[Contribution from the Isotope Department, The Weizmann Institute of Science]

The Isotopic Exchange between Hypohalites and Halide Ions. II. The Exchange between Hypochlorous Acid and Chloride Ions

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The rate of chlorine exchange between hypochlorite and chloride ions has been investigated in the range of *p*H 9.6–13.7. The reaction was found first order in hypochlorite and chloride concentrations and second order in hydrogen ion concentration. The rate constant for the expression $R = k(\text{HOCl})(\text{Cl}^-)(\text{H}^+)$ is 3.16×10^{13} l.² mole⁻² min.⁻¹ at 27°. The chlorine exchange proceeds at a slower rate than the chloride catalyzed oxygen exchange between HOCl and water (Anbar and Taube[2]). An intermediate $(\text{HOClCl})^-$ is suggested for the oxygen exchange reaction, which may exchange its oxygen with water without interchanging the chlorines. The same intermediate is postulated for the chlorine exchange reaction. Catalysis of the chlorine exchange by alcoholate ions demonstrates a direct exchange path through the respective hypochlorites. In contrast to the behavior of the free acid, the chlorine exchange between *t*-butyl hypochlorite and chloride ions was found both acid and base catalyzed, the acid catalysis being first order in H^+ and involving most probably $t\text{-BuOClH}^+$.

Introduction

In our preceding paper[1] we have described the kinetics of interaction of hypobromous acid with bromide ions as compared to the bromide catalyzed oxygen exchange of hypobromous acid. In an analogous manner we shall follow in this work the chlorine exchange between hypochlorous acid and its esters with chloride ions.[2] The catalytic effect of chloride ions on the rate of the reaction was found considerably slower than the interaction of bromide ions with hypochlorous acid.[3] This large difference in rates, compared with the fact that in the case of hypobromous acid the rate of interaction of chloride ions with hypobromous acid is faster than that of bromide ion, was rather surprising.[4] Further, there was an observation[5] that the rate of chloride exchange with hypochlorite ion at 0.1 *M* sodium hydroxide proceeds considerably *slower* than the chloride catalyzed oxygen exchange. It has been pointed out[6] that this result may exclude a straight forward substitution of the oxygen by the chloride ion. This result is also contrary to the findings in the case of hypobromous acid[1] where bromine was found to exchange *faster* than the catalyzed oxygen exchange.

The purpose of this work was to elucidate the mechanism of interaction of chlorine ions with hypochlorous acid by following the rates of chlorine exchange over an extended range of concentrations of the reagents. These results are to be compared with the kinetics of chlorine exchange between *t*-butyl hypochlorite and chloride ions.

Experimental

The chloride-free hypochlorous acid was prepared by extraction of a chlorine monoxide solution in carbon tetrachloride into a sodium hydroxide solution. The concentration of the sodium hydroxide was fixed so that the final alkalinity after extraction would be in the desired range of *p*H. The chlorine monoxide solution was prepared by shaking a chlorine solution in CCl_4 with analytical freshly prepared mercuric oxide. Care was taken to avoid moisture in the chlorine and in the HgO. The chlorine monoxide solution was analyzed for free chlorine before use. This was done by titrating the iodide released in the presence of an aliquot of standardized acid and then titrating the excess of the acid iodometrically by adding iodate in excess.[7] Stock solutions were discarded if the chlorine content exceeded 5% of the total oxidizing power. The concentration of the hypochlorite solutions was determined iodometrically, using standardized sodium thiosulfate.

Radioactive hypochlorous acid was prepared by hydrolysis of radioactive *t*-butyl hypochlorite. Radioactive chloride of high specific activity was added to a chloride-free hypochlorous acid solution, the solution was acidified to *p*H 9, *t*-butyl alcohol was added and the radioactive *t*-butyl hypochlorite formed, was separated, washed and dried.[8] In more recent experiments the direct exchange between *t*-butyl hypochlorite and chloride ions was used to produce labeled ROCl. This was achieved by shaking *t*-butyl hypochlorite with an acid solution containing radioactive chloride of high specific activity.

In the alkalinities under investigation, there is practically complete hydrolysis of *t*-butyl hypochlorite,[8] thus the ester could be used as a carrier of chloride-free hypochlorous acid. It has been shown that if the hypochlorous acid concentration does not exceed 0.1 molar, there is little effect of the alcohol formed by hydrolysis on the rate of exchange.

The anhydrous *t*-butyl alcohol for the $t\text{-BuOCl-Cl}^-$ exchange experiments was prepared from commercial purified alcohol. The alcohol was first fractionated and the fraction boiling in the range of 81–82.5° was separated. This was dried over crystalline sodium aluminum silicate (Linde Molecular Sieve Type 4a) and redistilled. Then about 1 g. of metallic lithium was added and the alcohol was fractionated again. The amount of water remaining was of the order of 10^{-1} molar (about 10 p.p.m.).

The chloride solution in absolute *t*-BuOH was prepared by dissolving analytical lithium chloride in the alcohol under reflux and using the saturated solution. Solutions of the order of 10^{-2} molar could be obtained. The BuO^- solutions were obtained by dissolving metallic lithium in the anhydrous alcohol. When the alcohol was extremely dry solutions of the order of 10^{-1} molar could be prepared, though traces of moisture made these solutions unstable and LiOH, possibly together with LiOBu, was precipitated. The acid solutions in absolute *t*-BuOH were prepared by preparing a 0.1 molar solution of *p*-toluenesulfonic acid in *t*-BuOH. This solution, which contained water, was fractionated with benzene and most of the water was removed in form of the azeotrope. The solution finally contained less than 0.5% water. This solution was now diluted with absolute *t*-BuOH to the desired range of acidities (10^{-6}–10^{-8} molar). Thus the water was diluted to same order of magnitude as in the basic solutions.

The radioactive chlorine used, chlorine 36, was used at two levels of specific activities. Potassium chloride^{36} obtained from Harwell and having a specific activity of 1 microcurie per gram, was recrystallized. HCl^{36}, having a specific activity of about 100 microcuries per gram, was obtained from The Radiochemical Centre, Amersham, and was used for preparing radioactive *t*-butyl hypochlorite. All other reagents were of analytical grade.

In the acidity range up to *p*H 12 the alkalinity was kept constant by phosphate buffer and was determined with an alkaline glass electrode using the Beckman Model G *p*H Meter, with an accuracy of ±0.05 *p*H unit. At higher

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(1) M. Anbar and R. Rein, This Journal, **81**, 1813 (1959).

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

(3) L. Farkas, M. Lewin and R. Bloch, *ibid.*, **71**, 1988 (1949).

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(5) R. A. Silverman and H. Taube, unpublished experiments, 1956.

(6) H. Taube, *Am. Rev. Nucl. Sc.*, **6**, 283 (1956).

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TABLE I

THE EXCHANGE OF CHLORINE BETWEEN HYPOCHLORITE AND CHLORIDE IONS

No.	*p*H	(OCl^-)	(Cl^-)	Phosph. buf. mole/l.	$t_{1/2}$, min.	k' l. mole^{-1} min.$^{-1}$	k''[f] l.^{3} mole^{-3} min.$^{-1}$	Remarks
1.01	9.6	0.0017	0.0017[e]	0.1	8.7	23.5	0.38	[a]
1.02	9.8	.00043	.0017[e]	.1	26	12.5	.50	[a]
1.03	9.9	.002	.0026[e]	.1	18	8.4	.53	[a]
1.04	10.2	.47	.05	.2	0.3	4.43	1.08	[a]
1.05	10.5	.21	.033	.2	3.0	0.96	0.96	[a]
1.06	10.6	.53	.05	.2	2.1	.57	0.91	[a]
1.07	10.7	.30	.25	.2	3.0	.42	1.05	[b]
1.08	10.7	.08	.05	.2	24	.23	0.58	[c]
1.09	10.8	.15	.09	.2	14	.21	.81	[a]
1.10	10.8	.73	.05	.05	4.8	.19	.76	[a]
1.11	10.8	.65	.05	.8	6	.17	.68	[a]
1.12	10.8	.37	.05	.2	6.3	.27	1.08	[a]
1.13	11.1	.47	.05	.2	20.0	.67	1.06	[a]
1.14	11.3	.37	.17	.2	42	.031	1.24	[b]
1.15	11.3	.45	.05	.2	50	.028	1.12	[a]
1.16	11.3	.45	.05	.2	60	.023	0.92	[a] 1 *M* F^-
1.17	11.6	.70	.05	.2	120	7.7×10^{-3}	1.23	[a]
1.18	11.8	.35	.20	.2	312	4.0×10^{-3}	1.60	[b]
1.19	12.1	.50	.05	.2	2760	0.45×10^{-3}	0.57	[a]
1.20	12.5	.05	1.00	..	5870	0.12×10^{-3}	0.38	[a,d]
1.21	13.0	.05	1.00	..	50500	1.25×10^{-5}	1.25	[a,d]
1.22	13.0	.05	5.00	..	9900	1.4×10^{-5}	1.40	[a,d]
1.23	13.3	.05	5.00	..	35500	0.38×10^{-5}	1.52	[a,d]

[a] Kinetics followed chloride activity. [b] Kinetics followed hypochlorite activity by the *t*-butyl hypochlorite method. [c] Kinetics followed hypochlorite activity by the *p*-cresol method. [d] Kinetics started with radioactive hypochlorite. [e] Concentration determined by dilution analysis. [f] $k'' = k'/(H^+)^2$.

alkalinities no buffer was used and the OH^- concentration was determined by potentiometric titrations.

The BuO^- concentrations in the *t*-BuOCl–Cl^- exchange experiments were determined by potentiometric titrations after introducing an aliquot of the alcoholic solution into CO_2-free distilled water.

The reaction mixtures containing hypochlorite and chloride ions in a buffered or unbuffered solution were kept in a thermostat at 27 ± 0.2°. Aliquots were withdrawn at different time intervals and their activity was determined by the following methods.

1. **Radioassay of the Hypochlorous Acid up to *p*H 11.5.**—An aliquot of 1 ml. was added to a 5-ml. aqueous suspension containing 1 g. of silver phosphate and was mechanically shaken. Then the silver chloride and the excess of silver phosphate were separated by centrifugation. The solution, which was now chloride-free, was acidified to *p*H 8 and *t*-butyl alcohol was added. The *t*-butyl hypochlorite formed was extracted by 2 ml. of toluene and the toluene solution was transferred into a 5-ml. volumetric flask and diluted to 5 ml. An aliquot was taken and introduced into a scintillation solution which was counted (*cf.* ref. 1). An aliquot was later taken from the scintillation mixture, was added to an acid iodide solution and titrated with standardized sodium thiosulfate. This procedure giving the specific activity of the sample was shown to yield a 98% counting efficiency of the radioactivity. Moreover, the scintillation mixtures containing the hypochlorite ester were shown to remain stable for hours in respect to the hypochlorite content, thus making the iodometric titrations quite reliable. There have been some attempts to use the reaction of hypochlorous acid with *p*-cresol for radioassay.[1] The results are satisfactory but, as the *t*-butyl hypochlorite method gives a direct measure of the specific activity, the *p*-cresol method was rejected.

2. **Radioassay of the Chloride Ion.**—The silver chloride-silver phosphate mixture obtained by centrifugation (see above) was washed with water, then dilute ammonium hydroxide was added. This dissolves the phosphate, as well as some silver oxide formed. The remaining silver chloride was filtered and the filter paper mounted for counting with a Geiger counter. This procedure was improved in later experiments by separating the silver chloride by centrifuge, dissolving it in concentrated ammonium hydroxide and evaporating the solution in a counting dish. When the *t*-butyl hypochlorite method was not applied, silver phosphate or silver acetate was used to precipitate all the chloride and the supernatant was rejected. At higher concentration of chloride, when large amounts of AgCl were to be counted, the silver chloride was dissolved in ammonium hydroxide solution and then the solution was evaporated in a counting dish on a rotatory dryer to obtain a homogeneous layer for counting. At higher alkalinity (*p*H > 11.5) formation of silver oxide interfered with the quantitative precipitation of silver chloride; thus in these cases, which were also runs of higher chloride concentrations, only a part (10-30%) of the total chloride was precipitated. The precipitation was done by adding a constant volume of silver perchlorate solution to the reaction mixture.

When the concentrations of radioactive chloride were very low (*p*H >10), the aliquots of the reaction mixture were quenched in 0.2 *M* sodium hydroxide solution containing 0.01 *M* chloride as carrier. In these runs the chloride concentration was determined by dilution analysis, comparing the specific activities at time zero and at equilibrium with the concentration of HOCl as determined iodometrically. The equilibrium values of activity for very long runs were obtained by acidifying the reaction mixture prior to the addition of the silver salt.

The kinetics of chloride exchange between *t*-BuOCl and Cl^- were followed by introducing aliquots of the reaction mixtures into a known volume of silver perchlorate solution in anhydrous acetone. Silver chloride precipitated and it was centrifuged, washed with dry acetone, centrifuged again and then dissolved in concentrated ammonium hydroxide solution and transferred to a counting dish for evaporation. At chloride concentration below 3×10^{-2} the aliquot of the reaction mixture were first mixed with a 5×10^{-2} molar chloride solution in anhydrous *t*-butyl alcohol and then the $AgClO_4$ solution was added. There was no induced exchange in this procedure.

Results

The rate of chlorine exchange between hypochlorite and chloride ions was investigated changing the chloride concentration 2500-fold, the hypochlorite concentration 1500-fold and the hydrogen ion concentration 10,000-fold. Over this wide range of concentration, half-lives of the exchange ranged from 12 seconds to over a year, but the rate law remained unchanged. Table I presents a selection of typical runs under different concentrations of the reagents. Each run consists of 5–10 points and the constants given are averages. The standard deviation in 90% of the runs does not exceed 25%. All the exchange results are given in Fig. 1 as function of *p*H.

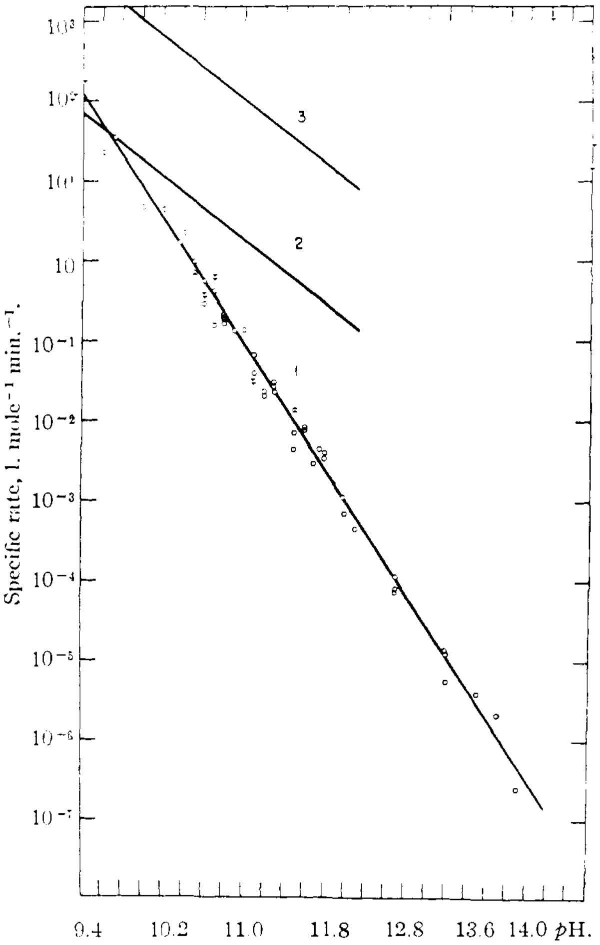

Fig. 1.—The rate of HOCl–Cl$^-$ exchange reactions as function of *p*H: (1) HOCl–Cl$^-$ chlorine exchange; (2) Cl$^-$ catalyzed oxygen exchange with water[2]; (3) HOCl–Br$^-$ → HOBr + Cl$^-$ reaction[3] (Ordinate = specific rate l. mole^{-1} min.$^{-1}$).

From Table I it may be seen that the rate of exchange is proportional both to hypochlorite and to chloride concentration and to the second power of hydrogen ion concentration. Also it is found at $p\text{H} < 12$ that there is no substantial effect of the buffer concentration, (it should be noted that phosphate buffer is both a general acid and general base) (*cf.* 1.10, 1.11, 1.12). On the other hand a small negative salt effect may exist (*cf.* 1.15, 1.16). In the more alkaline region, however, a kind of general base catalysis to be described in a following paragraph is detected. The dependence on the hydrogen ion concentration is clearly demonstrated in Fig. 1 which displays data extending over four *p*H units and over nine orders of magnitude of the rate constant k'. Using all our data k'' is $9.3 \pm 2.8 \times 10^{20}$ l.^{3} mole^{-3} min.$^{-1}$.

The rate law, rate $= k'' (\text{H}^+)^2(\text{ClO}^-)(\text{Cl}^-)$, can be presented in the equivalent form $k'(\text{H}^+)(\text{HOCl})(\text{Cl}^-)$. Taking the dissociation constant of hypochlorous acid $K_a = 3.4 \times 10^{-8}$ (*cf.*[2]) into account, k' becomes $3.16 \pm 0.95 \times 10^{13}$ l.^{2} mole^{-2} min.$^{-1}$.

The effect of *t*-butyl alcohol, ethyl and methyl alcohol on the rate of chlorine exchange, are presented in Table II.

TABLE II

THE EFFECT OF ALCOHOLS ON THE RATE OF CHLORINE EXCHANGE

	(OH$^-$)	(ROH)	(OCl$^-$)	(Cl$^-$)	k', l. mole^{-1} min.$^{-1}$
2.01	0.1		0.05	1.0	7.5×10^{-6}
2.02	.1	0.2^a	.05	1.0	1.1×10^{-5}
2.03	.1	1^a	.05	1.0	1.6×10^{-5}
2.04	.1	2^a	.05	1.0	2.9×10^{-5}
2.05	.1	3^a	.05	1.0	4.4×10^{-5}
2.06	.1	2^b	.05	1.0	7.3×10^{-6}
2.07	.5	..	.05	1.0	2.5×10^{-7}
2.08	.5	1^a	.05	1.0	2.5×10^{-6}
2.09	.5	2^a	.05	1.0	4.5×10^{-5}
2.10	.5	1^c	.05	1.0	2.6×10^{-6}
2.11	.5	1^d	.05	1.0	2.6×10^{-6}
2.12	.5	2^b	.05	1.0	9.1×10^{-7}

[a] *t*-BuOH. [b] Dioxane. [c] EtOH. [d] MeOH.

It may be seen that alcohols have a catalytic effect on the rate of exchange which is not a solvent effect (*cf.* 2.01, 2.04, 2.06; 2.09, 2.12). In the case of *t*-butyl alcohol the effect can be shown to be directly proportional to its concentration and inversely proportional to the hydroxyl ion concentration.

From the rate coefficients of runs 3.01–3.05 and 3.07, one can compute the specific rate coefficient k for $R = k(t\text{-BuOH})(\text{OCl}^-)(\text{Cl}^-)$; k is found 1.1×10^{-5} l.^{2} mole^{-2} min.$^{-1}$ at 0.1 molar OH$^-$ and 2.2×10^{-6} at 0.5 molar OH$^-$.

Table III presents the effect of acetate ion concentration on the rate of chlorine exchange. The results of these series were not as reproducible as those in unbuffered or in phosphate buffered solutions, thus they allow us only a qualitative interpretation.

TABLE III

THE EFFECT OF ACETATE IONS ON THE RATE OF CHLORINE EXCHANGE

	(OH$^-$)	(AcO$^-$)	(OCl$^-$)	(Cl$^-$)	k', l. mole^{-1} min.$^{-1}$
3.01	0.006	..	0.05	1.0	4.4×10^{-3}
3.02	.006	1.0	.05	1.0	2.2×10^{-2}
3.03	.006	3.0	.05	1.0	1.4×10^{-2}
3.04	.03	..	.05	1.0	8.0×10^{-5}
3.05	.03	0.5	.05	1.0	2.4×10^{-4}
3.06	.03	1.0	.05	1.0	1.3×10^{-3}
3.07	.03	3.0	.05	1.0	6.3×10^{-4}
3.08	.1	..	.05	1.0	5.5×10^{-6}
3.09	.1	3M NaClO$_4$	.05	1.0	4.4×10^{-6}
3.10	.1	0.5	.05	1.0	4.2×10^{-6}
3.11	.1	3.0	.05	1.0	4.1×10^{-5}
3.12	.1	1.0	.05	5.0	1.7×10^{-5}
3.13	.25	..	.05	5.0	1.6×10^{-6}
3.14	.25	1.0	.05	5.0	6.9×10^{-6}

We see here a definite catalytic effect of acetate ions on the rate of exchange. The effect becomes more pronounced with the rise of alkalinity (*cf.* 3.02, 3.06; 3.05, 3.10; 3.03, 3.07). The catalytic effect of acetate ion is smaller at higher chloride concentrations (*cf.* 3.10, 3.12; 3.14). It seems that at higher acetate concentrations there is a decrease in the catalytic effect of acetate ions (*cf.* 3.02, 3.03; 3.06, 3.07) which cannot be accounted for by a simple salt effect (*cf.* 3.08, 3.09, 3.11).

The kinetics of *t*-BuOCl–Cl$^-$ exchange studied in anhydrous *t*-butyl alcohol are represented in Tables IVa–IVc. The reproducibility of these kinetic data is limited due to the effect of traces of water on the rate of exchange and due to the fact, that both butoxide and chloride solutions in the range used were oversaturated. Therefore we will consider these results on a semiquantitative basis only.

Table IVa represents the effects of *t*-BuOCl, *t*-BuO$^-$ and Cl$^-$ ions on the rate of chlorine exchange.

TABLE IVa

THE EFFECT OF *t*-BuOCl, Cl$^-$ AND BuO$^-$ ON THE RATE OF CHLORINE EXCHANGE BETWEEN *t*-BuOCl AND Cl$^-$ IN ANHYDROUS *t*-BuOH

	(BuO$^-$) × 10^3	(Cl$^-$) × 10^2	(BuOCl$^-$) × 10^2	$t_{1/2}$, min.	k' × 10^2, l. mole^{-1} min.$^{-1}$
4.11	3.5	6	25.0	20	11.2
4.12	3.5	6.1	12.5	30	12.5
4.13	3.5	6.1	5	35	17.8
4.14	3.5	6	2.5	44	18.6
4.15	3.5	6	1.0	120	8.3
4.16	3.5	6.1	0.5	150	7.1
4.17	3.5	6	0.25	210	5.3
4.21	2.5	35.0	4	11.5	15.5
4.22	2.5	14	4	13.5	28.5
4.23	2.5	7	4	15	42
4.24	2.5	3.5	4	27	31
4.25	2.5	1.4	4	42	31
4.26	2.5	0.7	4	61	24
4.31	50	7	5	19	31
4.32	25	7	5	22	26.5
4.33	12.5	7	5	28	20.4
4.34	5.0	7	5	34	17
4.35	2.5	7	5	45	13
4.36	0.5	7	5	144	4
4.41	.35	6	4	98	7.1
4.42	.23	6	4	245	2.8
4.43	.077	6	4	675	1.03
4.44	.037	6	4	1240	0.56

The consistency within a series of runs performed with the same reagent at the same time is better than that between different series.

From series 4.11–4.17 it may be seen that the exchange does not deviate appreciably from the second-order rate law. Thus changing *t*-BuOCl concentration one hundred fold did not affect the calculated rate constant by more than a factor of two; the same is true of the effect of chloride ion, the concentration of which is changed fifty fold. As may be seen in series 4.31–4.44, increasing the concentration of butoxide ions increases the rate of exchange, but not in a simple manner. Comparing 4.31 with 4.44 we see that changing butoxide concentration by a factor of over one thousand, induces a rate catalysis by a factor of sixty only. On the other hand comparing runs 4.35 with 4.42 we see a fivefold change in rate following a ten-fold change in butoxide concentration; morover comparing 4.41, 4.42, 4.43, 4.44 shows a first-order proportionality between the rate of exchange and butoxide concentration. It should be borne in mind that at the higher butoxide concentrations we are concerned with saturated or nearly saturated solutions of lithium butoxide. It may be suggested that at these concentrations most of the butoxide exist in form of ion pairs, thus we obtain a reduced catalytic effect.

Table IVb demonstrates the effect of water and acetate ions on the rate of exchange.

TABLE IVb

THE EFFECT OF WATER AND OF ACETATE IONS ON THE RATE OF CHLORINE EXCHANGE BETWEEN *t*-BuOCl AND CHLORIDE IONS

	(BuO$^-$) × 10^3	(Cl$^-$) × 10^2	(BuOCl) × 10^2	(H$_2$O) × 10^2	(AcO$^-$) × 10^{-3}	$t_{1/2}$, min.
4.51	3.8	7	5	264	..	3.3
4.52	3.8	7	5	88	..	6.5
4.53	3.8	7	5	26	..	7.8
4.54	3.8	7	5	8.8	..	9.3
4.55	3.8	7	5	2.6	..	12.7
4.56	3.8	7	5	0.9	..	13.5
4.61	20	4	2	...	1.4	22
4.62	20	4	2	...	2.8	45
4.63	20	4	2	...	5.6	26
4.71	8	6	0.8	...	1.4	58
4.72	8	6	0.8	...	2.8	107
4.73	8	6	0.8	...	5.6	115

From Table Vb it can be seen that water has a positive catalytic effect on the rate of exchange and that acetate ion has no effect on the rate of reaction. The behavior of the *t*-BuOCl–Cl$^-$ system in the acid region is summarized in Table IVc.

TABLE IVc

THE EFFECT OF TOLUENESULFONIC ACID ON THE RATE OF CHLORINE EXCHANGE BETWEEN *t*-BuOCl AND CHLORIDE IONS IN ABSOLUTE *t*-BuOH

	(H$^+$) × 10^8	(Cl$^-$) × 10^2	(BuOCl) × 10^2	$t_{1/2}$	k'	k''^a	k''(H$^+$) × 10^5
4.81	800	6	5	3	2.1	2.05	2.6
4.82	500	6	5	6.6	0.95	0.90	1.8
4.83	240	6	5	14	.45	.40	1.7
4.84	200	6	5	9	.69	.64	3.2
4.85	80	6	5	16.5	.38	.33	4.1
4.86	40	6	5	28	.23	.18	4.5
4.87	16	6	5	38	.164	.11	6.9
4.88	8	6	5	65	.097	.047	5.9
4.89	4	6	5	115	.055	.005	1.2
4.90	..	6	5	125	.050		

$k = 3.6 \pm 1.8 \times 10^5$ l.^{2} mole^{-2} min.$^{-1}$

[a] $k'' = k' - k'_{\mathrm{BuOH}}$; k'_{BuOH} is the rate constant of the non-catalyzed reaction as it appears in run 5.90.

It can be seen from Table IVc that the chlorine exchange is acid catalyzed and that there is a first-order dependence on (H$^+$)

$$R = k(\mathrm{H}^+)(\mathrm{BuOCl})(\mathrm{Cl}^-),\ k = 3.6 \times 10^5 \text{ l.}^2 \text{ mole}^{-2} \text{ min.}^{-1}$$

Discussion

The interaction between hypochlorous acid and chloride ions in aqueous solutions may lead to three different results: (1) chlorine may be formed; (2) the chlorine atoms may exchange; (3) there may be an induced oxygen exchange between hypochlorous acid and water. In fact the first interaction $HOCl + Cl^- \rightleftarrows Cl_2 + OH^-$ will result in a simultaneous chlorine exchange and a chloride induced oxygen exchange. Kinetic studies of the chloride induced oxygen exchange[2] and the chlorine exchange between hypochlorite and chloride ions presented in this paper may be compared with the kinetic study of chlorine hydrolysis[9] which implies, by using the equilibrium constant for the chlorine hydrolysis,[10] the rate of chlorine formation from $HCl + HOCl$. We do see that the above-mentioned three interactions proceed at different rates

(1) The chlorine formation[9,10]; rate = $k_1(HOCl)(Cl^-)(H^+)$

(2) The chlorine exchange; rate = $k_2(HOCl)(Cl^-)(H^+)$; $k_2 \gg k_1$

(3) The chloride induced oxygen exchange[2]; rate = $k_3(HOCl)(Cl^-)$ does not lead to chlorine exchange. (Reactions 2 and 3 are compared in Fig. 1.)

The mechanism of reaction 3 has been discussed in a previous paper[2] and it has been concluded that the chlorine atoms in the activated complex ($H_2O \cdot HOCl \cdot Cl^-$) do not become equivalent whereas the oxygens may exchange. Next we have before us an activated complex ($H_3O^+ \cdot HOCl \cdot Cl^-$) which leads to a chlorine exchange.[11] This activated complex, having the same composition of the activated complex of reaction 1 must behave differently and no free chlorine is formed by its decomposition. The difference between the two modes of decomposition of two similar activated complexes may be due to a different position and role of the water molecule. In the case of chlorine exchange the water molecule is probably attached to the terminal chlorine which subsequently becomes a hypochlorite chlorine

$$(H_2{}^+OCl^*Cl^- \cdot H_2O) \rightleftarrows H_2O + Cl^- + {}^*ClOH_2{}^+ \rightleftarrows H_2O + Cl^- + Cl^*OH + H^+$$

In the case of chlorine formation the water molecule may be attached to the hypochlorous acid end of the complex ($H_2O \cdot H_2OCl \cdot Cl^-$) $\rightleftarrows 2H_2O + Cl_2$.

The precursor of the ($H_2O \cdot ClClH_2O$) complex is probably the ($HOClCl^-$) ion the role of which in hypohalite chemistry has been discussed elsewhere.[2] The rate-determining step in this case will be therefore a proton transfer to this trihalide-like ion. Assuming arbitrarily that the equilibrium constant for the formation of $HOClCl^-$ is equal to unity, we end up with a rate constant of 3×10^{13} l. mole^{-1} min.$^{-1}$ for the proton transfer, which is comparable to the value obtained by Eigen for fast proton transfer reactions.[12] The precursor for the formation of the second type activated complex is probably the hydrated H_2OCl^+ which exists only in much more acid solutions than those studied by us.[8,13]

Comparing the four reactions $HOCl + Cl^-$, $HOCl + Br^-$, $HOBr + Cl^-$ and $HOBr + Br^-$ we note, that the $HOCl$–Br^- reaction[3] proceeds at a higher rate than Cl^- catalysed oxygen exchange.[2] Assuming that the rate determining step in the chloride catalyzed oxygen exchange is most probably the nucleophilic attack on $HOClCl^-$ which itself may be formed at a much higher rate, there is no inconsistency between the $HOCl$–Cl^- and $HOCl$–Br^- interactions.[4] It has been suggested that BrCl is formed as intermediate in the $HOCl$–Br^- reaction.[14] It seems probable that when a bromide ion attacks an HOCl molecule, a $HOClBr^-$ is formed, this ion is capable of losing its OH^- and forming a ClBr molecule which hydrolyzes instantly to HOBr and Cl^-. Remembering that the Br^- will attack HOCl on the Cl side because this is slightly positively polarized[15] and assuming that the $(HOClBr)^-$ ion is linear in analogy to trihalide ions, we may exclude the possibility of releasing a Cl^- ion from the $(HOClBr)^-$ ion in a single step. The comparable rates of the HOCl–Br, HOBr–Br, $HOBr$–Cl^- reactions, namely 1.77, 1.8 and 4.8×10^5 l. mole^{-1} min.$^{-1}$, respectively,[2,3] may point to a similar rate-determining step in the three reactions. In the case of $HOCl$–Cl^- interaction to form $HOClCl^-$, only the original Cl^- may split off, whereas the OH^- may interchange with the solvent without affecting the polarity of the chlorine bound to it.

The catalytic effect of the alcohols may be explained by the formation of the corresponding esters as intermediates

$$HOCl + RO^- \overset{\text{fast}}{\rightleftarrows} ROCl + OH^-;$$

$$ROCl + Cl^- \overset{k}{\rightleftarrows} RO^- + Cl_2$$

The RO^- group may polarize the ROCl molecule sufficiently to enable an attack of a chloride ion on its chlorine. As the ROCl concentration is proportional to the first power of hydrogen ion concentration, $(ROCl) = K(OCl^-)(ROH)(H^+)$, we observe a first-order dependence on H^+ concentration. The different mode of chlorine exchange between *t*-butyl hypochlorite and chloride ions is probably due to the polarizing effect of the *t*-butyl group on the chlorine. This chlorine is accessible to a nucleophilic reagent, without requiring an additional proton. The difference between ROCl and HOCl is manifested again by the fact that a nucleophilic reagent like OH^- attacks *t*-BuOCl at the chlorine end,[8] whereas an analogous attack on HOCl, which would lead to oxygen exchange, could not be detected.[2]

The exchange reaction of *t*-BuOCl with Cl^- studied in non-aqueous solutions confirms the difference in behavior of ROCl as compared to HOCl. We do observe in this system both an acid and a base catalysis. The deviations from linearity at the higher electrolyte concentrations may be attributed to the formation of ion pairs. The cata-

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(9) E. Shilov and S. N. Solodushenkov, *J. Phys. Chem.* (*USSR*), **21**, 1159 (1947).

(10) W. M. Latimer, "Oxidation Potentials," Prentice–Hall, New York, N. Y., 1952, p. 54.

(11) Whether oxygen exchanges simultaneously with chlorine at *p*H values below 9.5 where reaction 3 should dominate has not been proven (*cf.* Fig. 1) because of experimental limitations, but it is most probable that this is actually the case.

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lytic effect of small amounts of water on the rate of exchange, points to an effect of ion pair dissociation.

In the acid region we pick up a reaction path involving acid catalysis, but we see that the presence of an acid is no prerequisite for the ROCl–Cl^- chlorine exchange, as it is in the case of the HOCl–Cl^- exchange. The acid path becomes appreciable only at acid concentrations above 10^{-7}-molar where we may assume t-BuOCl$^+$ as intermediate. Estimating the dissociation constant of t-BuOHCl$^+$ at 10^2 we derive a specific rate constant for this reaction $k = 4 \times 10^7$ l. mole^{-1} min.$^{-1}$ at 27°.

In the basic region we are surprised by the well established catalytic effect of t-BuO$^-$ concentration on the rate of exchange. We suggest three ways to explain this effect: one is to assume that a butoxide ion forms a complex with t-BuOCl which facilitates the interaction with Cl^-. It is hard however to see, why should $(t\text{-BuO})_2Cl^-$ be more liable to a nucleophilic attack than t-BuOCl; if such a complex would be formed, it might probably suppress the rate of exchange. An alternative explanation may be by the reaction t-BuOCl + t-BuOLi $\rightleftarrows$ $t\text{-Bu}\underset{\text{Li}}{\text{O}}\text{Cl}^+$ + tBuO$^-$ whereafter $t\text{-Bu}\underset{\text{Li}}{\text{O}}\text{Cl}^+$ is attacked by Cl^-; $t\text{-Bu}\underset{\text{Li}}{\text{O}}\text{Cl}^+ + Cl^- \rightleftarrows t\text{-BuOLi} + Cl_2$. This assumption would require a second-order effect of LiCl concentration, which has not been observed. The third explanation may be the effect of BuO$^-$ on the availability of free Cl^- ions in our system. If we assume that the LiCl exists in solution in an undissociated form, then by the reaction LiCl + BuOLi $\rightleftarrows$ BuOLi$_2^+$ + Cl^- more chloride ions are available for exchange. Still there is no evidence available for the existence of complexes of the type t-BuOLi$_2^+$. We conclude that it is hard to offer an explanation for the t-BuO$^-$ effect.

The effect of acetate ions on the rate of chlorine exchange is not clear. It is hard to assume acetyl hypochlorite as intermediate because its rate of formation is slower[8] than the catalytic effect of acetate ions on the chlorine exchange. The pH dependence here is not well established, whereas the dependence on the chloride ion concentration points to competing reactions between AcO$^-$ and Cl^- ions. We may conclude that the effect of acetate ions on the chlorine exchange requires further investigation.

Conclusion

Our results give more evidence that the HOCl system differs basically from the HOBr system. Having a much stronger HO–X bond, HOCl follows different mechanisms of interaction with nucleophilic reagents the HOCl molecule requires occasionally an additional proton to make its chlorine accessible. Next it has been shown that the trihalide like ions HOX^-_2 or $HOXY^-$ may occasionally occur as intermediates in HOX reactions.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE AGRICULTURAL AND MECHANICAL COLLEGE OF TEXAS]

The System NaF–HF–H_2O at 0 and -15°[1]

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The system NaF–HF–H_2O has been studied at 0 and −15°. The solid phases include NaF·HF, NaF·2HF, NaF·3HF and NaF·4HF at both temperatures. NaF exists in the 0° case and presumably at −15°.

Introduction

Ternary systems involving an inorganic fluoride, hydrogen fluoride and water have been studied by relatively few workers. Tananaev has investigated systems involving hydrogen fluoride, water and lithium fluoride,[2] potassium fluoride,[3] zirconium(IV) fluoride[4] and iron(III) fluoride.[5] Clark[6] has listed some data on the solubility of sodium fluoride in various concentrations of aqueous hydrogen fluoride.

Our interest in the ternary system sodium fluoride–hydrogen fluoride–water (NaF–HF–H_2O) was stimulated by the lack of complete data for this system and the disagreement in the literature concerning the fluorides in this system. Simons[7] states that, with aqueous or anhydrous HF, the acid salt NaF·HF results and is the only acid fluoride of sodium known. According to Jache and Cady,[8] the analysis of the solid phase in equilibrium with HF saturated with NaF indicated the presence of 1 mole of NaF to 4.10 of HF at −24.3°. Tananaev[9] has also studied part of this system but his results seem not to have been noted by later workers.

We have studied this system at 0 and −15° using the Schreinemakers wet residue method.[10]

Experimental

Samples were made up from reagent grade NaF and aqueous HF. When HF of concentration greater than 48% was needed it was made up from mixtures of anhydrous HF

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[1] Presented at the 133rd National Meeting of the American Chemical Society, San Francisco, California.

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