The extent of reaction, $([\mathrm{Br(III)}]_0 - [\mathrm{Br(III)}])/[\mathrm{Br(III)}]_0$, is given by $p(K/[\mathrm{Br(III)}]_0)$ and was calculated for several values of $[\mathrm{Br(III)}]_0/K$. Furthermore, we calculated $(1 - q_\infty)$, *i.e.*, that fraction of the steady state concentration which is not reached when $t = \infty$, for the same values of $[\mathrm{Br(III)}]_0/K$.[23] The results are shown in Table I (*cf.* Table III of Benson's paper[19]). Our values of $[\mathrm{Br(III)}]_0/K$ lie between 4 (for the highest bromide concentration) and 58 (for low bromide or high initial bromite concentration). An inspection of the table shows, therefore, that the steady-state concentration of hypobromite is practically reached in all the experiments, except that having the highest bromide concentration; for this experiment, expression 10 is not applicable. Furthermore, the steady state is seen to be approached earlier the higher the initial concentration and the lower the bromide concentration, as borne out by our experiments.

We are indebted to Dr. G. Stein for helpful discussion.

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(23) The calculation was based on the assumption that the rate of reaction I can be neglected in comparison with that of reaction I′, even when $[\mathrm{Br(III)}] \rightarrow 0$. This assumption is clearly not justified; nevertheless, the values of $(1 - q_\infty)$ can serve to decide to what extent the steady state concentration is approached in a given case.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, OREGON STATE COLLEGE]

Isotopic Exchange Reactions in Liquid Sulfur Dioxide. III. The Catalyzed Sulfur Exchange between Thionyl Bromide and Sulfur Dioxide[1]

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In sharp contrast to previously reported results on the almost utter absence of isotopic exchange in the systems SO_2–$SOCl_2$ and SO_2–$SOBr_2$ (excess SO_2), it has now been found that the addition of a number of ionic halides to the SO_2–$SOBr_2$ system produces a strong catalysis of the exchange. The catalysis is homogeneous, with exchange rates apparently first order in catalyst concentration and zero order in thionyl bromide concentration. Tetramethylammonium bromide, rubidium bromide, rubidium chloride, cesium bromide, potassium bromide and potassium chloride act as catalysts, although the last two are limited by low solubility. Roughly comparable k values, based on the expression, rate = k(catalyst concn.), are obtained at a given temperature, irrespective of which of the first four catalysts are employed, average values for tetramethylammonium bromide being (1) 5.8×10^{-2} min.$^{-1}$ at 25°, and (2) 6.2×10^{-3} min.$^{-1}$ at 0°; a representative exchange half-time for this catalyst is 80 minutes at 25° (0.163 mmole in 9.9 and 1.24 mmoles each of SO_2 and $SOBr_2$). The reaction is interpreted as involving basic catalysis by halide ions. Pyrex glass powder also shows a weak catalysis (half-time 307 hours at 25°).

In an earlier communication[3] it was reported that, using S^{35} as tracer, neither thionyl chloride nor thionyl bromide, dissolved in liquid sulfur dioxide, showed a significant rate of sulfur exchange. The bromide, at a mole fraction of *ca.* 0.090 gave an exchange half-time of about 1.9 years at 25°. In the same paper were recorded some observations of anomalous exchange effects obtained when potassium bromide (relatively insoluble) was added to thionyl chloride dissolved in sulfur dioxide (thionyl bromide and potassium chloride being obtained by double decomposition). Further investigation has now shown that there is here involved a striking catalysis of the thionyl compound–sulfur dioxide exchange. In this paper we report the results of an investigation of the catalysis by several halide salts of the thionyl bromide–sulfur dioxide exchange.

Experimental

Techniques used were in general similar to those in previous work.[3] Radiosulfur was obtained from the Atomic Energy Commission. All samples were counted as thin layers of barium sulfate under an end window counter, all appropriate corrections being applied.

Preparation of Reactants.—**Sulfur dioxide** from a cylinder was purified by successive passage through concentrated sulfuric acid and phosphorus pentoxide. Freezing with liquid air and pumping to a high vacuum ensured the absence of permanent gases.

Potassium chloride (Mallinckrodt Analytical Reagent) was pulverized and dried at 140°. The powder was sieved through standard mesh screens, that portion passing a 250 micron, but retained by a 177 micron screen being collected for use.

Potassium bromide (J. T. Baker Reagent) was treated in the same manner as the chloride. **Rubidium and cesium halides** (99% purity, from A. D. Mackay, Inc.) were pulverized and dried at 140° for an hour. **Tetramethylammonium bromide** (Eastman Kodak Co., White Label) was dried at 140° for 20 minutes. **Thionyl bromide** was prepared essentially by the method of Hibbert and Pullman[4] and was fractionally distilled under reduced pressure in an all-glass, ground joint-free system at room temperature. The middle 60% of the distillate was collected in glass tubes, which were sealed off and stored in a refrigerator until ready for use.

Anal. Calcd. for $SOBr_2$: S, 15.42; density expected (25°) 2.672.[5] Found: S, 15.43; density, 2.67 (24°).

Pyrex glass powder was prepared from tubing which had been carefully cleaned with chromic acid cleaning solution, washed with distilled water and dried. Thin glass "balloons," blown from the tubing, were crushed and ground up. The powder so obtained was sieved in the same manner as the potassium bromide and chloride.

Labeled sulfur dioxide was prepared either by the method of Johnson and Huston[6] or, more recently, Masters and Norris.[7]

Labeled thionyl bromide was prepared by a method based on the results of the present work. In a typical preparation 10 millimoles of active sulfur dioxide, 5 millimoles of thionyl

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(2) Taken from the thesis of Rolfe H. Herber, submitted in partial fulfillment of the requirements for the Ph.D. degree, at Oregon State College, September, 1952.

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

(4) H. S. Booth, "Inorganic Syntheses," Vol. 1, McGraw-Hill Book Co., Inc., New York, N. Y., 1939, p. 113.

(5) H. A. Mayes and J. R. Partington, *J. Chem. Soc.*, 2594 (1926).

(6) Rowland E. Johnson and J. L. Huston, THIS JOURNAL, **72**, 1841 (1950).

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

bromide and 0.5 millimole of tetramethylammonium bromide catalyst were put together in a reaction bomb. Twenty-four hours at 25° sufficed for virtually complete randomization of sulfur activity. The bomb contents were then fractionated, the relatively non-volatile thionyl bromide fraction was "washed" with inactive sulfur dioxide to eliminate residual activity of that compound, and the preparation was finally distilled into an all-glass storage bomb. Roughly 50% recoveries of thionyl bromide were effected, with measured specific activities of the order of 100 c./min./mg. (as barium sulfate).

Run Procedure.—Methods used, involving standard high vacuum techniques, consisted of obvious modifications of those previously employed.[3] The first runs were made with labeled sulfur dioxide in sealed bombs, filled on the vacuum line. Runs at 25° were in a thermostat, at 0° in an ice-bath, and at −21° in an ice–salt-bath. At the end of a run, the bombs' break-off tips were crushed and the volatile contents distilled *in toto* from the catalyst into a cold trap. From this material the bulk of the sulfur dioxide was then evaporated off in a reproducible manner. The small residue of active sulfur dioxide in the relatively non-volatile thionyl bromide led to moderately reproducible, small blanks (*ca.* 2–3% apparent exchange), for which correction was made. All samples were converted to barium sulfate for counting, and the fraction of exchange equilibrium attained calculated from the expression $F = (S_t - S_0)/(S_\infty - S_0)$.[8] The S's refer to the thionyl bromide fraction specific activities at zero time (the blank, assumed a constant), at the end of a run, and for complete exchange (calculated from the initial sulfur dioxide activity and the known dosages of reactants). Values of F from several bombs, run for various times, were plotted as log $(1-F)$ *vs.* time; from this, then, the exchange rate was calculated by the usual first-order exchange rate law.[9]

It was convenient to make calculations using millimole *amounts* of reactants and catalysts rather than concentrations (hence the units of mmoles min.$^{-1}$ for the rates). Since, however, the total amount of reactants remained always substantially constant, the runs are directly intercomparable, just as though expressed in concentration units. This procedure does not, of course, affect the equation 1 k values (see Results) since, in their calculation, concentrations cancel.

In the tetramethylammonium bromide catalyst experiments, we could not recover the dry salt on evaporating off the volatile reactants, varying amounts of the latter apparently being retained to form a dark oily liquid. Although we had difficulty in obtaining satisfactory analytical data, the retained material appeared to consist at least three-fourths of thionyl bromide, in a mole ratio of total sulfur to salt of three or four to one. The predominance of thionyl bromide was also shown by comparison of the retained material's specific activity with that of the recoverable thionyl bromide.

Since, for various length runs, these last two specific activities remain rather similar, any possible "addition compound" in the solution must be in rapid exchange equilibrium with the rest of the thionyl bromide; hence, the rate calculation according to the first-order exchange rate law is not affected. Also, the interpretation of the reaction kinetics is not complicated since the rate appears to be independent of thionyl bromide concentration. Finally, we may assume that the formation of an "addition compound" is not directly related to the catalysis, since rubidium halides have catalytic effects comparable to tetramethylammonium bromide, yet are easily recoverable as dry salts from the evaporation of the volatile solvent reactants.

The purpose in labeling the solvent was to avoid simulation of exchange by any possible decomposition of thionyl bromide. It was later found, however, that, with the latter labeled, rates of substantially the same magnitude were obtained, at least at 0°. (Compare in Table I, for example, among the tetramethylammonium bromide, 0° experiments, those with 0.430 and 0.488 mmole of catalyst, in which thionyl bromide and sulfur dioxide, respectively, were labeled.) The labeling of thionyl bromide had two significant advantages: (1) The occurrence of the tetramethylammonium bromide "addition compound" did not inhibit the use of relatively small amounts of thionyl bromide in some cases; (2) it was now possible to follow the exchange by withdrawing successive sulfur dioxide vapor samples from a single bomb.

The labeled thionyl bromide runs were made in tubes provided with high pressure stopcocks and four or five samples of reproducible size (0.439 mmole of sulfur dioxide) were withdrawn during a run. Since this procedure led to a significant drain on the total initial sulfur dioxide (*ca.* 10 mmoles), it was necessary to correct for it in calculating F values.

Results

Potassium Chloride as Catalyst.—After it became evident that the exchange reaction was strongly catalyzed by such compounds as potassium chloride, we set out to test for heterogeneity. Table I gives the results of three experiments with widely varying amounts of potassium chloride, all greatly in excess of its solubility (*ca.* 0.0011 millimole[10]). When plotted as log $(1 - F)$ *vs.* time, the data gave no indication of a dependence of rate on catalyst amount, the points all falling (with some scatter) along a straight line corresponding to a 15-hour half-time.

Thus, while there is evidently a strong catalysis (compare the no-catalyst control and also the uncatalyzed half-time of 1.9 years reported earlier[3]), it appears to be a homogeneous one by dissolved salt, a constant in these saturated solutions. So assuming, we have used the approximate solubility value quoted above to calculate the rate constant, k (see next section), shown in the last column. This figure cannot be taken too seriously, however, since no allowance has been made for the effect of added thionyl bromide on the solubility of the catalyst.

Tetramethylammonium Bromide as Catalyst.—The more soluble tetramethylammonium bromide was also found to be an effective catalyst and we have used this material to study some details of the reaction in homogeneous solutions. All results are presented in Table I.

1. The increased rate due to the greater solubility of tetramethylammonium bromide than potassium chloride is apparent from the experiments at 25°. These three runs show the variation in rate with catalyst concentration. A log–log plot of these two quantities against each other gives a good straight line of slope 1.19 with an estimated uncertainty of perhaps 12%. Thus an approximate first-order dependence on catalyst concentration seems indicated. Taking

$$\text{rate} = k(\text{catalyst concn.}) \qquad (1)$$

we have calculated the rate constants shown in the last column of the table.

2. The first five tabulated experiments at 0° were also designed to test the rate dependence on catalyst concentration. A log–log plot of these data gives a slope of 0.94 ± ~0.09, a first order dependence again being indicated. The rate obtained in the sixth experiment, in which a very much smaller amount of catalyst was used, is unfortunately quite rough and was not used in making the plot. However, it is of interest that, including this run, the equation 1 k values show a

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[8] R. J. Prestwood and A. C. Wahl, This Journal, **71**, 3131 (1949).

[9] R. B. Duffield and M. Calvin, *ibid.*, **68**, 557 (1946).

[10] This figure is for pure sulfur dioxide at 25°: A. I. Shatenstein and M. M. Viktorov, *Acta Physicochim. U.R.S.S.*, **7**, 883 (1937).

TABLE I

EXCHANGE RATES

Catalyst, mmoles	$SOBr_2$, mmoles	SO_2, mmoles	$t_{1/2}$, hr.	Rate × 10^4, mmoles/min.	$k \times 10^3$, min.$^{-1}$
KCl catalyst, 25.0°					
0.0	1.24	9.7[a]	$\lesssim$400[c]	$\lesssim$0.3	
0.067	1.24	9.7[a]	15 ± 3	8	(700[d])
2.02	1.24	9.8[a]			
11.8	1.24	9.8[a]			
Me_4NBr catalyst, 25.0°					
0.065	1.24	10.0[a]	4.2	30.6	47.1
.163	1.24	9.9[a]	1.33	95.7	58.9
.488	1.24	10.4[a]	0.38	334	68.6
				Average	58.2
Me_4NBr catalyst, 0.0°					
0.142	1.24[b]	10.3	10.6	12.1	8.47
.247	1.24[b]	10.4	6.84	18.8	7.60
.430	1.24[b]	10.2	4.00	32.0	7.44
.587	1.24[b]	10.4	2.53	50.7	8.65
.920	1.24[b]	10.0	2.11	60.5	6.58
.005[e]	1.24[b]	10.1	~920	~0.14	~3
.488	1.24	9.8[a]	3.4	37.5	7.68
.0649	0.62[b]	10.1	28.5	2.37	3.65
.0649	1.24[b]	10.1	47.3	2.70	4.16
.0649	2.48[b]	10.1	76.7	3.00	4.63
				Average	6.18
Me_4NBr catalyst, −21.3°					
0.488	1.24	10.4[a]	27.0	4.74	0.973
KBr catalyst, 0.0°					
Excess	0.62[b]	10.1	10.4	6.50	(32[f])
Excess	1.24[b]	10.0	12.3	10.4	
Excess	2.48[b]	9.8	29.6	7.74	
RbBr catalyst, 0.0°					
0.0145	1.24[b]	9.9	402	0.318	2.19
.0641	1.24[b]	10.3	74.2	1.73	2.69
.161	1.24[b]	10.0	12.1	10.6	6.56
.355	1.24[b]	10.3	6.78	18.9	5.32
.005[e]	1.24[b]	10.1	~2300	~0.06	~1
				Average	3.55
RbCl catalyst, 0.0°					
0.0207	1.24[b]	10.1	380	0.336	1.63
.005[e]	1.24[b]	10.1	~570	~0.2	~4
CsBr catalyst, 0.0°					
0.005[e]	1.24[b]	10.1	~1100	~0.11	~2
Glass catalysis, 25.0°					
880 mg.	1.24	9.5[a]	307	0.41	

[a] Sulfur dioxide initially labeled. [b] Thionyl bromide initially labeled. [c] Based on a 24-hour control with no KCl which showed < 4% exchange. [d] Based on an estimated KCl solubility of 0.0011 mmole.[10] [e] Rough experiments: uncertainty of rates perhaps ±40%. [f] Based on an estimated KBr solubility of 0.0256 mmole.[11]

fair degree of constancy over a concentration range of almost 200.

3. The last three 0° experiments were made to find the effect of varying the thionyl bromide concentration. Evidently a fourfold variation in this quantity yields but little change in rate, any drift, apart from being well within experimental accuracy, being readily rationalized in terms of a variation in the nature of the solution with thionyl bromide content at these very high concentrations of the latter (relative to solvent sulfur dioxide). We conclude, therefore, that the reaction is zero order with respect to thionyl bromide.

The k values for these experiments, while reasonably consistent with those of the first five runs, appear somewhat low. This discrepancy is treated under Discussion.

4. The three experiments with 0.488 millimole of catalyst were used to determine the activation energy from a semi-log plot of rate against $1/T$. The three points fall rather well on a straight line, indicating the occurrence of but a single rate-determining step over this temperature range. On the basis of the plot, together with averages of all the k values, one may summarize the tetramethylammonium bromide data in terms of the expression $k = 2.50 \times 10^8 e^{-13,200/RT}$ min.$^{-1}$.

Other Alkali Halide Catalysts. 1.—Potassium bromide catalyst experiments were performed with saturated solutions (excess solid present), with an intent to check the zero-order dependence on thionyl bromide concentration. It is evident from Table I not only that this salt is also an effective catalyst, but further that the zero-order dependence is again indicated. This conclusion might possibly be criticized on the basis of a probable variation in the solubility of the catalyst in the different solutions of varying composition. The data appear to indicate this to be a small effect, however. The k value given in the table is computed on the basis of the reported solubility of potassium bromide in pure sulfur dioxide,[11] and consequently, as with potassium chloride, must be somewhat discounted, no allowance having been made for the effect on the solubility of added thionyl bromide.

2. Rubidium and cesium halides are sufficiently soluble to be tested for catalytic activity in homogeneous solutions, and experiments showed these also to be effective, rates roughly comparable to those observed with tetramethylammonium bromide being obtained. The rubidium bromide data again suggest an approximate first-order dependence on catalyst concentration, the actual apparent order obtained from a log–log plot of the first four runs (Table I) being 1.35 ± ~0.15.

Catalysis by Pyrex Glass.—A glass catalysis experiment was done, using a charge of pulverized Pyrex, in an effort to test for heterogeneity. Runs in the dark lasting from 4 to 424 hours showed a slow exchange, with the indicated half-time. Presumably the catalysis is heterogeneous, although variation in the amount of added glass powder would be desirable. In view of the mildness of this exchange catalysis, however, it has not seemed important immediately to pursue such experiments in the current context.

Although comparison of the rate found here with that observed for the "uncatalyzed" exchange is difficult because of uncertainty in the absolute amount of glass surface, an approximate extrapolation of the present result to a surface area equal to that of the "no catalyst" reaction bombs yields

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(11) G. Jander, "Die Chemie in Wasserähnlichen Lösungsmitteln," Springer-Verlag, Berlin, 1949, p. 231.

a half-time considerably greater than the 1.9 year figure observed in the latter case[3] (despite the presence of only a fused glass surface in that instance). Such a situation seems reasonable, since the very long half-time of 1.9 years would be critically dependent on possible traces of catalytically effective dissolved impurities.

Discussion

The foregoing experiments clearly demonstrate a strong catalysis by ionic halide compounds. It is further evident from the *k* values given in Table I that all four soluble catalysts are more or less equally effective, within the precision of our data. The situation with regard to the potassium halides is beclouded because of uncertainty in their solubilities.

Although we have been unable to account entirely for the scatter in the data, part of the difficulty may be due to a drift in *k* with catalyst concentration, the tetramethylammonium bromide runs being in general at higher concentration than the others. A plot of all 0° *k* values *vs.* concentration (Fig. 1) suggests such a drift, the slope being such as possibly to indicate an exponential dependence of rate on concentration nearer 1.3 than unity. The source of this drift (if real), possibly a salt effect or, alternatively, reaction mechanism complexity, is not clear from the present data.

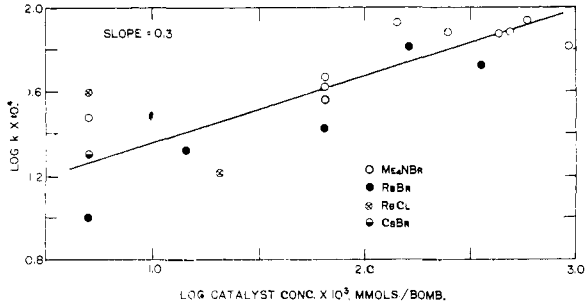

Fig. 1.—First-order rate constants, all catalysts, 0°.

The approximate first order of the reaction appears to indicate that halide ions are equally effective irrespective of degree of dissociation (free ions, ion pairs, etc.). A comparable situation was found by Bartlett and Herbrandson[12] in their study of a system bearing resemblances to the present one. Alternatively one might suppose an associated species (ion pairs?) to be the active material, due to the paucity of free ions at these high catalyst concentrations (*ca.* 0.01–2 molar); this might correlate with the concentration drift in *k*. The uniform activity of the different catalysts further suggests a non-dependence on free halide ions, whose concentrations would vary from case to case.

The following may be postulated as a tentative mechanism

$$\mathrm{Me_4NBr + SO_2 \rightleftharpoons (Me_4N)(SO_2Br)} \quad \text{fast} \quad (2)$$

$$\mathrm{(Me_4N)(SO_2Br) + SO_2 \rightleftharpoons SOBr^+ + Me_4N^+ + SO_3^=} \quad \text{slow} \quad (3)$$

$$\mathrm{Me_4NBr \rightleftharpoons Me_4N^+ + Br^-} \quad \text{fast} \quad (4)$$

$$\mathrm{SOBr_2 \rightleftharpoons SOBr^+ + Br^-} \quad \text{fast} \quad (5)$$

The rapidity of equilibria 4 and 5 is consistent with the observed rate independence of thionyl bromide concentration and is reasonable in view of results recently obtained in this Laboratory[13] on the immeasurable rapidity of chloride exchanges, even at −20°, between thionyl chloride and tetramethylammonium chloride, dissolved in sulfur dioxide. In the proposed mechanism, equation 3 is rate-determining, which is consistent with the observed first-order dependence on the catalyst. The slowness of this step might be related to the smaller relative likelihood of loss by the ion SO_2Br^- of an $O^=$ as compared with a Br^- (to an SO_2 acceptor).

The foregoing scheme is all the more attractive both in view of the known formation of solvates between tetramethylammonium bromide and sulfur dioxide,[14] and the formal analogy borne to the exchange system $(Me_4N)_2SO_3$–SO_2. The much greater rapidity of exchange observed in the latter case[3] might be related, in part, to a greater basicity for $SO_3^=$ than SO_2Br^-. (The $SO_3^=$ exchange was explained in terms of a mobility of oxide ions, which is also involved in the above mechanism.)

The above discussion evidently implies the operation of a basic catalysis. Hence one might expect an acid halide, *e.g.* aluminum chloride, to be of much lower catalytic activity. Incomplete results obtained in the study of the thionyl chloride–sulfur dioxide exchange system[13] seem to support this view; we plan to pursue this point. Bartlett and Herbrandson[12] in their study report that, in contrast to benzylpyridinium chloride, hydrogen chloride is catalytically ineffective.

Our experiments have all been done with excess sulfur dioxide: using excess thionyl halide would make possible variation of sulfur dioxide concentration, which would yield valuable kinetics data. Such an experiment might, of course, be quite vitiated by so drastic a change in the solvent environment; this would be a question for exploration. Alternatively one might work in an inert solvent. We plan to continue investigations of this and similar problems involving the sulfur dioxide system.

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[12] P. D. Bartlett and H. F. Herbrandson, THIS JOURNAL, **74**, 5971 (1952). This research consists of an investigation of the kinetics of the reaction between thionyl chloride and dibutyl sulfite in nitrobenzene, which is found to be strongly catalyzed by benzylpyridinium chloride.

[13] B. J. Masters and T. H. Norris, to be published. In this system catalysis of sulfur exchange is also found to occur, but with a rate much lower than that of the chloride exchange. It is of interest that the sulfur exchange rate is roughly comparable to the corresponding rates given in this paper.

[14] G. Jander, ref. 11, p. 219.