Discussion

From Fig. 1 it can be seen that the calculated and experimental potentials differ at 7.80 and 18.01 atm. total pressure by no more than a few millivolts up to 150°. This is probably within experimental error. At higher temperatures the deviation becomes as large as 10 mv. The experimental points at 41.82 atm. total pressure are lower than the calculated curve by 6 to 10 mv. up to 150° and then drop increasingly farther below the calculated curve until the value at 250° is 58 mv. below the calculated value.

Two possible explanations of the discrepancy between the calculated and experimental potentials at the higher temperatures and pressures are: (1) Hydrogen reduction of part of the AgCl of the Ag, AgCl electrode. This would increase the acid concentration and hence lower the potential of the system. Also the silver thus formed could poison the platinum electrode.

(2) A lowering of the silver chloride electrode potential by hydrogen. The fact that this effect can be very appreciable was experimentally demonstrated by Choudhury and Bonilla.[2] The mechanism of the potential lowering would probably involve the extablishment of hydrogen electrode sites on the silver metal of the silver, silver chloride electrode. This effect would be most pronounced at higher temperatures at constant pressure and at higher hydrogen pressures at constant temperature. Figure 1 shows that the deviations between the experimental and calculated values are in these directions.

OAK RIDGE, TENN.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, OREGON STATE COLLEGE]

Isotopic Exchange Reactions in Liquid Sulfur Dioxide. IV. Kinetics of the Catalyzed S^{35}-Exchange between Thionyl Chloride and Sulfur Dioxide[1]

BY B. J. MASTERS[2] AND T. H. NORRIS

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Extending earlier work, a study has been made of the kinetics of the chloride-catalyzed S^{35} exchange reaction between liquid sulfur dioxide and thionyl chloride. Whereas rubidium and tetramethylammonium chlorides are effective catalysts, acid chlorides (aluminum and hydrogen chlorides) are found to be far less, if at all, active. A basic catalysis by chloride ion is proposed. Experiments both in excess sulfur dioxide and in excess thionyl chloride indicate the rate law Rate = k_3 (catalyst)($SOCl_2$)(SO_2). With tetramethylammonium chloride in excess sulfur dioxide the rate constant is about 0.06 l.^{2} mole^{-2} hr.$^{-1}$ (0°), while rubidium chloride gives *ca.* 0.03 l.^{2} mole^{-2} hr.$^{-1}$; in a large excess of thionyl chloride tetramethylammonium chloride gives about 0.22 l.^{2} mole^{-2} hr.$^{-1}$. For these three systems, activation energies are, respectively, 14.7, 14.7 and 13.6 kcal./mole and entropies of activation are -28.1, -29.5, and -29.6 cal. deg.$^{-1}$ mole^{-1}. A mechanism for the reaction is suggested. Comparison with the thionyl bromide–sulfur dioxide exchange reveals that, whereas the latter system shows, with tetramethylammonium bromide, a comparable activation energy of 13.2 kcal./mole, the rate is only about one-seventh as great as in the present case, possibly explicable in terms of a greater basicity for chloride than for bromide ion.

Whereas in pure liquid sulfur dioxide, thionyl halides do not exchange S^{35} at a significant rate with the solvent,[3] similar solutions containing certain soluble halide salts exhibit a rapid exchange. This observation, previously reported, led to an investigation of the kinetics of the catalysis involving the solute thionyl bromide.[4] The present research consists of a study of the kinetics of the catalyzed exchange reaction in the related thionyl chloride–sulfur dioxide system. The experiments, more extensive than the earlier ones, include results for solutions over the entire range from excess sulfur dioxide to excess thionyl chloride.

Experimental

Techniques were generally similar to those of previous work.[3,4] Radiosulfur, S^{35}, was obtained from the Atomic Energy Commission in the form of neutron-irradiated potassium chloride. Samples were counted as thin deposits of barium sulfate with an end window counter, all appropriate corrections being applied. In general, planchets were prepared and counted in duplicate.

Preparation of Reactants.—Sulfur dioxide was purified as previously described.[4] In addition a final rough fractional distillation of the liquid was done (*in vacuo*), only the middle third being retained.

Labeled sulfur dioxide was prepared as previously described,[5] and was generally shaken with concentrated sulfuric acid and then passed through phosphorus pentoxide. The resulting high specific activity material was either used directly to prepare labeled thionyl chloride, or was diluted several hundredfold with inactive sulfur dioxide to *ca.* 1000 c./min./mg. (as $BaSO_4$).

Thionyl chloride (Matheson, Coleman and Bell, b.p. range 75–76°) was distilled successively from quinoline and boiled linseed oil.[6] The resulting clear, colorless product was fractionated in the vacuum system, the middle third being collected in sealed glass tubes provided with break tips, in which it was stored in darkness until used.

Labeled thionyl chloride was prepared by an exchange, in which 100 mmoles of inactive material, 10 mmoles of high activity dioxide, and 3 mmoles of tetramethylammonium chloride catalyst were left together in a sealed tube in darkness for three days at room temperature. The volatile material, after complete distillation from the catalyst, was then fractionated in the vacuum system, the middle third, about 4 ml., being retained and diluted about tenfold with inactive thionyl chloride to give a final specific activity of *ca.* 4,000 c./min./mg. Traces of $S^{35}O_2$ left by this procedure were almost completely eliminated by a process of further fractionation, used in filling the exchange bombs.

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[1] Presented before the Physical and Inorganic Division of the American Chemical Society in New York, September, 1954. Published with the approval of the Oregon State College Monographs Committee, Research Paper No. 259, Department of Chemistry, School of Science.

[2] Taken from the thesis of B. J. Masters, submitted in partial fulfillment of the requirements for the Ph.D. degree, at Oregon State College, June, 1954.

[3] R. E. Johnson, T. H. Norris and J. L. Huston, THIS JOURNAL, **73**, 3052 (1951). Also E. C. M. Grigg and I. Lauder, *Trans. Faraday Soc.*, **46**, 1039 (1950); R. Muxart, *Compt. rend.*, **231**, 1489 (1950).

[4] R. H. Herber, T. H. Norris and J. L. Huston, THIS JOURNAL, **76**, 2015 (1954).

[5] B. J. Masters and T. H. Norris, *ibid.*, **74**, 2395 (1952).

[6] L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., Boston, Mass., 1941, p. 381.

Anal. Calcd. for $SOCl_2$: d^{20}_4, 1.638.[7] Found: d^{20}_4, 1.630.

Tetramethylammonium Chloride.—A few of the last experiments were done with Matheson, Coleman and Bell material, freed of its strong amine odor by a double wash with chloroform and recrystallization from an absolute ethanol–chloroform mixture. Most of the work, however, involved material prepared by metathesis from tetramethylammonium bromide (Eastman, White Label). Excess freshly precipitated silver chloride was shaken in a darkened flask with the bromide solution. After removal of the solid, the supernatant was shaken several times with chlorine water and carbon tetrachloride, until no further bromine coloration appeared in the latter, and was then evaporated to dryness. The crystals, washed with chloroform, recrystallized from absolute ethanol and dried at 130° for one hour, were snow-white and odorless. The hygroscopic product was stored in a opaque desiccator.

Anal. Calcd. for Me_4NCl: Cl, 32.40. Found: Cl, 32.30.

Rubidium chloride (99% purity from A. D. Mackay, Inc.) was used without purification other than drying.

Aluminum chloride (Baker C.P., anhydrous) was resublimed several times in vacuum down a long tube, through glass wool, and finally, still *in vacuo*, transferred directly into the reaction bombs.

Hydrogen chloride (Matheson, anhydrous, 99.0%) was passed from a cylinder through phosphorus pentoxide and, after condensation, was separated by distillation into three equal fractions, the middle one being finally frozen with liquid nitrogen and pumped to a high vacuum.

Water, freshly distilled, was first pumped upon while frozen with liquid nitrogen, and then, as liquid, was allowed to boil under vacuum to eliminate permanent gases.

Run Procedures.—These involved standard high vacuum techniques and were generally similar to those of previous work.[4] All distillations were accomplished without elevation of temperature, either by cooling receivers with liquid nitrogen, or in some cases by evaporating a portion of the material into large evacuated volumes.

Two general procedures were followed, 5–18 mmoles of the major solution component being used in all cases. In the first method (procedure 1), sets of about five all-glass bombs were filled with almost identical portions of labeled sulfur dioxide, thionyl chloride and catalyst, sealed, and run for various times. Reaction was terminated by distilling the two volatile reactants away from the catalysts. A following fractional distillation gave sufficient separation for calculation of the percentage exchange. In the excess thionyl chloride experiments, simple distillation down to a fraction of the initial volume yielded relatively pure thionyl chloride, whose specific activity, together with that of the more volatile fraction, led to the percentage exchange. Where sulfur dioxide had been in excess, a similar procedure yielded a "thionyl chloride" sample significantly, but reproducibly, contaminated with active sulfur dioxide. Appropriate corrections were applied to obtain the true thionyl chloride activity.[8]

In the second and more frequently used method (procedure 2), reaction bombs equipped with pressure stopcocks were filled with a reaction mixture employing labeled thionyl chloride. With this arrangement, used only for runs with excess sulfur dioxide, it was possible periodically to withdraw a series of about five vapor samples, presumably almost pure sulfur dioxide. The growth of activity in these samples, compared to that of the final residue, was used to calculate the exchange rate.

In experiments using either procedure, with the effective catalysts (RbCl or Me_4NCl), samples were taken up to something over 50% exchange. Depending on conditions, total elapsed times ranged from about 1 to 170 hours. That variation in results does not stem from procedural differences is shown by intercomparison of such experiments as no. 6 and 17, representative, respectively, of the two procedures. The similarity in k_3 values (see Results) is evident.

As a further check on the possible effect of stopcock grease, present in procedure 2, two all-glass bombs, each with six break-tips (procedure 3), were run in a manner similar to that for the stopcock bombs (rubidium chloride and labeled thionyl chloride). Comparison of k_3 values for Runs 32 and 37, for example, shows the lack of any effect of this modification. Further cross checks on procedure are provided by experiment pairs 7–18, 30–31, and 30–40.

For the three temperatures used, constancy was maintained with an ice–salt-bath, an ice-bath, or at 25°, a regulated thermostat. All runs were either in subdued light or darkness, although indications are that ordinary indoor illumination has no effect on the rate.

Because of the very small amounts employed, the two active catalysts were usually measured into the bombs as weighed portions of aqueous solutions, which were then evaporated to dryness and baked under high vacuum (*e.g.*, Me_4NCl, 120°, 4 hr.) before dosing in the reactants. Observations by us as well as by others,[9] indicate no resulting decomposition of tetramethylammonium chloride. All reaction solutions were clear and colorless, although it was necessary to dissolve rubidium chloride overnight in the sulfur dioxide before adding thionyl chloride. With both catalysts, evaporation of volatile material at the end of a run left a dry, white salt, there being no difficulty with retention of solvent such as was experienced with tetramethylammonium bromide in thionyl bromide–sulfur dioxide solutions.[4] This point was further checked by analysis of a tetramethylammonium chloride residue. Obsd. 32.02% Cl; calcd. for Me_4NCl, 32.40. In another case the same catalyst, recovered from a radiosulfur-containing solution, showed, on examination, no activity.

In the case of the aluminum chloride runs, the salt was handled entirely *in vacuo*, as indicated under Reactants, in an effort to obtain consistent data. Solutions, although initially clear and colorless, often, over considerable periods of time, became faintly pinkish. In view of the trifling catalytic activity involved, this phenomenon was not further investigated. Possibly it may be related to a slow solvolysis[10] to yield aluminum oxychloride, a material which, dissolved in nitrobenzene or acetone, gives brown and red solutions, respectively.[11] Evaporation of volatile material from the aluminum chloride solution left a sirupy mass of light yellow crystals which could be "dried" (still *in vacuo*) only at an estimated temperature of somewhat over 100° (obtained by brushing with a flame). Although additional compounds with aluminum chloride both of sulfur dioxide[12] and of thionyl chloride[13] have been reported, the latter apparently considerably the more stable,[13,14] sulfur analyses of the wet residue failed to yield any consistent results as to amount of sulfur retention. Radioassay of residues from an active run indicated a specific activity intermediate between that of the two sulfur compounds, suggesting retention of both to be involved.

Calculations.—For runs in individual bombs, with labeled sulfur dioxide, the fractional exchange was computed from the expression $F = S/S_\infty$, where S refers to thionyl chloride specific activity, that for infinite time having been calculated from the measured activities of the two separated fractions. These data were plotted as log $(1 - F)$ *vs.* time, good straight lines being obtained, from which finally the exchange rates were computed by the usual first-order exchange rate law.[15]

In the case of the runs with labeled thionyl chloride, in pressure stopcock (or multiple break-tip) bombs, from which successive vapor samples were withdrawn, a more involved calculation was required. Since the samples, *ca.* 0.8 mmole each, made a significant drain on the 18.0 mmoles of sulfur dioxide used in all cases, it was necessary to apply corrections in calculating the rate. The process consisted essentially of computing the fractional exchange between pairs of successive samples by means of the expression $F = (S_2 - S_1)/(S_\infty - S_1)$, and from this obtaining the corresponding *amount* of exchange, $R_0 \times \Delta t$, *via* the first-order rate law.

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[7] "International Critical Tables," Vol. 3, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 22.

[8] Blank experiments indicated the resulting uncertainty at zero per cent. exchange to be *ca.* ± 2–3% absolute, the uncertainty decreasing with increasing exchange.

[9] A. A. Vernon and R. E. Walker, Jr., THIS JOURNAL, **73**, 5915 (1951).

[10] For examples of such reactions see L. F. Audrieth and J. Kleinberg, "Non-aqueous Solvents," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 221–224.

[11] W. Menzel and M. Froelich, *Ber.*, **75**, 1055 (1942).

[12] O. Ruff, *ibid.*, **35**, 4454 (1920).

[13] H. Hecht, *Z. anorg. Chem.*, **254**, 44 (1947).

[14] F. Ephraim and I. Kornblum, *Ber.*, **49**, 2020 (1916).

[15] R. B. Duffield and M. Calvin, THIS JOURNAL, **68**, 557 (1946).

The R_c values were then corrected to initial conditions in the bomb, on the basis of the experimental rate law (see Results), to give $R^\circ_c \times \Delta t$. The values so obtained were added cumulatively from zero time, to give a series of $R^\circ_c \times t$ values which, finally, were plotted against time, yielding a straight line, the slope of which gave the exchange rate.[16] From the rate, the half-time was obtainable *via* the expression $t_{1/2} = 0.693ab/R^\circ_c\,(a + b)$, where a and b represent concentrations of the two reactants.

R_c refers to a rate in concentration units, the latter being calculated from the measured amounts of reactants, on the basis of the following densities[17] at −21.0, 0.0 and 25.17°, respectively: SO_2, 1.487, 1.434, 1.369; $SOCl_2$, 1.718, 1.677, 1.628. It was assumed that, for mixed solutions, the volumes were additive.

Results

Kinetic details were investigated with the two catalytically effective ionic materials, tetramethylammonium and rubidium chlorides. Results are shown in Tables I and II.

Dependence on Catalyst Concentration.—A number of experiments were run at 0° at varying concentrations of each of the catalysts, the concentrations of thionyl chloride and sulfur dioxide being held constant. For excess sulfur dioxide solutions, consideration of experiments 8–13 and 32–38 show the rates to increase progressively with concentration. Log-log plots of these data (Fig. 1) indicate a first-order dependence in each case, with tetramethylammonium about twice as effective as rubidium chloride.

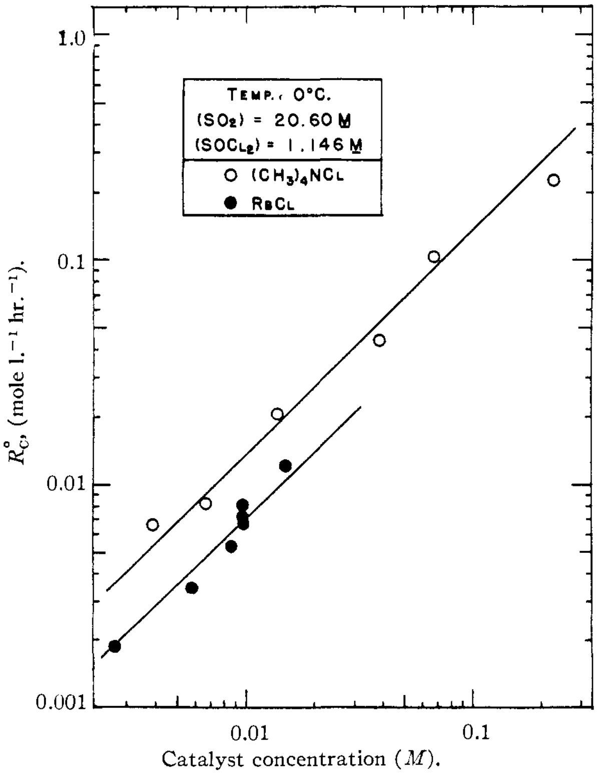

Fig. 1.—Catalyst concentration dependency in excess sulfur dioxide.

TABLE I

EXCHANGE RATES WITH TETRAMETHYLAMMONIUM CHLORIDE CATALYST

Expt. no.	Me_4NCl, mole/l. × 10^2	$SOCl_2$, mole/l.	SO_2, mole/l.	$t_{1/2}$, hr.	Rate × 10^2, mole l.$^{-1}$ hr.$^{-1}$	k_3 × 10^2 l.^{2} mole^{-2} hr.$^{-1}$
			Experiments at 0.0°			
6[a]	65.2	2.04	19.12	0.676	189	7.25
8[b]	0.665	1.146	20.6	89.4	0.842	5.25
9[b]	1.372	1.146	20.6	36.3	2.07	6.39
10[b]	0.388	1.146	20.6	113	0.664	7.24
11[b]	6.65	1.146	20.6	7.31	10.3	6.57
12[b]	22.6	1.146	20.6	3.36	22.4	4.20
13[b]	3.85	1.146	20.6	17.2	4.37	4.81
14[b]	3.31	2.95	17.72	16.4	10.7	6.18
15[b]	4.12	0.422	21.8	10.9	2.63	6.97
16[b]	4.63	0.245	22.0	10.4	1.61	6.45
17[b]	2.73	4.88	14.64	20.3	12.5	6.38
20[a]	1.410	4.88	14.63	38.7	6.56	6.53
21[a]	0.927	8.04	9.65	60.4	5.04	7.00
					Av.	6.25
22[a]	1.181	10.21	6.14	35.0	7.60	10.3
23[a]	1.560	13.60	0.815	14.5	3.68	21.3
24[a]	1.612	13.92	0.279	12.0	1.58	25.2
25[a]	1.450	12.50	2.50	16.7	8.65	19.1
26[a]	0.336	13.60	0.815	68.0	0.784	21.0
27[a]	4.92	13.60	0.815	4.48	11.9	21.9
					Av.	21.7
			Experiments at other temp.			
7[a,c]	67.1	2.12	19.65	8.56	15.5	0.554
18[b,c]	4.68	1.182[a]	21.3	127	0.613	0.520
28[a,c]	1.622	13.92	0.835	102	0.536	2.84
19[b,d]	4.10	1.090[a]	19.62	1.66	43.0	49.0
29[a,d]	1.527	13.18	0.790	1.70	30.4	191

[a] Procedure 1, SO_2 initially labeled. [b] Procedure 2, $SOCl_2$ initially labeled. [c] Temperatures: no. 7, −20°; no. 18 and 28, −21°. [d] Temperature, 25.2°.

TABLE II

EXCHANGE RATES WITH RUBIDIUM CHLORIDE CATALYST

Expt. no.	RbCl, mole/l. × 10^2	$SOCl_2$, mole/l.	SO_2, mole/l.	$t_{1/2}$, hr.	Rate × 10^2 mole l.$^{-1}$ hr.$^{-1}$	k_3 × 10^2 l.^{2} mole^{-2} hr.$^{-1}$
			Experiments at 0.0°			
32[c]	0.965	1.146	20.6	112.4	0.67	2.95
33[b]	0.970	1.146	20.6	93.2	0.809	3.54
34[b]	0.268	1.146	20.6	401	0.188	2.97
35[b]	0.576	1.146	20.6	220	0.342	2.52
36[b]	1.480	1.146	20.6	62.3	1.21	3.46
37[b]	0.965	1.146	20.6	107.6	0.700	3.08
38[b]	0.865	1.146	20.6	142.7	0.528	2.59
					Av.	3.02
			Experiments at other temperatures			
39[b,d]	0.997	1.182	21.3	1410	0.055[f]	0.22[f]
30[a,e]	1.692	1.990	18.20	7.18	17.3	28.3
31[c,e]	0.918	1.090	19.62	10.60	6.75	34.4
40[b,e]	0.920	1.090	19.62	14.60	4.90	24.9

[a] Procedure 1, SO_2 initially labeled. [b] Procedure 2, $SOCl_2$ initially labeled. [c] Procedure 3, $SOCl_2$ initially labeled. [d] Temperature, −21.5°. [e] Temperature: no. 30 and 31, 25.0°; no. 40, 25.2°. [f] Rough approximation. Estimated reliability ±40%.[18]

The first-order dependence is further indicated by the constancy of the rate constants, k_3 (see below) shown in the last column of each table. Because of the limited solubility of rubidium chlo-

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[16] For further details see the Ph.D. thesis of B. J. Masters, Oregon State College, 1954.

[17] Reference 7, pp. 22 and 236.

ride, concentrations could be varied only about sixfold. With tetramethylammonium chloride, however, a 60-fold range was covered. Furthermore, by including experiment 6 (a small correction for thionyl chloride–sulfur dioxide concentration ratio is necessary—see below), the range becomes about 170-fold, with k_3 still substantially constant.

Experiments 23, 26 and 27 show the effect in excess thionyl chloride (*i.e.*, with this material as "solvent") of varying tetramethylammonium chloride concentration fifteen-fold. Again a first-order dependence is indicated by the plot in Fig. 2 and by the k_3 values of Table I.

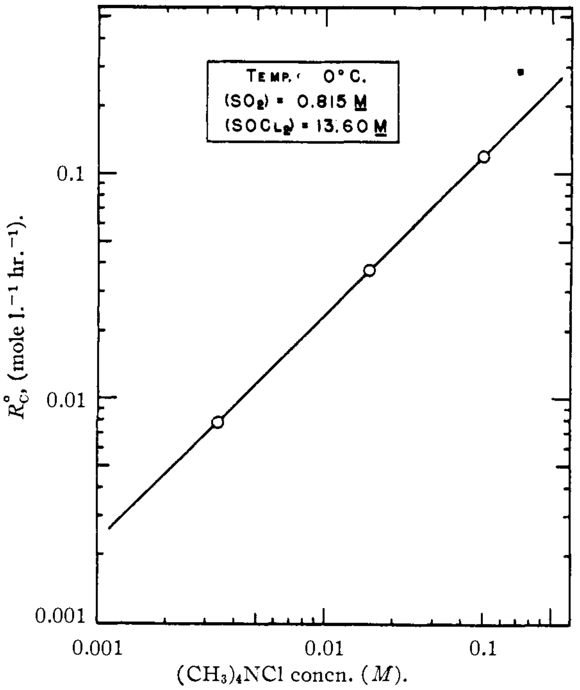

Fig. 2.—Catalyst concentration dependency in excess thionyl chloride.

Dependence on Thionyl Chloride and Sulfur Dioxide Concentrations. The Rate Law.—Table I includes runs with tetramethylammonium chloride catalyst over the range from moderately low concentrations of thionyl chloride in sulfur dioxide to moderately low concentrations of sulfur dioxide in thionyl chloride. For the sake of direct intercomparison, all rates may be divided by catalyst concentration. The resulting quantities have been used to make the log-log plots given in Figs. 3 and 4, showing, respectively, the relationship to thionyl chloride and sulfur dioxide concentrations.

In each case, the slope appears to approach unity at low solute concentration, indicating that for both types of solution the rate is first-order in the minor component. The fact that in the more concentrated solutions, the curve falls away from unit slope well before the point of equimolar mixtures is presumably related to the decrease in *solvent* concentration, which suggests that the rate is simultaneously first order in each of the two compounds. On this assumption, one may compute $[R_c^\circ/(\text{catalyst})]_{\text{cor.}}$ values, corrected for decrease in solvent concentration from that for infinite dilution. The dashed lines in Figs. 3 and 4 represent such a correction applied to the solid curves. Considerable improvement is apparent, in the case of excess sulfur dioxide solutions (Fig. 3) a straight line of essentially unit slope being obtained.

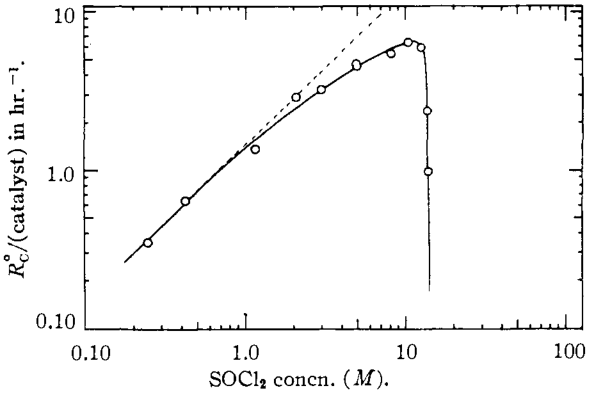

Fig. 3.—Thionyl chloride concentration dependency, Me_4NCl catalyst, 0°.

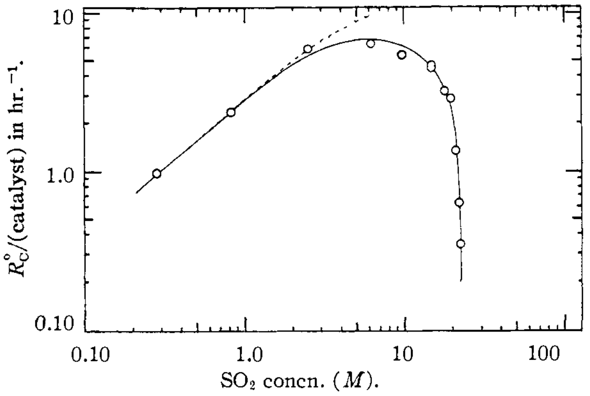

Fig. 4.—Sulfur dioxide concentration dependency, Me_4NCl catalyst, 0°.

On the basis of the foregoing, the experimental rate law becomes

$$\text{Rate} = k_3\,(\text{catalyst})(SOCl_2)(SO_2)$$

Although this equation appears to be valid for both excess sulfur dioxide and excess thionyl chloride solutions, k_3 is about three times as great in the latter case as in the former. The value of k_3 also depends on the catalyst, being about twice as great for tetramethylammonium as for rubidium chloride.

Temperature Dependence.—Using in each case runs at constant sulfur dioxide (or thionyl chloride) concentration only, the −21 and 25° experiments, together with an average of 0° rate constants, have been plotted as log k_3 *vs.* $1/T$ (Fig. 5[18]) for each of the three situations: (1) Me_4NCl, or (2) RbCl in sulfur dioxide, or (3) Me_4NCl in thionyl chloride. These plots, together with averages of all the appropriate k_3 values, yield for the three cases, respectively, the expressions

$$k_3 = 1.08 \times 10^7 e^{-14{,}700/RT}\ \text{l.}^2\ \text{mole}^{-2}\ \text{sec.}^{-1} \qquad (1)$$
$$k_3 = 5.31 \times 10^6 e^{-14{,}700/RT}\ \text{l.}^2\ \text{mole}^{-2}\ \text{sec.}^{-1} \qquad (2)$$
$$k_3 = 5.11 \times 10^6 e^{-13{,}600/RT}\ \text{l.}^2\ \text{mole}^{-2}\ \text{sec.}^{-1} \qquad (3)$$

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[18] Low solubility in the −21.5° RbCl run, no. 39, led to a quite low rate and hence to considerable experimental error, estimated at ±40% as shown in Fig. 5.

TABLE III

OTHER EXCHANGE RATES[d]

Expt. no.	Cat.	Cat., mole/l. × 10^2	Time, hr.	Exch.,[f] %	$t_{1/2}$, hr.	Rate × 10^2, mole/l.$^{-1}$ hr.$^{-1}$
43[a]	$AlCl_3$	65	100	1.4	2460	0.052
			100	−0.8		
			1011	23.9		
44[a,e]	$AlCl_3$	63	435	79.4	191	0.65
			528	85.8		
45[b]	HCl	8	71	1.8	>2500	<0.03
47[a]	HCl + H_2O	10.5[c]	8	3.1	....	Undetectable
48[a,e]	HCl + H_2O	10.0[c]	10	2.3	....	Undetectable
49[a,e]	HCl + H_2O	10.0[c]	2400	9.4	>25,000	<0.005
			2400	3.3		
50[b]	None		163	−0.7	....	−0.005
51[b]	None		0	0.6	>5,000	<0.015
			100	1.6		
			100	1.8		
			170	2.2		

[a] Procedure 1; concn.: SO_2 (initially labeled), 18.2–19.1; $SOCl_2$, 2.0 mole/l. [b] Procedure 2; concn.: SO_2, 20.6; $SOCl_2$ (initially labeled), 1.15 mole/l. [c] Concn. of H_2O. Concn. of HCl was 10.4 times these figures. [d] Temperatures 0° except as indicated. [e] Temperatures: no. 44 and 49, 23°; no. 48, 25°. [f] Estimated reliability of low apparent percentage exchange figures, ±2–3.

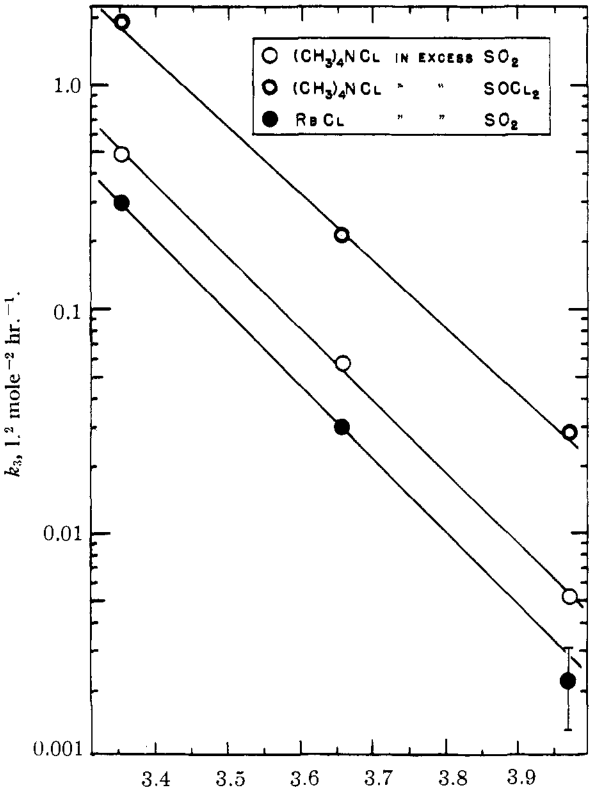

Fig. 5.—Temperature dependency of rate constants.

The activation energies are probably good to *ca.* ±500 cal./mole.

The corresponding entropies of activation, based on the equation[19]

$$k_3 = e \frac{kT}{h} e^{-E\ \mathrm{exp}/RT} e^{\Delta S\ddagger/R}$$

are (1) −28.1, (2) −29.5, and (3) −29.6 cal./deg. mole. Alternatively, assuming the reaction bimolecular in the two solutes in each case, these values become (1) −22.3, (2) −23.5 and (3) −24.7 cal./deg. mole.

Acid Catalysts.—Experiments performed with hydrogen chloride, hydrogen chloride plus water, and aluminum chloride are recorded in Table III, along with the results of two blank runs made using procedure 2. In the first two cases there appears to be no clear evidence for any exchange at all, even after 2400 hours in the second instance. That the exchange in no. 45 is, in fact, essentially zero is emphasized by a comparison with blank run no. 51, which shows an apparent minimum half-time of comparable magnitude.

With aluminum chloride, on the other hand, although the rate is exceedingly low, and although insufficient points were obtained to give good plots of log (1 − *F*) *vs.* time, it would seem that a weak catalysis does occur. Assuming here the same rate law as for Me_4NCl and RbCl, one obtains k_3 values for aluminum chloride of 2 × 10^{-5} (0°) and 2.8 × 10^{-4} (23°), *ca.* 2–3000 times smaller than for Me_4NCl. These figures lead to the expression $k_3 = 3.3 \times 10^6 e^{-18,400/RT}$ l.^{2} mole^{-2} sec.$^{-1}$. It is of interest that the pre-exponential term here does not differ greatly from that for the two active catalysts, the lower rate resulting primarily from a higher activation energy. The entropy of activation for aluminum chloride is −30.4 (or −24.6) cal./deg. mole on a termolecular (or bimolecular) basis.

Discussion

The present results show marked similarities to those for the catalysis of the thionyl bromide–sulfur dioxide exchange.[4] The interpretation of the reaction, made in the earlier report, as involving a basic catalysis by halide ions, is clearly applicable here, in view of the marked contrast in relative effectiveness of tetramethylammonium and ru-

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(19) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 199.

bidium chlorides, as compared to aluminum and hydrogen chlorides. The uncertainty over the exact order of the reaction with respect to catalyst and also the question of whether different halides have different catalytic activities, are both clarified by the greater precision of the newer data. Careful measurements over a considerably greater concentration range than before now indicate a strict first-order dependence, with tetramethylammonium chloride clearly more active than rubidium chloride.

The principal difference between the two sets of results is the present finding of a first-order dependence on thionyl chloride in contrast to zero order for the bromide. It is unfortunate that the thionyl bromide data are not more extensive, covering as they do a much narrower range of concentrations than in the present instance and including no measurements with thionyl bromide as the major solution component. Nonetheless, there appears at present to be no obvious reason to question the validity of the thionyl bromide order. Hence it would seem that somewhat different mechanisms must operate in the two cases.

Quantitatively, comparison may be made with the thionyl bromide exchange by calculating, from the present data, first-order rate constants (rate/(catalyst)) for the same thionyl chloride concentration as prevailed in most of the thionyl bromide work. For corresponding tetramethylammonium halide catalysts, the rate so obtained, 2.70 hr.$^{-1}$, is about seven times greater than the average 0° figure for thionyl bromide of 0.370 hr.$^{-1}$. This occurs despite a lower apparent activation energy for the latter of 13.2 kcal./mole and implies for it a lower pre-exponential term than for the thionyl chloride exchange as shown in the two expressions

$$k_{1(\mathrm{SOCl_2})} = 4.63 \times 10^{8} e^{-14{,}700/RT}\ \mathrm{sec.}^{-1} \quad \text{and}$$
$$k_{1(\mathrm{SOBr_2})} = 4.17 \times 10^{6} e^{-13{,}200/RT}\ \mathrm{sec.}^{-1}$$

The following represents a mechanism consistent with the present data

$$\mathrm{S^*O_2 + Cl^- = S^*O_2Cl^-} \quad \text{fast}$$
$$\mathrm{S^*O_2Cl^- + SOCl_2 = S^*OCl_2 + SO_2Cl^-} \quad \text{slow}$$

The first step in this mechanism is essentially the same as that suggested for the thionyl bromide exchange. In view of the difference in the observed kinetics, however, thionyl chloride replaces sulfur dioxide here as the oxide ion acceptor in the second, slow step.

This mechanism leads to an activated complex in which oxide and chloride ions are simultaneously interchanged, possibly *via* a ring structure. Alternatively, it is possible, of course, that only an oxide transfer would occur, yielding the ions $SOCl^+$ and $SO_2Cl_2^{=}$. The latter, however, corresponding to the double addition of chloride ion to sulfur dioxide, seems an unlikely species. Probably two such ions, if formed at all, would exchange a chloride before diffusing out of the solvent cage; the net effect would then be the same as in the proposed mechanism. Such a picture would be consistent with the apparent ready mobility of chloride ions in these solutions, shown by radiochlorine tracer experiments in this Laboratory.[20]

The foregoing mechanism allows for a reasonable explanation of the greater catalytic activity of tetramethylammonium chloride as compared to rubidium chloride. Assuming ion pairs to be the dominant form of the salt in each case, it may be supposed that the larger, more loosely bound organic cation would permit of a more ready donation of chloride ion to sulfur dioxide than would the alkali cation. It must be conceded that a difficulty exists relative to this interpretation, however, since the strict first-order dependence on catalyst over a large concentration range would seem to require that chloride ion have the same catalytic activity whether free or associated in ion pairs. Further data on the relative activity of various other chlorides as a function of the nature of the cation would be of real interest, although low solubilities pose a serious experimental difficulty to such work.

While the calculation should not be taken too seriously, it is interesting to attempt to compute an approximate equilibrium constant for the first equation in the proposed mechanism. Comparing the observed pre-exponential term for tetramethylammonium chloride in excess sulfur dioxide with a "normal" bimolecular value of *ca.* 10^{11} l./mole sec.,[21] and neglecting the contribution of the heat of the first equation to the observed activation energy, one arrives at an approximation of *ca.* 10^{-4} for this equilibrium constant. For what it is worth, it may be noted that this figure is almost of the same order of magnitude as ionization constants given by Jander[22] for a number of bromides and iodides in sulfur dioxide.

The proposed mechanism is assumed to be valid in excess of either sulfur dioxide or thionyl chloride, although not unexpectedly, the specific rate constants differ somewhat for the two cases. While quantitative interpretation of this difference is difficult, it seems likely that it may be related to a considerable increase in the acidity of the environment as thionyl chloride replaces sulfur dioxide. Thus possibly solvation of sulfur dioxide molecules by thionyl chlorides, in preference to other sulfur dioxides, would, by increasing their acidity, increase their tendency to accept chloride ions to form the intermediate $S^*O_2Cl^-$.

While an understanding of the difference between the rates of the present reaction and of the bromide-catalyzed, thionyl bromide exchange is obscured by the apparent difference in the mechanisms, it seems probably related to a greater basicity for chloride as compared to bromide ion catalyst.

Finally, reference should be made to the experiments with water–hydrogen chloride mixtures. These experiments were prompted by the observation of Bagster and Cooling[23] that the addition of water to a non-conducting solution of hydrogen bromide in sulfur dioxide yielded a conducting solution, which was presumed to contain hydronium bromide, $(H_3O^+)(Br^-)$. Jander[24] reports that at low temperatures thionyl chloride in sulfur dioxide

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[20] B. J. Masters and T. H. Norris, to be published.

[21] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 72.

[22] G. Jander, "Die Chemie in Wasserähnlichen Lösungsmitteln," Springer-Verlag, Berlin, 1949, p. 240.

[23] L. S. Bagster and G. Cooling, *J. Chem. Soc.*, **117**, 693 (1920).

[24] Reference 22, p. 295.

is not hydrolyzed by water. Consequently, it seemed of interest to find whether one might observe catalysis by the salt, hydronium.chloride, which presumably would be comparable in effectiveness to the two active catalysts of this research. It is assumed our failure to observe such catalysis implies that hydrolysis did occur. Possibly experiments at a lower temperature might be more successful.

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CORVALLIS, OREGON

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF DUKE UNIVERSITY]

A Spectrophotometric Study of the Hydrolysis of Iron(III) Ion. II. Polynuclear Species[1]

BY RONALD M. MILBURN AND W. C. VOSBURGH

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The hydrolysis of iron(III) ion has been investigated at 25° over a wide range of iron(III) concentrations and ionic strengths. The results give direct evidence for the importance of polynuclear iron(III) species at total iron(III) concentrations of 10^{-3} M or greater. The most reasonable postulate consistent with the data involves dimerization of the first hydrolysis product. The first hydrolysis and dimerization equilibrium constants have been determined over the ionic strength range studied. With increasing ionic strength the first hydrolysis constant decreases while the dimerization constant increases, in qualitative accord with Debye–Hückel theory. The absorption spectrum of the pure hydrated iron(III) ion has been redetermined through the range 320–360 mμ with care to avoid interference by polynuclear species.

An earlier report described a spectrophotometric determination of the first hydrolysis constant of iron(III) ion.[2] It was believed that polynuclear species would not be important in the 10^{-4} M iron(III) solutions used. The presence of polynuclear species in more concentrated solutions was suggested as an explanation for the failure of Bjerrum's method of corresponding solutions.

We have extended the work of Siddall and Vosburgh to cover a wide range of iron(III) concentrations. In accord with previous findings, optical densities of 10^{-4} M iron(III) solutions indicate that over the greater range of acidities studied the first hydrolysis is alone important. But results for 10^{-3} and 10^{-2} M iron(III) solutions cannot be explained on the basis of mononuclear species alone. The simplest postulate in agreement with experiment involves dimerization of the first hydrolysis product. This is in agreement with Hedström,[3] who assumes existence of the dimer to explain e.m.f. data on iron(III) perchlorate solutions. Hedström has evaluated equilibrium constants for the dimerization and first and second hydrolysis reactions at 25° and the high ionic strength of 3. In the present study equilibrium constants at 25° have been evaluated for the first hydrolysis and dimerization reactions over a wide range of ionic strengths. Our results for the ionic strength of 3 are in good accord with Hedström. However, the dimerization is strongly dependent on ionic strength, the constant decreasing to approximately one-fiftieth its former value as the ionic strength is reduced from 3 to zero.

Experimental

Materials.—Water was purified by refluxing ordinary distilled water with potassium dichromate and sulfuric acid for three to four hours and redistilling in an all-glass apparatus. Standard perchloric acid and sodium perchlorate solutions, prepared as previously described,[2] were used for the adjustment of hydrogen ion concentration and ionic strength. The solutions gave negative tests for chloride and iron(III) ions.

A stock iron(III) perchlorate solution was used for the preparation of other iron(III) solutions. Reagent grade hydrated iron(III) perchlorate was recrystallized from perchloric acid solution. The resulting crystals were filtered in a sintered glass crucible and some of the excess perchloric acid was washed away with water. The remaining iron(III) perchlorate was dissolved in water and the solution was analyzed for iron(III) by the iodometric method.[4] After diluting to approximately one tenth molar, the solution was reanalyzed for iron(III). The perchloric acid content was determined by titrating with standard sodium hydroxide to a phenolphthalein end-point. Toward the end of the titration, after each addition of alkali, the precipitated iron(III) hydroxide was allowed to settle and the color of the supernatant liquid was observed. The excess perchloric acid was calculated from the total alkali required and the known iron(III) concentration. The stock solution was 0.1002 M in iron(III) and 0.0122 M in perchloric acid.

Technique.—Optical density measurements were made with a model DU Beckman spectrophotometer, provided with a thermostat to allow the temperature of solutions to be held at 25 ± 0.1°. Most measurements were made in 10-cm. Corex cells or in 1-cm. quartz cells. For some solutions with large optical densities 0.9-cm. cell spacers were placed in the 1-cm. cells to give a path length of approximately 0.1 cm. The exact path length was determined by comparing the optical densities of a solution as measured with and without the spacers. Test cells were calibrated against blanks over the wave length range used. In no case did the optical densities vary sufficiently with wave length for the recorded value to depend on the slit width.

All measurements were made after the iron(III) perchlorate solutions, prepared from the stock iron(III) solution, had been allowed to mature for about five days. No evidence was found for changes with time after dilution, except when the acidity was too low and hydroxide ultimately precipitated. In this case the results were discarded. The time for maturing was allowed in view of changes in properties reported by other workers.[5-8]

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[1] From a thesis by R. M. Milburn in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Duke University.

[2] T. H. Siddall and W. C. Vosburgh, THIS JOURNAL, **73**, 4270 (1951).

[3] B. O. A. Hedström, *Arkiv Kemi*, **6**, 1 (1953).

[4] A. I. Vogel, "Quantitative Inorganic Analysis," Longmans, Green and Co., London, second edition, 1951, p. 356.

[5] A. B. Lamb and A. G. Jacques, THIS JOURNAL, **60**, 967, 1215 (1938).

[6] A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1322 (1949).

[7] T. V. Arden, *J. Chem. Soc.*, 350 (1951).

[8] T. Ito and N. Yui, *Sci. Rep. Tohoku Univ.*, Series 1, **37**, 19 (1953).