

Summary

The dielectric constants and specific conductances of 2,2-dichloropropane and methyl chloroform have been measured over a wide range of temperature at frequencies of 0.5, 5 and 50 kilocycles. Temperature-time curves have been run with falling and rising temperature and the substances have been observed over a wide range of temperature with a polarizing microscope. These as well as the other three substances with methyls or chlorines attached to a central carbon solidify to cubic crystals in which the molecules have much the same freedom of rotation as in the liquid state.

With decreasing temperature, the isotropic form undergoes a sharp transition to an anisotropic form in which the molecules have lost their rotational freedom.

Temperature-time curves show that *t*-butyl chloride and carbon tetrachloride form a complete series of solid solutions. When the temperature of the rotational transition which occurs throughout these solid solutions is plotted against composition, the curve obtained shows two eutectoids with a maximum at the composition of the most stable solid solution.

PRINCETON, NEW JERSEY

RECEIVED JUNE 29, 1940

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 776]

The Rate of Exchange of Elementary Radiosulfur with Sulfur Monochloride

BY ROBERT A. COOLEY AND DON M. YOST

Introduction

The reactions between sulfur or sulfur monochloride and chlorine have been the subject of investigation since 1782. The mechanisms that have been suggested for the reactions usually involve intermediates having the general formula S_mCl_n , or even ions,¹ but of these compounds only S_2Cl_2 , SCl_2 , and SCl_4 have been isolated, the evidence for the existence of such substances as S_3Cl_4 , S_4Cl_2 , S_2Cl , S_3Cl_2 , and chloride or sulfur chloride ions being of an indirect nature. In the interpretations of the results of both equilibrium and kinetic studies of the sulfur chlorides, the existence of one or more of the compounds not capable of isolation, in slow or rapid equilibrium with sulfur, frequently is assumed, but has never been proved directly. The use of radiosulfur makes it possible for the first time to establish the existence of such equilibria.

In this paper are described the results of experiments made on the slow rate of interchange of radiosulfur in solutions of sulfur dissolved in sulfur monochloride. The experiments show that exchange of dissolved sulfur with the combined sulfur does take place at a measurable rate, and some light is thrown on the mechanism of the reaction, but further investigation will be necessary to establish the steps in other reactions of the sulfur-chlorine system.

Preparation of Materials and Experimental Procedures

Materials.—The radiosulfur was obtained from iron sulfide which had been bombarded with 8 MEV deuterons in the cyclotron at the University of California Radiation Laboratory. To remove radioactive contaminants completely, the irradiated sulfide was treated with acid, the resulting hydrogen sulfide was passed into an acid solution of cupric ion, and the precipitate of cupric sulfide was filtered and washed. Continued digestion of the cupric sulfide with concentrated nitric acid converted it into sulfate and this was precipitated as barium sulfate. The barium sulfate was completely reduced at 900° to barium sulfide with hydrogen. Addition of hydrochloric acid to the barium sulfide produced hydrogen sulfide which was oxidized to elementary sulfur by passing through a solution of triiodide ion. Finally, the elementary sulfur was converted into a form completely soluble in carbon disulfide by heating in an autoclave.²

The sulfur monochloride was prepared by causing accurately weighed, equivalent amounts of pure dry liquid chlorine and purified sulfur to react at 100° for one hour in the sealed evacuated tube B of Fig. 1. The sulfur monochloride was completely distilled, after breaking the tip at C with the glass-enclosed magnetic hammer M, at room temperature into the evacuated tube F which contained a weighed amount (usually 6 mg.) of radiosulfur. The operations of preparation and distillation without losses were facilitated by using liquid air-baths. After sealing the reaction vessel at D and E, it was brought to the temperature at which the exchange was to be measured.

Rate Measurements.—The first experiments made showed the rate of exchange of the dissolved radiosulfur with the sulfur in the monochloride to be extremely slow at

(1) See, for example, Spang, *J. Chem. Soc.*, 1283 (1934).

(2) Cooley, Yost and McMillan, *This Journal*, **61**, 2970 (1939).

25°. In subsequent runs the reaction vessel was completely submerged in a bath of boiling water for a measured time (usually ten minutes), and immediately after removal the side arm G was immersed in liquid air until about one-third of the liquid had distilled over. Only the monochloride and not the uncombined sulfur is sufficiently volatile to distill over in this operation. F, G, and H were then cooled in liquid air and G was sealed off at its constriction. The reaction vessel was again placed in the boiling water-bath for a measured time and the distillation procedure repeated. This distillation procedure effected the separation of the solvent sulfur monochloride from the dissolved sulfur; a simpler method of separating the two substances is desirable, but no satisfactory one was hit upon.

In order to measure quantitatively the radioactivity of the sulfur monochloride removed from the reaction mixture, the former was converted to lithium sulfate. This was accomplished by breaking the removed side arm G, after weighing and cooling in liquid air, in a glass stoppered flask containing a known amount of silver nitrate dissolved in concentrated nitric acid, and then boiling the resulting mixture until oxidation to sulfate was complete.³ After removing and weighing the glass fragments, the calculated amount of hydrochloric acid was added to the sulfate solution to precipitate all of the silver as the chloride, and the precipitate was then filtered off and washed. To the filtrate was added the exact amount of lithium carbonate necessary to convert the sulfuric acid to lithium sulfate, and the resulting solution was then evaporated to dryness. The dry lithium sulfate prepared in this way was ground to a fine powder in an agate mortar, and with the aid of absolute alcohol a thin, uniform layer of the dry powder was placed in a definite area on a metal sample holder. Although the layer was thin, it was of such a thickness, 15 mg./sq. cm. or greater, that the beta particles of maximum energy, 0.107 MEV, originating on the lower side could not penetrate to the top of the layer. The activity of the samples was measured in a lead-shielded Lauritsen quartz fiber electroscopie whose ionization chamber was covered with a 0.15 mg./sq. cm. aluminum foil.

The activities of the samples and of the background were determined in terms of the time necessary for the quartz fiber to pass between two fixed scale positions; in this way the necessity for a calibration of the scale for linearity was eliminated. The background, about 0.0016 div./sec., was determined before and after each measurement on a sample.

The time intervals found for the samples of lithium sulfate are, after correcting for background and rate of radioactive decay, directly related to the concentration of radiosulfur in the samples. Since the weights of the sulfur monochloride used to make up the lithium sulfate were known, it is clear that the measurements will yield quantities proportional to the concentration of radiosulfur in the sulfur monochloride.

Treatment of the Experimental Results

G. Bruni⁴ has shown that sulfur dissolved in sulfur monochloride exists mainly in the form of

(3) H. Endoh, *J. Soc. Chem. Ind. Japan.*, **33**, 287B (1930); J. Frank and E. Marckwald, *Gummi Ztg.*, **28**, 1580.

(4) G. Bruni, *Z. anorg. allgem. Chem.*, **149**, 387 (1925).

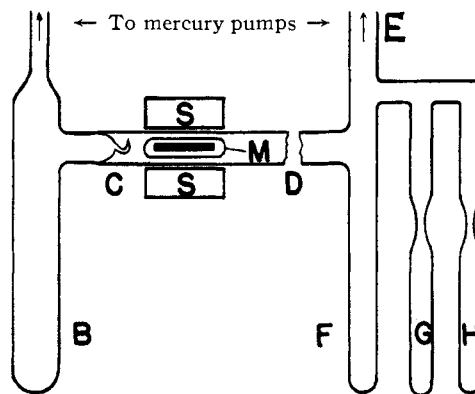
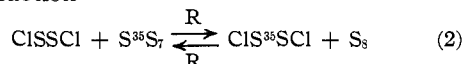


Fig. 1.—Reaction vessel.

S_8 molecules. If (S_2Cl_2) and (S_8) are the concentrations, respectively, of sulfur monochloride and sulfur in atomic weights of sulfur per liter of solution, and if α and β are the fractions of the sulfur atoms in the monochloride and the dissolved sulfur, respectively, that are radioactive, then the conservation of radiosulfur, S^{35} , is expressed by the relation

$$\Sigma(S^{35}) = \alpha_0(S_2Cl_2) + \beta_0(S_8) = \alpha(S_2Cl_2) + \beta(S_8) \quad (1)$$

where the subscript zero refers to the initial time. Without reference to the order of the exchange reaction, let R be the constant rate at which sulfur atoms pass from S_8 to S_2Cl_2 or the reverse. Since the concentration of radiosulfur atoms, S^{35} , is extremely small, practically no S_8 molecules will contain more than one S^{35} atom; consequently in the reaction



one-eighth of the reactions going to the right and one-half of those going to the left will involve an S^{35} atom. It is assumed here, in accordance with the results of crystal structure and electron diffraction investigations,^{5,6} that the sulfur atoms in both S_2Cl_2 and S_8 are equivalent.

Inasmuch as the probability that an S^{35} will be transferred from $S^{35}S_7$ to S_2Cl_2 is $\beta/8$, and the probability of transfer from $S^{35}S_2Cl_2$ to S_8 is $\alpha/2$, we may write for the net rate of transfer of S^{35} atoms

$$d(\alpha(S_2Cl_2))/dt = (\beta/8 - \alpha/2)R \quad (3)$$

On using (1) to eliminate β and then integrating, there results the relation

$$R = \frac{8(S_8)/(S_2Cl_2)}{t\{(S_2Cl_2) + 4(S_8)\}} \ln \frac{(\beta_0 - 4\alpha_0)(S_8)}{(S_2Cl_2)(\alpha_0 - \alpha) + \beta_0 - 4\alpha} \quad (4)$$

(5) Ackermann and Mayer, *J. Chem. Phys.*, **4**, 377 (1936).

(6) K. J. Palmer, *THIS JOURNAL*, **60**, 2360 (1938).

which can be evaluated from the experimental data.⁷ Both α and β may be evaluated to within the same multiplicative constant from the electro-scope measurements and the known weights of sulfur and sulfur monochloride in the samples. The principal errors in the results are believed to arise from uncertainties in the time required for the reaction mixtures to come to the temperature of the bath. The background of the electro-scope averaged about 0.0016 div./sec., and the activities of the lithium sulfate samples varied from 0.0380 to 0.0030 div./sec. Repeated measurements on a sample of the time interval required for the electro-scope fiber to move nine divisions showed the error in the interval to be from 1 to 2%. The error in the rate constants k_1 of Table I that result from the errors in the electro-scope measurements amounts to about 10%. When account is taken of the fact that the energies of the beta particles from radiosulfur are low and that the amount of radioactive material available is small, the stated error is about as small as can be attained with an electro-scope.

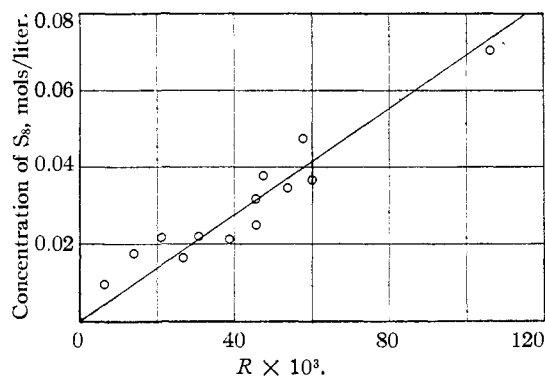


Fig. 2.—Curve showing dependence of R on $[S_8]$.

Discussion of the Results

It will be assumed that equilibrium between the molecular species present in the solutions is effectively established at all times. R , which is the constant rate at which sulfur atoms pass from S_8 to S_2Cl_2 or from S_2Cl_2 to S_8 , will be some function of the concentrations of these two compounds. A study of the experimental results showed that they were in best accord with the relations

$$R = k_1[S_8] \text{ or } R = k_2[S_8][S_2Cl_2]^n \quad (5)$$

where $[S_8]$ and $[S_2Cl_2]$ are the concentrations of the species indicated in moles per liter of solu-

(7) For the analysis for a somewhat similar case see J. N. Wilson and R. G. Dickinson, *THIS JOURNAL*, **59**, 1358 (1937).

tion. The second expression reduces to the first in the present case, since the concentration of the sulfur monochloride solvent was effectively constant in all experiments.

The results of the experiments together with the values of k_1 are presented in Table I. The constants k_1 show appreciable variation, but this variation is not correlated with changes in concentration, and it is believed to be due to the errors mentioned above. In Fig. 2 the values of R are shown plotted against $[S_8]$; it is clear that a linear relationship is indicated, and that therefore the rate R is first order with respect to $[S_8]$.

From the results at the two temperatures an approximate value of the energy of activation was calculated to be 33 kcal.

Experiment 7, the results of which are not plotted in Fig. 2, differed greatly from the other experiments in the concentration of S_8 , and in that initially there was no elementary radiosulfur present, all the radiosulfur being introduced in the form of S_2Cl_2 .

TABLE I

THE RATE OF EXCHANGE OF SULFUR BETWEEN S_8 AND S_2Cl_2

	Moles S_8 per liter of soln. $[S_8]$	Time for exchange, in reciprocal min., $1/t$	Temp. at which exchange occurred, °C.	$R \times 10^3$	$k_1 = R/[S_8]$
	0.0316	0.00114	25 0	0.023	2.3×10^{-5}
1	.0378	.20	98.5	47.2	1.3
	.0477	.0667	98.5	57.7	1.2
	.0704	.0667	98.5	106	1.5
4	.0212	.20	98.3	38.6	1.8
	.0319	.10	98.3	45.3	1.4
2	.0097	.20	98.5	6.36	0.7
	.0165	.10	98.5	26.7	1.6
3	.0177	.10	98.5	14.0	0.8
	.0250	.05	98.5	45.4	1.8
5	.0218	.20	98.5	21.1	1.0
	.0345	.05	98.5	53.6	1.6
6	.0220	.20	98.5	30.8	1.4
	.0364	.10	98.5	60.0	1.7
7	.4606	.0677	98.5	188	0.4
	.6921	.0677	98.5	181	0.3

In arriving at a mechanism for the exchange reaction only the first form of the rate equation will be considered. It will be assumed, in accord with the fact that the rate is first order with respect to the concentration of S_8 , that the rate determining step consists in the slow reversible dissociation of S_8 into S_6 and S_2 , $S_8 = S_2 + S_6$. The exchange is assumed to be accomplished by the rapid reversible step, $2S_2Cl_2 = S_2Cl_4 + S_2$, a reaction postulated

by Patrick and Hackerman⁸ to explain their results on the boiling points of solutions of sulfur monochloride in various solvents. The first step recalls the slow reactions that have been postulated to explain the well-known equilibria between S_λ and S_μ in liquid sulfur.

Since the dependence of R on $[S_2Cl_2]$ in the second form of the rate equation is not known, it is not possible to give an unambiguous mechanism for the case that the monochloride is involved in the slow step of the exchange. A different kind of investigation will be required to settle this point, namely, one in which both the sulfur and the sulfur monochloride are present in small concentrations in a common solvent.

We wish to express our gratitude to Professor Edwin McMillan and Dr. Martin Kamen of the

(8) Patrick and Hackerman, *J. Phys. Chem.*, **40**, 679 (1936).

Radiation Laboratory of the University of California for furnishing us with radiosulfur, and to Dr. J. Norton Wilson for helpful suggestions.

Summary

In solutions of radiosulfur in liquid sulfur monochloride the rate of exchange of sulfur between solute and solvent is very slow at room temperature but is measurably rapid at 100°. From quantitative measurements it was found that the rate at which sulfur atoms pass from S_8 to S_2Cl_2 is directly proportional to the concentration of S_8 . If the rate is not dependent on the concentration of sulfur monochloride, a satisfactory mechanism for the reaction consists in the slow dissociation $S_8 = S_8 + S_2$ followed by the rapid reversible reaction $S_2 + S_2Cl_4 = 2S_2Cl_2$.

PASADENA, CALIF.

RECEIVED MAY 20, 1940

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 778]

The Structure of Thionyl Bromide

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In this communication we report the results of an electron diffraction investigation of the structure of thionyl bromide. The structure of this molecule is of particular interest since it is, as far as we are able to ascertain, the only molecule possessing a sulfur-bromine bond which is sufficiently stable to permit the preparation of electron diffraction photographs of the vapor.

Experimental

The electron diffraction apparatus used in this investigation has been described by Brockway.¹ The camera distance was 10.85 cm. and the wave length of the electrons, determined in the usual way¹ from transmission photographs of gold foil ($a_0 = 4.070 \text{ \AA}$), was 0.0618 \AA .

The thionyl bromide was prepared by the reaction of thionyl chloride with dry hydrogen bromide at 0° as described in "Inorganic Syntheses."² The product was twice distilled *in vacuo*, generous first and last portions being discarded. Analysis of the final material by the precipitation and weighing of silver bromide gave 76.88% bromine (theoretical 76.88%). After standing for thirteen weeks the sample showed 76.90% bromine, indicating that no appreciable decomposition had taken place.

The high temperature nozzle was used to form the gas jet in order to avoid the long gas path and resultant condensation difficulties which accompany the use of the low

temperature nozzle. It was found that a temperature of from 40 to 60° sufficed to give the vapor pressure necessary for the preparation of the electron diffraction photographs.

The photographs showed eight measurable rings whose s ($s = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$) values are given in Table I. The appearance of the photographs is very satisfactorily reproduced by curve C of Fig. 1.

TABLE I

Max.	Min.	C_n	s_0	s_0^a	s_0/s_0^b
	1	-7	1.69	1.64	(0.970) ^b
1		6	2.54	2.63	(1.035)
	2	-5	3.23	3.25	1.006
2		13	4.16	4.10	0.986
	3	-17	5.10	5.11	1.002
3		20	6.20	6.18	0.997
	4	-15	7.53	7.38	0.980
4		18	9.10	9.08	0.998
	5	-22	10.28	10.48	1.019
5		19	11.57	11.61	1.003
	6	-12	12.89	12.77	0.991
6		14	14.58	14.92	1.023
	7	-15	15.86	16.10	1.015
7		12	17.33	17.24	0.995
	8	-10	18.52	18.32	0.989
8		8	19.95	19.30	(0.967)
Average of 13 features					1.000 ± 0.009

^a Model of curve C of Fig. 1. ^b Values in parentheses omitted from average because of unreliability of the measurements.

(1) L. O. Brockway, *Rev. Mod. Phys.*, **8**, 231 (1936).

(2) H. S. Booth, "Inorganic Syntheses," McGraw-Hill Book Co., Inc., New York, N. Y., 1939, pp. 113 and 151.