nometer having a volume of one liter (radius *ca.* 6.2 cm.) and claim that wall effects were thereby eliminated. They do not report absolute light intensities, but they do report rate constants for the percentage change in concentration of hydrogen molecules. Rodebush and Klingelhoefer[13] claim that at 18° only one out of about 4×10^4 collisions between chlorine atoms and hydrogen molecules leads to reaction. A combination of this figure with the rate data permits an estimate of the photostationary concentration of chlorine atoms in any of the runs by Kramers and Moignard. Such calculations indicate that the root mean square displacement of a chlorine atom during its mean lifetime[14] ranged from 0.7 cm. (when the rate of reaction was proportional to the square root of the light intensity) to 16 cm. (when the rate was directly proportional to the light intensity). We have attempted to analyze the kinetic data in more detail. So many assumptions must be made that the conclusions are not of much value. However, if one admits errors of up to 5% in the ratio of two light intensities and a possibility of an error of the same order in the ratio of rate constants from two individual runs, then all of their results can be explained by the assumption of a wall reaction with a recombination coefficient of 5×10^{-5}.

We are thus unable to find any data with carefully prepared gases which necessitate the assumption of a homogeneous impurity in order to account for the first order chain-termination process. A conclusive decision between homogeneous and heterogeneous processes would require experiments in systems containing several atmospheres of inert gas, and no such investigations appear to have been reported.

(13) W. H. Rodebush and W. C. Klingelhoefer, Jr., THIS JOURNAL, **55**, 130 (1933). Bodenstein and Winter (ref. 3) obtained almost the same result from completely independent considerations.

(14) T. L. Hill, *J. Chem. Phys.*, **17**, 1125 (1949).

NEW YORK, N. Y. RECEIVED NOVEMBER 21, 1950

[CONTRIBUTION NO. 115 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

The Role of Halide Ions in the Ferric–Stannous Reaction

BY FREDERICK R. DUKE AND RICHARD C. PINKERTON

(1) It is confirmed that the reaction of ferric ion with stannous ion in the presence of chloride ion is first order in ferric concentration. This is also the case when bromide or iodide ions are added. (2) In the range of chloride ion concentrations studied, fourth order dependence on chloride is dominant. It is probable that a minimum of three is required in the activated complex for any appreciable reaction rate. When bromide is added, a third order dependence is observed. Only two iodide ions appear necessary for reaction, but third order dependence is more important at higher iodide concentrations. (3) The reaction rate is depressed when large amounts of metal ion are present due to the complexing and removal of halide ions. This is markedly so in the case of high stannous ion concentrations. Approximate values for the equilibrium constants for the formation of $SnCl^+$ and $SnBr^+$ have been estimated. (4) In the order of increasing effectiveness in promoting reaction we have that Cl^- is less than Br^- is less than I^-. Attention is directed to the fact that the complexing affinity of the halides for both ferric and stannous ions decreases in this order, while the order observed is the order of increasing ease of oxidation of the halide ions.

The reaction between ferric and stannous ions was observed by Gorin[1] to be very slow in perchloric acid solutions, particularly at high hydrogen ion concentrations where hydrolysis is suppressed. One possible reason for the failure of the unhydrolyzed ions to react is the coulombic repulsion between them.[1,2,3] Many studies have been made of the reaction in chloride solutions.[4] In this case it is rapid and kinetics measurements have indicated that chloride complexes of ferric and/or stannous ions are involved. No definite conclusions concerning the order in chloride ion may be drawn from the data in these papers. It would likewise be desirable to determine the exact species which participate. Although it is theoretically impossible to obtain such information for this reaction from kinetic data several views have been advanced. Thus Gorin has stated that the probable reactants are $FeCl_3$ and tin chloride complexes, while Weiss[3] believes them to be Fe^{+++} and $SnCl_4^{--}$. The latter opinion is maintained by Krishna[5] who has observed that increasing the ionic strength depresses the rate and concludes that the reaction is between oppositely charged ions.

More recent data on the equilibrium constants for the formation of ferric[6] and stannous[7] chloride complexes enable a more exact evaluation of the chloride ion dependence. In this paper, the order in chloride ion is investigated and the studies extended to the systems in which bromide and iodide ions are used to catalyze the reaction.

Experimental

Materials.—A solution of 2.03 *N* $HClO_4$ was prepared and used to make up all stock solutions and dilutions. An approximately 0.3 *N* solution of $Sn(ClO_4)_2$ was made by dissolving the salt in 2.03 *N* $HClO_4$ and was standardized before each series of runs against standard ceric sulfate solution. A solution of 0.150 *N* $Fe(ClO_4)_3$ was prepared by dissolving the salt in 2.03 *N* $HClO_4$ and was standardized by tin reduction and titration with standard ceric sulfate. A solution of 2.01 *N* HCl was made and diluted when necessary with 2.03 *N* $HClO_4$. Solutions of 0.5 *N* NaBr and NaI were made by dissolving the salts in water and standardizing by means of a Fajans titration.

---

(1) M. H. Gorin, THIS JOURNAL, **58**, 1787 (1936).

(2) F. R. Duke, *ibid.*, **70**, 3975 (1948).

(3) J. Weiss, *J. Chem. Soc.*, 309 (1944).

(4) (a) A. A. Noyes, *Z. physik. Chem.*, **16**, 546 (1898); (b) W. F. Timofeew, G. E. Muchin and W. G. Gurewitsch, *ibid.*, **115**, 161 (1925); (c) R. A. Robinson and N. H. Law, *Trans. Faraday Soc.*, **31**, 899 (1935).

(5) B. Krishna, *J. Chem. Phys.*, **17**, 846 (1949).

(6) E. Rabinowitch and W. H. Stockmayer, THIS JOURNAL, **64**, 335 (1942).

(7) F. R. Duke and W. G. Courtney, "Iowa State Journal of Science," **24**, 397 (1950).

Procedure.—With the stock solutions made up as described, all reacting mixtures were of ionic strength 2 except for negligible contributions from the metal salts themselves and small corrections in the cases where NaBr or NaI were added. By using high acidity hydrolysis was suppressed and the ionic strength remained essentially unchanged during the reaction. All reactions were carried out in a 200-ml. flask immersed in a water-bath held at 25.0 ± 0.2°. The metal constituent to be present in the smaller concentration was usually added last to start the reaction, although the order was found to be unimportant. Usually 7 samples of 5 ml. each were withdrawn, quenched in $HgCl_2$ solution using diphenylamine as indicator. Quenching with $HgCl_2$ has been repeatedly shown not to catalyze the reaction, and this was confirmed before attempting these experiments. In the case of runs reported in Table V, 25-ml. samples were taken.

Results and Discussion

The rate expression used was

$$dx/dt = k'(a - x)(2b - x) \qquad (1)$$

where x is the concentration of ferrous ion at time t, a the initial concentration of ferric ion and b the molar concentration of stannous ion. Included in k' are functions of chloride concentration. The integrated form is

$$\frac{2.303}{a - 2b} \log_{10} \frac{a - x}{2b - x} = k't + \text{constant} \qquad (1a)$$

In the tables, the quantity S reported is the slope of a plot of $\log_{10}(a - x)/(2b - x)$ *vs.* the time in minutes. Then

$$k' = \frac{2.303}{a - 2b} S \qquad (2)$$

There has been some disagreement in the past as to the exact order in ferric ion, since, when a plot is made as above to test for the order, the reaction rate as indicated by the slope S appears to decrease toward the end of the reaction. Yet as shown below the actual order in ferric ion is one, and not two. Since the apparent decrease in rate must be due to some other effect (such as the consumption of free chloride ion due to stronger complexing by the stannic species formed) the slopes have been found for the initial phase of the reaction.

To determine the true order in ferric ion, a series of runs were made in which the initial ferric ion concentration was varied (Table I). The results show that the dependence is first order as concluded by Gorin.[1] All concentrations are moles per liter in the tables.

TABLE I

EFFECT OF VARYING INITIAL FERRIC CONCENTRATION

Initial stannous concn. 0.00875; total chloride concn. 0.136 (c_t)

$[\mathrm{Fe}^{+3}]$	S	k'	k'/c_t^3
0.101	0.0720	1.96	822
.0812	.0590	2.14	898
.0609	.0455	2.42	1014
.0406	.0226	2.28	956
.0203	.00280	2.32	976

Because it is known that stannous ion forms relatively stable complexes with chloride ion, the determination of the rate dependence on chloride concentration was carried out in solutions of low tin content. An examination of the quantity k'/c_t^3 in Table II shows that there is an apparent third order dependence. The symbol c_t refers to the total chloride ion concentration.

TABLE II

THE EFFECT OF VARYING CHLORIDE CONCENTRATION WITH FERRIC ION IN EXCESS

Initial ferric concn., 0.101; initial stannous concn. 0.00875

$[\mathrm{Cl}^-]$ or c_t	S	k'	k'/c_t^3
0.217	0.265	7.27	715
.163	.112	3.07	715
.136	.0694	1.90	800
.108	.0358	0.982	771
.0813	.0137	0.377	701
.0542	.00398	0.109	686

Next the effect of varying the initial stannous ion concentration was studied. The results in Table III show that the rate actually decreases when stannous ion concentration is increased, although the reaction is first order in tin. This is the consequence of the removal of chloride ion from action by the formation of complexes with stannous ion. If the chloride ion concentration is varied in a series of high stannous ion concentration, the third power dependence on chloride is obscured (Table IV). However, if one assumes that the true dependence in this particular range is third order, one may use the results to estimate a value of the equilibrium constant

$$K_1 = y/(b - y)(c_t - y)$$

for the reaction $\mathrm{Sn}^{++} + \mathrm{Cl}^- \rightleftarrows \mathrm{SnCl}^+$. Here y refers to the concentration of SnCl^+ ion. This is done by taking a value of k'/c_t^3 under conditions in which there is a minimum of complexing (for example the last value of Table I). This value may then be used to calculate the value of chloride concentration under conditions where much of it is present as SnCl^+ (for example, the first run of Table III). The difference between the total chloride and "free" chloride as determined from the rate may then be taken as the concentration of SnCl^+, and K_1 may be evaluated. At first approximation, $K_1 = 13$. Duke and Courtney[7] have since used an improved concentration cell

TABLE III

EFFECT OF VARYING INITIAL STANNOUS CONCENTRATION

Initial ferric concn. 0.0188; total chloride concn. 0.125

$[\mathrm{Sn}^{+}]$	S	k'	k'/c_t^3	$k'/(c_t - y)$
0.121	0.0320	0.329	167	911
.0809	.0352	.567	237	903
.0607	.0337	.756	383	907
.0405	.0258	.954	483	858
.0202	.0129	1.374	697	932

TABLE IV

THE EFFECT OF VARYING CHLORIDE CONCENTRATION WITH STANNOUS ION IN EXCESS

Initial ferric concn., 0.0188; initial stannous concn. 0.0809

$[\mathrm{Cl}^-]_t$ or c_t	S	k'	k'/c_t^3	$k'/(c_t - y)^3$
0.251	0.333	5.36	399	722
.201	.163	2.62	325	780
.151	.0620	0.998	292	828
.125	.0352	.567	287	903
.100	.0166	.267	265	938
.0752	.00584	.0940	221	899

to measure the constants for the stannous chloride complexes and have found a value of $K_1 = 11.3$ in 2 N $HClO_4$. If this latter value is used to correct for the chloride ion concentration for $SnCl^+$ a major improvement is brought about in the agreement of the data. This is seen in the quantity $k'/(c_t - y)^3$.

From the above approximations it is seen that the formation of complexes can be ignored when determining the chloride ion dependence. A more exact treatment will now be undertaken. This becomes necessary when it is realized that the actual dependence may be higher than third order, due to the large proportion of the metal ions present in the complexed form. In the following treatment it is assumed that the reaction occurs between chloride complexes of iron and tin, due to the high improbability of the simultaneous collisions of more than two bodies. Next, those reactions occurring between complexes containing less than a total of three chloride ions are neglected, since the data show that no significant portion of the reaction can occur by those paths. We may then write the rate expression

$$1\mathrm{d}x/2\mathrm{d}t = k_{03}[Fe^{+++}][SnCl^-{}_3] + k_{12}[FeCl^{++}][SnCl_2] + k_{21}[FeCl^+{}_2][SnCl^+] + k_{30}[FeCl_3][Sn^{++}] + k_{04}[Fe^{+++}][SnCl^-{}_4] + k_{13}[FeCl^{++}][SnCl_3^-] + k_{22}[FeCl^+{}_2][SnCl_2] + \ldots + k_{05}[Fe^{+++}][SnCl_5^{---}] + \ldots \text{etc.}^8 \qquad (3)$$

Next the concentrations of each of these species is solved for in terms of total ferric ion, total stannous ion, and "free" or uncomplexed chloride ion. For example, $[SnCl_2] = K_1^sK_2^s[Sn^{++}]_t/(1 + K_1^sc + K_1^sK_2^sc^2 + K_1^sK_2^sK_3^sc^3)$. When this is done, each term is found to contain in its denominator the product of two polynominals which we shall call $f(c)$

$$f(c) = (1 + K_1^fc + K_1^fK_2^fc_2 + K_1^fK_2^fK_3^fc_3)$$
$$(1 + K_1^sc + K_1^sK_2^sc^2 + K_1^sK_2^sK_3^sc^3)$$

Higher terms in c have been neglected. The K's are the constants for the complexing of one, two and three chloride ions successively with the metal ion and the superscripts f and s refer to ferric and stannous ions, respectively. From the data of Rabinowitch and Stockmayer we have that $K_1^f = 3.8$ (corrected for ionic strength 2 by their equation) $K_1^fK_2^f = 4.94$, and $K_1^fK_2^fK_3^f = 0.198$. From Duke and Courtney, $K_1^s = 11.3$, $K_1^sK_2^s = 58.0$ and $K_1^sK_2^sK_3^s = 14.0$, all at ionic strength 2. We next collect all terms containing the same powers of chloride and write

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{(a-x)(2b-x)}{f(c)}(dc^3 + ec^4 \ldots) \qquad (4)$$

Here d, e, etc., are not specific rate constants, but linear combinations of rate constants multiplied by equilibrium constants. For example

$$d = k_{03}K_1^sK_2^sK_3^s + k_{12}K_1^fK_1^sK_2^s + k_{21}K_1^fK_2^fK_1^s + k_{30}K_1^fK_2^fK_3^f$$

The k's may not be separated. From equation (2) we see that

$$k^5f(c)/c^3 = d + ec + fc^2 + gc^3 + \ldots \qquad (5)$$

Data from Table II have been used to evaluate the constants d and e. The free chloride c has been calculated by subtracting the concentrations of $FeCl^{++}$ and $2FeCl_2^+$ (found by graphical methods) and $SnCl^+$ from the total chloride c_t. Concentrations of the other species are small compared with total chloride. Then $k'f(c)/c^3$ is plotted *vs.* (c), from which the intercept, d is found to be 1.2×10^3 while the slope at low values of c gives $e = 72 \times 10^3$ (Fig. 1). The range of chloride concentration in the graph has been extended by a series of runs reported in Table V, where the metal concentrations used are very small and c_t has been taken equal to (c). It is perhaps remarkable that the entire curve can be fit well with a value of $g = 27 \times 10^4$ estimated from these higher values and f taken to be zero. At any rate, a fit is not possible without considering that complexes containing more than four chlorides may participate at higher chloride concentrations.

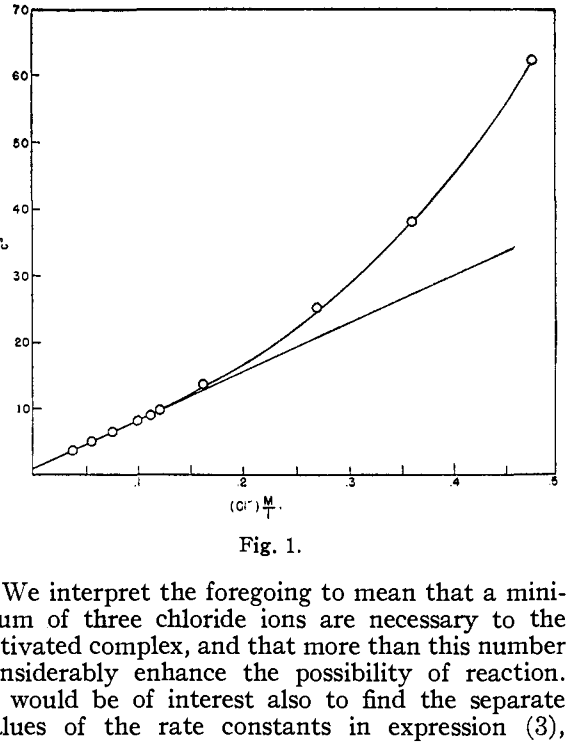

Fig. 1.

We interpret the foregoing to mean that a minimum of three chloride ions are necessary to the activated complex, and that more than this number considerably enhance the possibility of reaction. It would be of interest also to find the separate values of the rate constants in expression (3), but this cannot be done from the kinetic data alone. Certain assumptions are required concerning relationships among the k's themselves which are of a highly questionable character and will not be dis-

TABLE IIA

DATA FOR DETERMINING THE MORE EXACT DEPENDENCE ON CHLORIDE ION CONCENTRATION

$c = c_t - [FeCl^{++}] - 2[FeCl^+{}_2] - [SnCl^+]$ $f(c) = (1 + 3.8c + 4.84c^2 + 0.198c^3)(1 + 11.3c + 58.0c^2 + 14.0c^3)$
k' values are from Table II

k'	c	$f(c)$	$k'f(c)/c^3 \times 10^3$
7.27	0.158	7.428	13.59
3.07	.117	4.732	9.13
1.90	.0961	3.705	7.95
0.982	.0760	2.900	6.49
.377	.0564	2.244	4.72
.109	.0370	1.714	3.70

---

[8] After Gorin, it may be assumed that the product of these reactions is a form of Sn(III) which reacts immediately with more ferric ion. Since the initial reaction is rate determining in the ranges studied, nothing may be said of the following reaction.

TABLE V

THE EFFECT OF VARYING CHLORIDE AT HIGH CHLORIDE CONCENTRATIONS AND LOW METAL CONCENTRATIONS

$[Fe^{+3}]_0 = 2[Sn^{+2}]_0$	c_t	k'	$k'f(c_t)/c_t^3 \times 10^3$
0.00360	0.111	2.50	8.82
.00370	.270	24.1	25.0
.00351	.359	44.2	37.9
.00326	.476	80.9	62.3

cussed here. The question of which of the combinations containing three chloride ions in total are essential remains in doubt.

The criterion of charge repulsion seems one of slight importance here, since $SnCl_2 + Fe^{+++}$, containing two chloride ions in total, do not detectably react. The assumption of Krishna that oppositely charged complexes are involved is invalid, since increasing the ionic strength would be expected to decrease the magnitude of most of the complexing constants K^f and K^s and hence decrease the concentration of the activated complex regardless of the sign of the changes on the colliding species.

A factor of more importance is that the reaction may proceed by a mechanism in which chloride ions are effectively oxidized. For example, a chlorine atom (or units such as Cl_2^- or $Cl_3^=$) might be transferred from ferric to stannous ion. This is not the same as the formation of Cl^0 in solution, an event which would require too much energy. This mechanism would require that at least one chloride ion be strongly bound to ferric ion in the activated complex, since the energy of such a bond is related to the probability that an electron transfer will take place between ferric and chloride ions.[9] An investigation of the effects of bromide and iodide ions, which are more readily oxidized, is illuminating in this respect.

From the values of $k'/[Br^-]^3$ listed in Table VI

TABLE VI

THE EFFECT OF VARYING BROMIDE CONCENTRATION

$[Fe^{+3}]_0$	$[Sn^{+2}]_0$	$[Br^-]$	S	k'	$k'/[Br^-]^3 \times 10^4$
0.0739	0.00683	0.0676	0.308	11.8	3.81
.0739	.00683	.0541	.163	5.84	3.70
.0739	.00683	.0405	.0595	2.27	3.41
.0739	.00683	.0270	.0179	0.684	3.46
.0171	.239	.0375	.427	.427	0.810

it can be seen that the apparent order in bromide ion is three. From the last value in the table, a high stannous concentration is observed to depress the rate. The last figure may be used as before to make a rough approximation of the value of K_1 for the reaction

$$Sn^{++} + Br^- \rightleftharpoons SnBr^+$$

K_1 is found to be 2.7. The corresponding value for the formation of $FeBr^{++}$ (at ionic strength 1) is given as 0.5 by Rabinowitch and Stockmayer.[6] These values are quite small compared to those for the formation of the chloride complexes and we may conclude that third order terms are the important ones in the case of bromide. It should be noted that the values of $k'/[Br^-]^3$ show bromide ion to be much more effective than chloride ion even though the concentration of complexed forms is much smaller. In terms of the rate constants for the actual reactions, bromide complexes must be several thousands of times as reactive as chloride complexes.

When iodide ions are added, complications are introduced because of their oxidation to iodine by ferric ion. The values S_0 in Table VII are the initial slopes of plots of $\log_{10} (a - x)$ *vs.* t, that is,

TABLE VII

THE EFFECT OF VARYING IODIDE CONCENTRATION

$[Sn^{+2}]_0$	$[Fe^{+3}]_0$	$[I^-]$	S	$S_0/[I^-]^2 \times 10^3$	$k'/[I^-]^2 \times 10^4$
0.0650	0.0163	0.00120	0.00862	5.98	5.85
.0664	.0168	.00307	.0590	6.25	6.16
.0651	.0163	.00600	.242	6.71	7.15
.0635	.0159	.00879	.553	7.15	8.10
.00560	.0176	.00646	.129	3.09	

the reaction is treated as if it were independent of tin concentration. The behavior is second to third order in iodide. We then write down the possible paths

$$Fe^{+3} + 2I^- \xrightarrow{2k_0} Fe^{+2} + I_2^-$$

$$Fe^{+3} + 2I^- + Sn^{+2} \xrightarrow{2k_1} \text{products}$$

$$Fe^{+3} + 3I^- + Sn^{+2} \xrightarrow{2k_2} \text{products}$$

In these we set down only the ions which enter the activated complex and do not mean to infer higher than bimolecular collisions. The first reaction is the one studied by Hershey and Bray.[10] For constant iodide concentration and constant (high) stannous ion, the integrated form of the rate equation is

$$\ln(a - x)/2t = k_0[I^-]^2 + [k_1[I^-]^2 + k_2[I^-]^3][Sn^{+2}] = 2.303S_0 \quad (6)$$

From the last run in the table (low tin) and two of the higher runs we may solve algebraically for an approximate value of k_0 and get 6.2×10^3 min.$^{-1}$ $[I^-]^{-2}$ at ionic strength 2. This is high compared with the values of Hershey and Bray (3.8×10^3 at ionic strength 0.09) but is accurate enough for the purpose at hand. Rearranging (6) we obtain

$$k'/[I^-]^2 = (S_0/[I^-]^2 - k_0/2.303)/2[Sn^{+2}] = k_1/2.303 + k_2[I^-]/2.303$$

Plotting the quantity on the left *vs.* $[I^-]$ we obtain $k_1 = 5.5 \times 10^6$ min.$^{-1}[I]^{-2}[Sn^{+2}]^{-1}$ from the intercept and $k_2 = 2.7 \times 10^6$ min.$^{-1}$ $[I^-]^{-3}$ $[Sn^{+2}]^{-1}$ from the slope.

These values are probably not very accurate, but it is to be noted that k_2 so obtained is independent of the value of k_0 used. The reaction which goes *via* three iodide ions will not occur unless tin is present. It may be that the reaction at high tin concentrations is zero order in tin by virtue of there being a slow prior equilibrium for the formation of ferric iodide complexes. In that case the rate of reaction between ferric and stannous iodide complexes containing three iodides in total would be even faster than indicated by the quantity

---

(9) E. Rabinowitch, *Rev. Modern Phys.*, **14**, 112 (1942).

(10) A. V. Hershey and W. C. Bray, THIS JOURNAL, **58**, 1760 (1936).

$k_2 = 2.7 \times 10^6$. In any event this value is to be compared with the values 1.2×10^3 for chloride and 3.4×10^4 for the bromide system.

We may conclude that the rates of these reactions are correlated with the ease of oxidation of the particular halide used. Since these reactions undoubtedly take place between complexed forms of the metal ions, and since the complexing ability of the halides decreases as the rates increase, we may also conclude that charge repulsion is not a primary consideration.

AMES, IOWA RECEIVED SEPTEMBER 25, 1950

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF OREGON STATE COLLEGE]

Isotopic Exchange Reactions of Liquid Sulfur Trioxide and Sulfur Dioxide[1]

BY J. L. HUSTON

No isotopic exchange of sulfur takes place at room temperature when sulfur trioxide is dissolved in liquid sulfur dioxide or when sulfur dioxide is dissolved in liquid sulfur trioxide, and exchange occurs only slowly at 132°. It is suggested on the basis of these results and of work of Nakata that the two compounds undergo rapid exchange of oxide ions at room temperature, interacting as a Lewis acid and a Lewis base but not undergoing oxidation–reduction interaction. Sulfur trioxide reacts with potassium pyrosulfite at room temperature, converting it to potassium sulfate and potassium dipyrosulfate. The process induces a small amount of exchange between sulfur dioxide and sulfur trioxide, indicating that some oxidation–reduction interaction takes place under these conditions. Isotopic exchanges of sulfur trioxide with barium sulfate and with potassium sulfate were observed. When potassium sulfate and sulfur trioxide react to form potassium dipyrosulfate substantial, and possibly complete, exchange occurs between excess sulfur trioxide and the sulfur originally in potassium sulfate.

Isotopic exchange of radiosulfur between compounds containing sulfur (IV) and sulfur (VI) has been investigated in a number of cases[2,3,4] and in no instance has a rapid exchange at room temperature been observed. In contrast with this generalization, Nakata,[5] using O^{18} as a tracer, thus labeling oxygen in place of sulfur, has reported a rapid, room temperature exchange for sulfur dioxide dissolved in excess liquid sulfur trioxide. The present work, done in part under conditions used by Nakata, was undertaken with S^{35} as tracer, to clarify the situation concerning isotopic exchange between these two compounds as well as to obtain information on the nature of liquid sulfur dioxide as an ionizing solvent.

Experimental

Preparation of Materials.—Sulfur dioxide from a cylinder was freed of sulfur trioxide and moisture 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.

Radioactive sulfur dioxide was prepared by a method previously described.[6]

Sulfur trioxide was handled by all-glass technique without contact with stopcock grease. Kahlbaum material was vacuum distilled into several small containers fitted with break-off tips for use as needed. It was condensed at temperatures above 0° to obtain the low-melting α-form. Its only drying was that inherent in distillations of moderate temperatures (below 50°), but this sufficed to maintain largely the α-form for more than a year.

Radioactive sulfur trioxide was made by a heterogeneous exchange found to occur between the liquid and active barium sulfate. Since it developed that the presence of barium sulfate catalyzed polymerization to the high-melting β-form within a few hours, it was necessary, after solidification had occurred, to distil off the sulfur trioxide by warming; the liquid distillate was then poured or distilled back onto the barium sulfate. After repetition of this procedure eight times during three days, the sulfur trioxide was finally distilled off with liquid air into small containers with break-off tips. Using 127 mg. of barium sulfate, 28.5% of the activity was transferred to 3.9 g. of sulfur trioxide. The solid residue from the last distillation was washed with water and after filtration 89.6 mg. of barium sulfate was precipitated from the filtrate, containing 12% of the activity; this must have been present as relatively involatile trioxide and perhaps partly as barium pyrosulfate. The residual barium sulfate retained the rest of the activity. The exchange might better have been conducted at a higher temperature, perhaps *ca.* 60°, to avoid solidification of the trioxide.

Potassium pyrosulfite was made by a standard procedure,[7] modified to permit all operations, including terminal drying in high vacuum, to be done in the same container. Iodimetric determination of sulfur(IV) gave 99.1% of the calculated value, considerably better than results for commercial material.

Commercial potassium sulfate was recrystallized and dried at 150°.

Run Procedure.—High vacuum techniques were used for all gas handling operations, all-glass methods being applied for sulfur trioxide. Visually estimated quantities of sulfur trioxide were distilled into small ampules, which were sealed off and placed in an all-glass apparatus. Sulfur dioxide was condensed into a separate leg of this apparatus which was then sealed off and shaken to break the ampoule, after which the sulfur trioxide was condensed into the leg containing the sulfur dioxide. In certain cases appropriate amounts of potassium sulfate or potassium pyrosulfite had initially been weighed into this "reaction leg" before sealing onto the apparatus.

At the end of a run sulfur dioxide and trioxide were, if necessary, distilled away from solid material by warming to 100° for two hours and collecting the distillate at liquid air temperature in a different leg of the apparatus. Dilute hydrochloric acid was next admitted to this leg (the other having been sealed off) to dissolve the two reactants, and sulfur dioxide then distilled out of this aqueous solution into sodium hydroxide, care being taken to prevent bumping. The two fractions thus obtained were each converted to barium sulfate for radioassay.

Residual solid material from the first distillation was weighed *in situ*. Where potassium pyrosulfite was involved, it was then subjected to the dilute hydrochloric acid and vacuum distillation treatment described in the preceding paragraph. Thus was determined the degree of conversion of pyrosulfite to sulfate and of sulfate to dipyrosulfate.

Appropriate modifications were made for runs at 132°; these were executed in heavy-walled capillary tubing and were thermostated in the vapor of refluxing chlorobenzene.

---

[1] Presented before the Physical and Inorganic Division of the American Chemical Society in Chicago, September, 1950. Published with the approval of the Oregon State College Monographs Committee. Research Paper No. 176, Department of Chemistry, School of Science.

[2] H. Voge, THIS JOURNAL, **61**, 1032 (1939).

[3] J. L. Huston, Thesis, University of California, Berkeley, 1946.

[4] T. H. Norris, THIS JOURNAL, **72**, 1220 (1950).

[5] S. Nakata, *J. Chem. Soc. Japan*, **64**, 635 (1943).

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

[7] H. F. Johnstone, "Inorganic Syntheses," Vol. 2, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 167.