law $R = k(\text{HNO}_3)_f \times (\text{H}_3\text{O}^+) \times (\text{Cl}^-)$ with R changing over one thousand fold. The specific rate constant at 100° is $3.2 \pm 0.9 \times 10^{-1}$ mole⁻² l.² min.⁻¹ and from a similar series at 60° an average specific rate constant $9.4 \pm 1.8 \times 10^{-3}$ mole⁻² l.² min.⁻¹ has been obtained. The activation energy calculated from these values is 21.8 kcal./mole.

TABLE III
NITRIC ACID-WATER OXYGEN EXCHANGE CATALYZED BY
CHLORIDE IONS AT 100°

(N- O ₃) _{total} mole l. ⁻¹	(H ₃ O ⁺), mole l. ⁻¹	(HNO ₃) _f , mole l. ⁻¹	(Cl ⁻), mole l. ⁻¹	(ClO ₄ ⁻), mole l. ⁻¹	R × 10 ² , l. ⁻¹ min. ⁻¹	R - R ₀ / (H ₃ O ⁺) (HNO ₃) (Cl ⁻) × 10, mole ⁻² l. ² min. ⁻¹
1.0	0.96	0.04	0.1	..	0.079	2.1
1.0	0.96	.04	.2	..	0.23	3.0
2.0	1.80	.20	.2	..	2.4	3.3
2.0	1.80	.20	.3	1.0	2.6	2.4
4.0	1.60	.40	.4	..	6.1	2.4
3.0	2.50	.50	.2	..	10.0	4.0
4.0	3.0	1.0	.1	..	17	5.7
4.0	3.0	1.0	.2	..	18	3.0
4.0	3.0	1.0	.2	..	12	2.0
4.0	3.0	1.0	.3	..	29.4	3.3
4.0	3.0	1.0	.5	..	34	2.3
6.0	3.68	2.32	.2	..	75	4.4

In the chloride-catalyzed reaction undissociated nitric acid, H₃O⁺ and Cl⁻ are found to participate in the exchange process; as a triple collision is highly unlikely, a bimolecular reaction should be considered. The formation of undissociated HCl in a pre-equilibrium followed by its interaction with HNO₃ would show a stronger dependence on H₃O⁺ concentration than that observed, because in the range of acidities studied the concentration of undissociated hydrogen chloride increases faster than required by an ideal first power dependence.¹⁵ An alternative bimolecular reaction is a nucleophilic attack of chloride ions, the concentration of which is hardly affected by (H₃O⁺) in the acidity range involved, on H₂NO₃⁺ with the formation of NO₂Cl + H₂O. This process is analogous to the Sn2 mechanism postulated above and involves the cleavage of a N-O bond in the rate determining step. Comparing the energies

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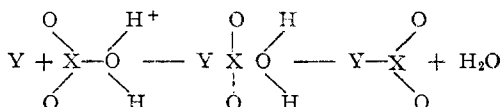
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of activation of the catalyzed and uncatalyzed reactions, it is evident that these are identical within experimental error; this strongly suggests that the two exchange reactions are similar SN2 processes where the N-O bond is broken in the rate-determining step. The chemical behavior of the NO_2Cl formed will be discussed later.

The conclusion that the uncatalyzed nitric acid exchange is proceeding by a Sn2 mechanism implies that at higher nitric acid concentrations, where NO_2^+ has been observed,^{1,2} this ion is formed also by a bimolecular process. It is suggested that when the concentration of free HNO_3 increases to about 50 mole% a new reaction becomes predominant, namely, the elimination of a water molecule from H_2NO_3^+ by the attack of an anhydrous HNO_3 molecule to form $\text{HNO}_3 \cdot \text{H}_2\text{O} + \text{NO}_2^+$. Another implication of the Sn2 exchange mechanism is that just below the 50 mole% HNO_3 the increase in the rate of oxygen exchange with increasing HNO_3 concentration should be smaller than at lower or at higher concentrations, because in this range H_2NO_3^+ increases rather slowly with rising acidity whereas the "free" water concentration decreases rapidly, owing to the formation of nitric acid monohydrate. It is obvious that bound water will be an inferior nucleophilic reagent, thus our reaction path is expected to be almost entirely inhibited before the NO_2^+ reaction path becomes of importance.

C. The Oxygen Exchange Between Bromate and Water Catalyzed by Chloride Ions.—This exchange reaction has been previously investigated³ in the same range of acidities where the chloride catalysis has been detected; still it was necessary to repeat some experiments on the uncatalyzed exchange because the temperature range has been extended. The bromate exchange was studied in the range 0–60°, and the energies of activation of the catalyzed and uncatalyzed processes were obtained. The results of the bromate exchange are summarized in Table IV.

From the data presented in Table IV it is evident that the bromate-water exchange proceeds⁵ according to the rate law $R = [\text{BrO}_3^-][\text{H}_3\text{O}^+]/(k_1 + k_2[\text{Cl}^-])$. The values of $k_1 = 5.6 \cdot 10^{-1} \text{ l.}^2 \text{ mole}^{-2} \text{ min.}^{-1}$ and $k_2 = 3.6 \times 10^1 \text{ l.}^3 \text{ mole}^{-3} \text{ min.}^{-1}$ were obtained at 30°. The energies of activation of the uncatalyzed and chloride catalyzed exchange reactions are 14.6 and 13.9 kcal./mole, respectively; the first value is in fair agreement with the value of 14.23 kcal./mole obtained by Hoering³ for a more limited range of temperatures (20–35°). As in the case of the nitric acid exchange, the values of activation energies of the two processes are identical within experimental error, and this strongly suggests a similar process in the rate determining step. The most plausible mechanism suggested is the nucleophilic replacement of a water molecule on the H_2XO_3^+ ion



where Y is H_2O or Cl^- . When ClXO_2 is formed it hydrolyzes rapidly to form again $\text{Cl}^- + \text{HXO}_3$.

TABLE IV
BROMATE-WATER OXYGEN EXCHANGE CATALYZED BY CHLORIDE IONS

Temp., °C.	pH	(BrO_3^-), mole l.^{-1}	(Cl^-), mole l.^{-1}	R, mole l.^{-1} min.^{-1} $\times 10^2$	$k' = R/$ (BrO_3^-) (H^+) ² , mole ⁻² l.^2 min.^{-1} $\times 10$	$k =$ $k' - k_1/$ (Cl^-) ³ , mole ⁻³ l.^3 min.^{-1} $\times 10^{-1}$
0	1.1	0.3	..	0.090	0.48	...
0	1.1	.3	0.2	1.83	0.7	0.46
0	1.1	.3	.5	3.90	20.7	0.40
25	1.1	.3	..	0.84	4.5	...
25	1.1	1.0	..	3.00	4.8	...
30	1.0	0.3	..	1.55	5.2	...
30	1.0	1.0	..	6.00	6.0	...
30	1.0	0.3	.05	7.6	25.3	4.0
30	1.0	.3	.1	12.0	40.0	3.5
30	1.0	.3	.3	31.4	105	3.3
30	1.0	.15	.5	30.6	204	4.0
30	1.0	.3	.9	107	357	3.9
30	1.25	.15	.1	18.3	39	3.2
30	1.75	.15	.2	4.0	82	3.8
30	2.15	.15	.3	0.81	107	3.4
30	2.25	.15	.3	0.56	119	3.8
60	1.1	.3	..	20.6	109	...
60	1.1	.3	.3	243	1290	39.4
60	1.1	.3	.6	477	2520	40.0

D. The Chemical Nature of ClXO_2 .—The oxygen exchange mechanism described in this study suggests the existence of ClNO_2 and ClBrO_2 as intermediates; it may be of interest to discuss the chemical behavior of these species. There has been some controversy about the structure and chemical behavior of nitryl chloride (NO_2Cl). On alkaline hydrolysis¹⁶ or ammonolysis¹⁷ this compound behaves as a carrier of a positively polarized halogen, or in other words, as the hypochlorite of NO^+ . On the other hand its hydrolysis in acid¹⁸ and its reaction with tetramethylammoniumazide¹⁹ suggest it as the chloride of NO_2^+ . It seems probable that two isomers do exist, one with a Cl-O bond which behaves as a hypochlorite derivative, whereas the isomer with a Cl-N bond acts as a chloride. The oxygen exchange reaction demonstrates the existence of the second isomer. The formation of the hypochlorite would not lead to an oxygen exchange; moreover it would have been consumed by the H_2O_2 present at a much faster rate than observed.

The possibility of existence of two isomers of the ClXO_2 type may be raised again, in the case of bromate. A second order reaction between H_2BrO_3^+ and chloride ions has been previously observed^{3,20} leading to a reduction of bromate to bromite and most probably hypochlorite. The specific rate of this reaction at 25° is $9.10 \cdot 10^{-2} \text{ l.}^3 \text{ mole}^{-3} \text{ min.}^{-1}$ as compared to our value of $3 \times 10^1 \text{ l.}^3 \text{ mole}^3 \text{ min.}^{-1}$ under similar conditions. This implies the formation of two different inter-

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mediates, ClBrO_2 and perhaps OBrOCl , in the two processes. ClBrO_2 may be of analogous structure to that of ClClO_2 investigated by Taube and Dodgen²¹; these authors consider, however, the terminal chlorine as positively charged, although they do not exclude the possibility that their intermediate has the structure OClOCl . It may be suggested therefore that whereas the chloride ions interact with H_2BrO_3^+ at a comparatively fast rate, the formation of BrO_2Cl requires another pre-equilibrium, namely, the dehydration of H_2BrO_3^+ . It should be noted that Y-BrO_2 might undergo a redox reaction by a different mechanism; if Y-BrO_2 is attacked by another Y^- , then $\text{OBrOY} + \text{Y}^-$ may be formed, which will eventually decompose to $\text{OY}^- + \text{BrO}_2^-$. This is consistent with the "third type" reactions formulated by Edwards²² and explains the catalytic effects of halide ions on the halate reduction reactions. This type of catalyzed reduction may occasionally proceed fast enough to consume the YBrO_2 as soon as it is

(21) H. Taube and H. Dodgen, *J. Am. Chem. Soc.*, **71**, 3330 (1949).
(22) J. O. Edwards, *Chem. Revs.*, **50**, 455 (1952).

formed; in this case the reaction will be first order in Y^- , but no $\text{XO}_3^- - \text{H}_2\text{O}$ oxygen exchange will be induced. Attempts to detect a catalytic effect of bromide ions on the bromate oxygen exchange have failed owing to the fast reduction of bromate; this is an analogous result to that of Hoering⁴ who failed to detect a catalytic effect of chloride in the chlorate-water oxygen exchange. On the other hand some induced $\text{BrO}_3^- - \text{H}_2\text{O}$ exchange was found on reduction of bromate by iodide ions.²³

It may be concluded that the mechanism of oxygen exchange by a bimolecular substitution is not limited to weak acids like hypochlorous and hypobromous acids²⁴ or to those of intermediate strength like nitrous⁶ or iodic acids,⁷ but it may be extended to include the conjugate acids of nitric or bromic acids; furthermore this mechanism includes cases where the formation of an acid anhydride originating from two acid molecules has been postulated, e.g. the formation of nitrogen trioxide in the nitrate water exchange.⁸

(23) M. Anbar and H. Taube, unpublished.

(24) M. Anbar and H. Taube, *J. Am. Chem. Soc.*, **80**, 1073 (1958).

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Invariability of the α -Parameter of Certain Salts with Change in Solvent

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The K_A -values of tetra-*n*-butylammonium perchlorate have been determined in seven one-component solvents ranging in *D*-value from 9.9 to 25.2. It is found that for five of the solvents, each of which consist of but one molecular species, the most probable relation between $\log K_A$ and $1/D$ is a linear one, thereby showing that the α -parameter of this salt has the same value in each of the solvents. The appreciable deviations from the straight line (so established), found for the solvents ethylene chloride and 1,2-dichloropropane, each of which consist of two molecular species, are shown to conform with the expectation that the effective dielectric constant of each of these solvents in the salt solution should be considerably greater than its macroscopic value. The K_A -values of tetra-*n*-butylammonium picrate, obtained by other investigators in seven one component solvents with *D*-values ranging from 5.04 to 34.69, are shown to vary linearly with $1/D$, thus warranting the same conclusion regarding the constancy of its α -parameter.

For many years prior to 1955 the most widely used theoretical expression for the relation between the dissociation constant of a salt in any solvent (of sufficiently low dielectric constant), the temperature, the dielectric constant of the solvent and the interionic distance in associated ion pairs (*viz.*, the α -parameter) was that derived by Bjerrum.³ As pointed out by Harned and Owen⁴ "the most noteworthy shortcoming of the Bjerrum model is its inability to follow the variation in the dissociation constant *K* with the dielectric constant *D* of the solvent without sometimes requiring highly specific dependence of the α -value upon the solvent." Some examples of this anomalous dependence of the α -parameter of a salt on the solvent are listed in a recent résumé of this subject by Kraus.⁵

It was recognized by those conversant with the Bjerrum theory that it had certain inherent

defects, partly mathematical and partly physical. These defects have been summarized and critically discussed by Fuoss.⁶ That aspect of this theory which is of particular interest in this investigation is the theoretical basis for obtaining the fraction of the pairs of oppositely charged ions which is to be counted as associated ion pairs. According to the Bjerrum theory the number of pairs of ions which are so counted is not restricted solely to those pairs which exist in "physical contact." Two oppositely charged ions are said to be in "physical contact" when the distance between them is sufficiently small to prevent the intervention of solvent molecules. (If, of course, the solvent molecules react to form a stable complex with either of the ions, then these complexing solvent molecules constitute an integral part of that ion.) Fuoss⁶ has given justification for his conclusion that this feature of the Bjerrum theory is untenable. In an earlier article⁷ the advantages of counting

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(3) N. Bjerrum, *Kgl. Danske Videnskab. Selskab.*, **7**, No. 9 (1926).

(4) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958, p. 294.

(5) C. A. Kraus, *J. Phys. Chem.*, **60**, 129 (1956).

(6) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958). See also R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishers, Inc., New York, N. Y., 1959, pp. 207-223.

(7) R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **79**, 3309 (1957).