367. *The Properties of the Chlorides of Sulphur. Part VI. Chemical Analysis.*

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In previous papers (J., 1929, 1421; 1930, 782, 1005) it has been shown that liquid sulphur chloride mixtures containing more than 50 atoms % of chlorine may be regarded as consisting entirely of sulphur dichloride, sulphur monochloride, and free chlorine. This fact, together with the relatively slow rate of reaction in such systems (J., 1931, 323), made the determination of these three constituents possible by chemical means; such a procedure had formerly appeared impracticable owing to the supposed greater complexity of the mixtures, but with ternary mixtures it suffices to determine the total chlorine and that part of it which is in the free condition.

The investigation was facilitated by Mr. A. E. Wadsworth's observation (private communication) that sulphur chloride in dilute solution in carbon tetrachloride is reduced on stirring with aqueous potassium iodide, iodine being liberated. The reduction is approximately quantitative, though the first product is not free iodine, since the solution in carbon tetrachloride is a reddish-orange, although the aqueous layer has the usual colour of a dilute solution of iodine in potassium iodide. The composition of the intermediate product has not been determined: it is perhaps a complex containing sulphur, chlorine, and iodine. If thiosulphate is added, the colour of the carbon tetrachloride phase becomes paler, finally passing through an extremely pale yellow to colourless, making the end-point very difficult to observe. Moreover, starch was useless as indicator, since it was apparently adsorbed at the carbon tetrachloride–water interface and merely retarded the transfer of iodine between the two phases. A back-titration method was therefore adopted, an excess of thiosulphate being first added and the excess then determined by means of a standard solution of iodine. This process affords a measure of the total chlorine.

A similar determination was then made, but β-naphthyl ethyl ether was added to the solution of sulphur chloride in carbon tetrachloride (before addition of aqueous potassium iodide) in order to remove free chlorine from the sphere of the reaction. The difference between this and the foregoing determination afforded a measure of the free chlorine.

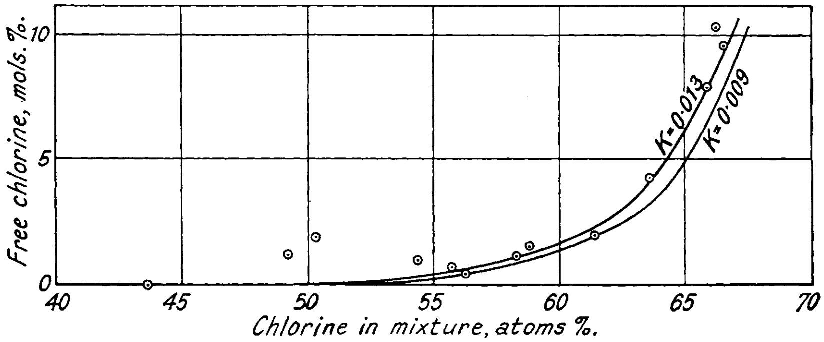
Since iodine catalyses the combination of sulphur monochloride and chlorine (J., 1927, 746; 1931, 323) and is therefore likely to catalyse also the dissociation of the dichloride, it might be thought that its presence would render invalid any determinations made by this method. This, however, appears unlikely, since the iodine, in the first place, is not liberated in the free condition, but in the form of a complex. The free iodine resulting from the dissociation of this complex will be largely transferred to the aqueous layer, on account of the considerable excess of potassium iodide present in that phase, and thus removed from the sphere of the reaction. Moreover, unpublished experiments indicate that the presence of moisture inhibits the reaction between sulphur monochloride and chlorine, even in the presence of the autocatalyst—an effect which is probably due to the products of hydrolysis of sulphur chloride.

The concordance of the analyses supports the view that the system is not disturbed by the presence of iodine, since, although no attempt was made to control the time interval between the addition of potassium iodide and the commencement of titration, the amounts of free chlorine found in a given mixture did not vary to any marked degree.

DISCUSSION.

1. *The Iodometric Determination of Total Chlorine.*—It will be seen from Table I that in general the later experiments show better agreement between the iodometric and the hydrolytic method, the proportion of chlorine titrated iodometrically approaching 98% of the total amount present. This may be due to improvements in technique, but the very low values recorded for mixtures 1—4 are perhaps due to some unsuspected reducing material in them. The amounts of free chlorine found in these mixtures are in good agreement with those found in later preparations.

There remain three likely sources of error: (i) Lack of sensitivity in the method; (ii) changes of composition during sampling; (iii) partial hydrolysis when the aqueous potassium iodide is added.



Free chlorine content of sulphur chloride mixtures.

(i) The sensitiveness of the method was tested by titrating known amounts of iodine in presence of carbon tetrachloride; the violet colour of the carbon tetrachloride solutions passed through pink to colourless, giving a sharp end-point, the error never amounted to more than one drop of thiosulphate, and the same end-point was obtained by addition of excess thiosulphate and back titration with iodine.

(ii) Changes in composition during sampling appear to be unimportant, since (*a*) except in the case of a solution of sulphur in sulphur monochloride, duplicate analyses showed satisfactory agreement, and (*b*) concordant values were obtained for earlier and later samples drawn from the same mixture, except for mixtures rich in chlorine, which easily lose this constituent. Mixtures of higher chlorine content than sulphur dichloride could not therefore be analysed in this way.

(iii) Partial hydrolysis is a more serious cause of error, since the aqueous layers were found to contain acid, which caused decomposition of the thiosulphate, unless they were diluted with a large excess of water before titration. Also, the typical smell of the products of hydrolysis of sulphur chloride can usually be detected after addition of the aqueous potassium iodide. The fact that the whole of the chlorine could not be titrated may be due to hydrolysis, but this would have no effect on the determination of free chlorine, which may be expected to react directly and instantaneously with the potassium iodide, the combined chlorine alone being subject to hydrolysis.

2. *The Estimation of Free Chlorine.*—The results of the analysis of a series of mixtures are plotted in the fig., where the curves represent values calculated according to the law of mass action from two possible values of the equilibrium constant. Over a considerable

part of the range of compositions examined, the results of analysis are in accordance with the view that equilibrium in the liquids is dominated by the dissociation $2SCl_2 \rightleftharpoons S_2Cl_2 + Cl_2$. The dissociation constant 0·013 is slightly higher than the value 0·009 found by colorimetric methods (J., 1929, 1421), but this only corresponds to a change in the degree of dissociation of SCl_2 from 16 to 18·5%. It is, however, also clear that, when the composition of the mixture approaches that of sulphur monochloride, a disturbing influence appears. This may be due to the dissociation of sulphur monochloride itself, for which various mechanisms have been suggested by previous workers (Aronstein and Meihuizen, *Verhand. Akad. Amst.*, 1898, **6**, No. 3; *Arch. néer.*, 1900, **3**, 89; Trautz, *Z. Elektrochem.*, 1929, **35**, 110).

For the present purpose it may be assumed that sulphur monochloride tends to dissociate according to the reversible equation :

$$3S_2Cl_2 \rightleftharpoons S_3Cl_2 + S_3Cl_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The two chlorides S_3Cl_2 and S_3Cl_4 are both known more or less definitely, and they are the nearest in composition to S_2Cl_2 of any of the possible products of its dissociation. The existence of S_3Cl_2 has already been postulated (see J., 1930, 1005) as a product of the dissolution of an excess of sulphur in the monochloride, and definite evidence of its presence in such solutions has been obtained from the refractive indices by Baroni (*Atti R. Accad. Lincei*, 1932, **15**, 305), who found no indication of any other polysulphide. It is probably a member of the series of covalent dichlorides, Cl–Cl, Cl–S–Cl, Cl–S–S–Cl, Cl–S–S–S–Cl, and would be expected to be relatively inert. S_3Cl_4 has been frozen out (J., 1927, 746) from mixtures containing 56·6—59·2 atoms % of chlorine. It is probably a perchloride of the same type as sulphur tetrachloride and would be expected to be equally reactive, dissociating readily according to the equation $S_3Cl_4 \rightleftharpoons S_3Cl_2 + Cl_2$. It may thus become the source of the chlorine found in the analysis of mixtures 5 and 9. A second dissociation of this compound is also possible, *viz.*,

$$S_3Cl_4 \rightleftharpoons S_2Cl_2 + SCl_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and there is evidence to show that this actually takes place at high temperatures. For instance, Trautz (*loc. cit.*) records that, when sulphur monochloride was heated, it first lost chlorine; but after long boiling the red colour of the dichloride sometimes appeared. The latter change, however, was never observed at temperatures below 100°.

Experiments on the changes of density in heated and irradiated sulphur monochloride (to be described in a later paper) are also in accord with this mechanism, and confirm the view that reaction (2) is normally very slow. It may also be pointed out that reaction (1) of this scheme is the only possible dissociation which meets the objection raised by Aronstein and Meihuizen (*loc. cit.*), that if polysulphides are formed it is difficult to account for the high vapour density found for sulphur monochloride by Marchand (*J. pr. Chem.*, 1841, **22**, 507).

EXPERIMENTAL.

Materials.—(*a*) Carbon tetrachloride, purified by shaking two or three times with concentrated sodium hydroxide solution, was washed with water and dried for some days over calcium chloride and finally for a few hours over phosphoric oxide. The liquid was then decanted and distilled through a fractionating column, the portion boiling at 76·70° ± 0·05° (corr.) being collected. In the recovery of residues, the washing with alkali was preceded by shaking two or three times with 98% sulphuric acid and once with water.

(*b*) Sulphur monochloride (from B.D.H. and from Kahlbaum) was redistilled in an all-glass apparatus under reduced pressure, with the addition of 1% of sulphur and 1% of freshly ignited charcoal. The distillate was stored in sealed tubes.

Mixtures richer in chlorine were prepared by passing chlorine through the redistilled monochloride. For this purpose, chlorine from a cylinder was purified by passing through aqueous solutions of copper sulphate and of potassium permanganate; it was then dried by passing through concentrated sulphuric acid and then over a layer (4 ft.) of calcium chloride previously ignited to its sintering point. The solutions were heated in sealed tubes and kept for some days to ensure the attainment of equilibrium.

A mixture containing an excess of sulphur was prepared by dissolving in the redistilled monochloride a suitable quantity of sulphur recrystallised from carbon disulphide.

All sulphur chloride mixtures were analysed by a procedure similar to that described in Part I (J., 1927, 746).

(*c*) β-Naphthyl ethyl ether was obtained from B.D.H. and used without further purification, its suitability being tested by titration of known amounts of iodine in presence of weighed quantities of the ether. Most specimens were without effect, but some (probably owing to traces of impurity) appeared to react slightly with the iodine. The extent of this reaction was shown to be independent of the amount of iodine present and a correction was therefore applied.

Method of Sampling.—The method described by Trautz (*loc. cit.*) was adopted. Small thin-walled bulbs having capillary stems were dried and weighed. They were then dipped in the liquid under examination. When a sufficient quantity of sulphur chloride had entered, the bulbs were withdrawn, rapidly sealed, wiped with filter-paper, and again weighed.

For the purpose of sampling, the mixtures were transferred from the sealed storage tubes to a wide-mouthed, well-stoppered bottle, previously cleaned and dried, which was kept, whilst samples were being taken, over sulphuric acid in a desiccator.

Determination of Total Chlorine.—The bulbs were broken under a quantity of carbon tetrachloride sufficient to give a concentration of about 0·06 g. in 100 c.c. (This dilution is necessary in order to prevent precipitation of sulphur when the potassium iodide is added, since Wadsworth finds that sulphur which cannot be dissolved in the carbon tetrachloride assumes a plastic form and adsorbs iodine, leading to a low titration.) 50 C.c. of 10% aqueous potassium iodide solution were then added as rapidly as possible, and the whole stirred by hand for a minute or two. 400 C.c. of water were next added, and the two phases thoroughly mixed by means of a mechanically-driven bulb stirrer. After stirring had been in progress for at least 5 minutes, addition of sodium thiosulphate from a burette was commenced, and was allowed to continue slowly for about 30 minutes. The thiosulphate should then be in excess and both layers colourless. The stirrer was now raised so as to stir only the aqueous layer, and the excess of thiosulphate was titrated with a standard solution of iodine in aqueous potassium iodide, starch being the indicator. By this method, concordant results can usually be obtained.

Long-continued stirring and gradual addition of sodium thiosulphate are essential, since the presence of excess thiosulphate appears to exert a retarding effect on the dissociation of the iodine complex. Nevertheless, the final addition of excess thiosulphate is apparently necessary in order to ensure the completion of this dissociation, and stirring should be continued for at least five minutes after all visible colour has disappeared from the carbon tetrachloride.

The results of experiments on a series of mixtures are in Table I. The material used in preparing mixtures 1—4 was different from that employed in the later preparations.

TABLE I.

The Iodometric Method of Analysis.

No.	Total Cl, % (hydrolytic method).	Titrated Cl, % (iodometric method).	$\frac{\text{Titrated Cl}}{\text{Total Cl}}$.
1	57·4	46·8	0·82
2	68·13	57·0	0·84
3	65·9	54·5	0·83
4	63·7	52·7	0·83
5	52·8	51·5	0·975
6	58·66	56·46	0·963
7	61·32	59·47	0·970
8	68·84	65·82	0·955
9	51·72	51·38	0·993
10	46·07	45·05	0·977
11	58·19	56·00	0·963
12	60·86	59·89	0·985
13	68·45	67·16	0·982

Determination of Free Chlorine.—To a sample, weighed and dissolved in carbon tetrachloride as already described, 3 g. of β-naphthyl ethyl ether were added and the liquid stirred for a few seconds. As soon as the ether had dissolved, 50 c.c. of 10% potassium iodide solution were added and the remainder of the experiment carried out as in the titration of total chlorine; from the difference, the free chlorine was calculated. Results of duplicate analyses were generally concordant within 0·5%. The results are in Table II, where the mol.-fractions of free chlorine found are compared with those calculated from two values of the equilibrium constant, $K = [S_2Cl_2][Cl_2]/[SCl_2]^2$ (J., 1929, 1421), *viz.*, 0·009 and 0·013 (see p. 1549), the latter being the most probable mean of the "constants" calculated from these mol.-fractions of free chlorine. The same comparison is also shown in the fig., where the points represent the experimental and the curves the calculated values.

TABLE II.

Variation of Free Chlorine Content with Composition of Mixture.

		Free Cl, mols. %.			
			Calc.		
No.	Total Cl, at. %.	Found.	From $K =$ 0·009.	From $K =$ 0·013.	K, found.
10	43·55	0·00	0·00	0·00	—
9	49·17	1·08	0·00	0·00	—
5	50·21	1·86	0·00	0·00	—
1	54·37	0·86	0·21	0·25	0·049
11	55·70	0·52	0·24	0·37	0·019
6	56·19	0·38	0·36	0·48	0·011
12	58·44	0·96	0·70	0·93	0·014
7	58·90	1·45	0·75	1·10	0·019
4	61·40	1·94	1·78	2·22	0·011
3	63·60	4·17	3·12	4·08	0·013
2	65·93	7·80	6·41	7·64	0·013
13	66·25	10·20	7·20	8·39	0·020
8	66·64	9·47	8·01	9·22	0·014

SUMMARY.

1. An iodometric method of determining total chlorine in sulphur chloride mixtures has been investigated and found to be fairly accurate.

2. Free chlorine can be removed from such mixtures by β-naphthyl ethyl ether, and the combined chlorine remaining then estimated, the free chlorine content being thus obtained by difference.

3. The results are in accord with the view that equilibrium in the liquids is dominated by the dissociation $2SCl_2 \rightleftharpoons S_2Cl_2 + Cl_2$. They also show, however, that sulphur monochloride is itself dissociated and a possible mechanism for this dissociation, based upon the equilibrium $3S_2Cl_2 \rightleftharpoons S_3Cl_2 + S_3Cl_4$, is discussed.

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