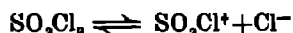


Formation of Acid-base Neutralisation Complexes in Sulphuryl Chloride

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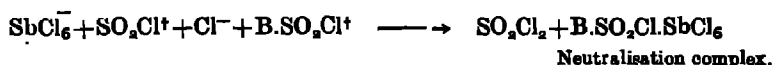
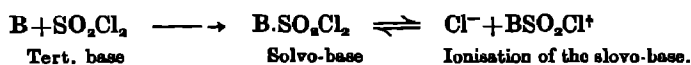
Formation of acid-base neutralisation complexes of solvo-acids and solvo- and ansolvo-bases in sulphuryl chloride has been investigated with a view to elucidating the polar character of sulphuryl chloride. The results obtained confirm the views of the earlier workers.

Gutman¹ from a study of the conductance of the Lewis acids antimony pentachloride, titanium tetrachloride, and stannic chloride in sulphuryl chloride has concluded that these combine with the solvent molecules to form solvo-acids. From a study of the conductance of the tertiary base pyridine in the same solvent, he concluded that it reacted with the solvent molecule to form a solvo-base. From this behaviour and from the conductometric titrations of solvo-acids and solvo-bases, he has pointed out that sulphuryl chloride ionises as



The present work describes the formation of acid-base neutralisation complexes of solvo-acids and solvo- and ansolvo-bases in sulphuryl chloride to elucidate the polar character of sulphuryl chloride and to confirm the views of earlier workers.

With the Lewis acid antimony pentachloride in the solvent sulphuryl chloride, complexes of isoquinoline, quinoline, pyridine, α - and β -picolines, and dimethylaniline have been prepared. Antimony pentachloride has already been used as a solvo-acid in phosphoryl chloride² and in arsenic trichloride³ where it has been shown to act as a mono-basic acid. The organic tertiary bases combine with sulphuryl chloride molecules to give solvo-bases. The formation of neutralisation complexes between the Lewis acid antimony pentachloride and the bases isoquinoline, quinoline, pyridine, α - and β -picolines, and dimethylaniline can be represented as follows:



1. *Monatsh.*, 1954, **85**, 393, 404.

2. Gutmann, *Z. anorg. allgem. Chem.*, 1952, **270**, 179; *Monatsh.*, 1954, **85**, 1077.

3. Gutmann, *Z. anorg. allgem. Chem.*, 1951, **266**, 331, *Monatsh.*, 1953, **84**, 1191.

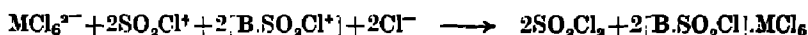
Thus the formation of the neutralisation complex is due to the combination of SO_2Cl^+ and Cl^- to give only feebly ionised SO_2Cl_2 molecules. Complexes of this structure have been isolated from the tertiary bases isoquinoline, quinoline, and pyridine. In the cases of α - and β -picolines and dimethylaniline, the complex molecules lose a molecule of the solvent to give desolvated complexes of the type B.SbCl_5 . The desolvation can be represented as:



Stannic chloride has a tendency to form hexachlorostannate ions which makes it a powerful Lewis acid. Gutmann⁴ has used it as a solvo-acid in sulphuryl chloride during the study of conductometric titrations in this solvent. Titanium tetrachloride also has a similar tendency and forms solvates in various solvents, e.g., phosphoryl chloride⁵, and acetyl chloride⁵. Gutmann^{4,5} has used titanium tetrachloride in sulphuryl chloride as a Lewis acid. The formation of solvo-acids in the case of both the tetrachlorides can be represented as:



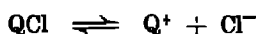
Formation of neutralisation complexes between these dibasic acids and mono-acid bases can be represented as :



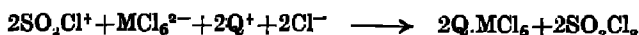
The complex may be desolvated in two stages to give the complexes of the following composition:



Quaternary ammonium chlorides will ionise in this solvent as :



i.e., these will directly increase Cl^- ion concentration in the solution and will thus act as ansolvo-bases. Formation of complexes between the dibasic solvo-acids and ansolvo-bases (quaternary ammonium halides) can be represented as :



In these complexes also the formation of the feebly ionised solvent molecules is responsible for the complex formation and in fact represents the neutralisation of the acidic species with basic species, both peculiar to the solvent.

In these compounds the tetrachlorides act as dibasic acids and these complexes correspond to normal salts. These normal complexes, however, dissolve on the addition of more of acidic solution to form probably the acidic complexes which are highly soluble and cannot be isolated. The formation of the acid salts can be represented as:

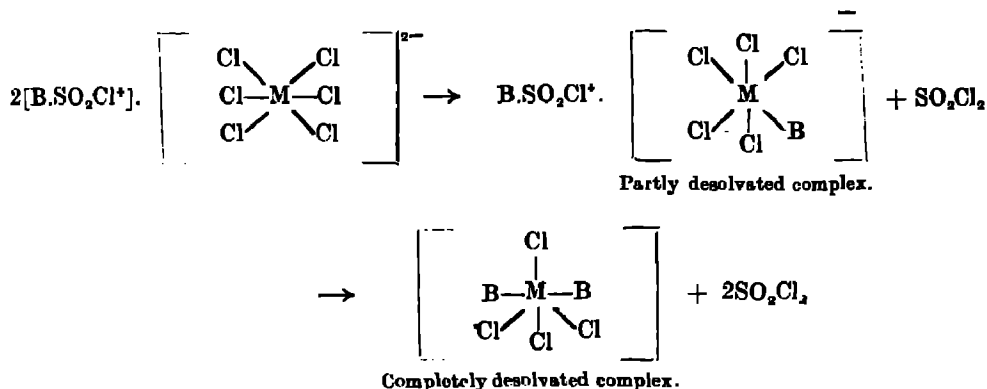


4. Gutmann, *Z. anorg. allgem. Chem.*, 1952, 269, 279.

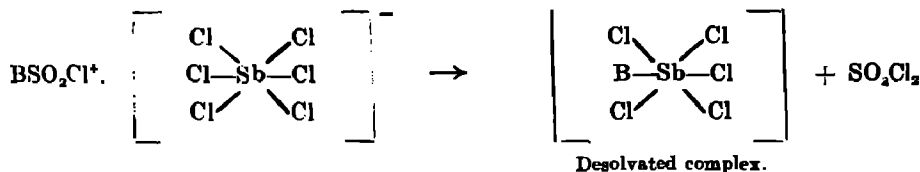
5. Manhas *et al.*, *J. Chem. Soc.*, 1959, 325.

where B represents a tertiary organic base, M represents Ti or Sn, and Q, a quaternary ammonium chloride.

The process of desolvation may not bring about a change in the co-ordination number of titanium and tin and may be due to the space and energy requirements. The process may be represented as:



whereas in the case of antimony pentachloride complexes, the desolvation can be represented as:



The various neutralisation complexes isolated are recorded in Table I.

EXPERIMENTAL

Sulphuryl chloride was fractionated in an all-glass standard joint apparatus and the fraction distilling between 67° and 69° was collected. The distillate was kept over a little mercury overnight to remove free Cl₂ or HCl. It was distilled over mercury and the fraction distilling at 68-68.5° was collected. It was distilled immediately before use at a take-off ratio of 1:10.

Titanium tetrachloride was kept over copper turnings to remove free chlorine present and it was freshly distilled over copper turnings in an all-glass apparatus in an atmosphere of dry nitrogen before use. The fraction distilling at 132.5°/735 mm was collected.

Stannic chloride was prepared by the action of dry chlorine gas on tin metal. Pure tin (100 g.) was taken in a retort, equipped with a long air condenser and a receiver having a calcium chloride guard tube to protect the product from moisture. A current of dry chlorine gas was passed slowly and the flask was heated gently on a low flame. The reaction, being exothermic, does not require continuous heating. The yellow fuming stannic chloride, thus formed, was collected in the ice-cooled receiver. The distillate was treated with pure

TABLE I

Name of the complex.	Formula.	Colour.	M.P.	% Metal.		% Chlorine.		% Nitrogen.	
				Reqd.	Found.	Reqd.	Found.	Reqd.	Found.
1. Sulphurypyridinium hexachloroantimonate	$C_5H_7N \cdot SO_2Cl_2SbCl_6$	White	Shrinks at 123°; melts at 138°(d)	23.67	23.50	48.41	48.01	2.86	1.97
2. α -Picolino-antimony pentachloride semi-solvate	$C_5H_7N \cdot SbCl_5 \cdot fSO_2Cl_2$	Very light yellow	158-03°	26.30	26.43	46.34	45.32	3.05	2.83
3. β -Picolino-antimony pentachloride	$C_5H_7N \cdot SbCl_5$	Black semisolid	..	31.03	28.02	45.25	45.02	3.57	3.07
4. Sulphurylquinolinium hexachloroantimonate	$C_9H_7N \cdot SO_2Cl_2SbCl_6$	Light yellow	124°	21.63	21.85	44.12	43.80	2.48	2.05
5. Sulphurylisoquinolinium hexachloroantimonate	$C_9H_7N \cdot SO_2Cl_2SbCl_6$	Brown	170° (d)	21.63	21.58	44.12	43.50	2.48	2.20
6. Dimethylamino-antimony pentachloride	$C_6H_5N(OH)_2 \cdot SbCl_5$	Light yellow	147°(d)	28.98	28.92	42.28	41.68	3.38	2.90
7. Dipyrilidino-stannic chloride monosulphuryl chloride	$(C_5H_3N)_2SnCl_4 \cdot SO_2Cl_2$	White	140° (d) Calc. Metal/Cl = 0.565.	21.44	18.73	38.80	33.10	5.05	3.93
8. Di- κ -picolino-stannic chloride monosulphuryl chloride	$(C_5H_7N)_2SnCl_4 \cdot SO_2Cl_2$	Light pink	116°(d)	20.40	20.50	36.60	36.98	4.80	4.00
9. Bis-sulphuryl- β -picolinium hexachlorostannate	$(C_5H_7N \cdot SO_2Cl)_2 \cdot SnCl_6$	Light orange	165°(d)	16.57	16.73	30.63	36.90	3.91	3.05
10. Diquinolino-stannic chloride monosulphuryl chloride	$(C_9H_7N)_2SnCl_4 \cdot SO_2Cl_2$	Cream	196°(d)	18.15	18.00	33.41	32.60	4.20	4.42

TABLE I (contd.)

Name of the complex.	Formula.	Colour.	M. P.	%Metal. Reqd. Found.	%Chlorine. Reqd. Found.	%Nitrogen. Reqd. Found.
11. Di-isquinolino-titanic chloride monosulphuryl chloride	$(C_9H_7N)_2SnCl_4 \cdot SO_2Cl_2$	Light yellow	170-80°	18.15 18.03	32.41 32.30	4.20 3.50
12. Tris-sulphuryldimethyl-anilinium sulphurylium bis-hexachlorostannate semisolvate	$[C_6H_5N(CH_3)_2SO_2Cl]_3 \cdot SO_2Cl \cdot (SnCl_6)_2 \cdot \frac{1}{2}SO_2Cl_2$	Dirty white	72°(d)	15.91 15.86	40.50 39.70	2.81 2.68
13. Bis-triethylbenzylammonium hexachlorostannate	$[(C_2H_5)_3N \cdot C_7H_7]_2SnCl_6$	Waxy white	80°(d)	16.58 17.45	20.76 20.00
14. Dipyrridino-titanium tetra-chloride monosulphuryl chloride	$(C_5H_5N)_2TiCl_4 \cdot SO_2Cl_2$	Lemon-yellow	163°(d)	9.94 8.42	44.10 37.54	4.43 3.2
15. Di- α -picolino-titanium tetrachloride monosulphuryl chloride	$(C_8H_7N)_2TiCl_4 \cdot SO_2Cl_2$	"	199°(d)	9.39 8.02	41.60 35.30	5.47 4.00
				Calc. Metal/Cl=0.225. Metal/Cl=0.224.		
				Calc. Metal/Cl=0.225. Metal/Cl=0.227.		
16. Di- β -picolino-titanium tetrachloride monosulphuryl chloride	$(C_8H_7N)_2TiCl_4 \cdot SO_2Cl_2$	Yellow	190°(d)	9.39 9.05	41.60 40.10	5.47 4.47
17. Diquinolino-titanium tetrachloride monosulphuryl chloride	$(C_9H_7N)_2TiCl_4 \cdot SO_2Cl_2$	"	100-213°	8.23 8.12	36.51 35.60	4.80 4.03
18. Diquinolino-titanium tetrachloride	$(C_9H_7N)_2 \cdot TiCl_4$	Light yellow	175°	10.71 10.00	31.60 31.00	6.00 5.40
19. Di-isquinolino-titanium tetrachloride	$(C_9H_7N)_2 \cdot TiCl_4$	Orange-brown	200°(d)	10.71 10.70	31.60 31.40	6.00 5.24
20. Dimethyl-anilino-titanium tetrachloride monosulphuryl chloride	$C_6H_5N(CH_3)_2TiCl_4 \cdot SO_2Cl_2$	"	165°(d)	8.46 7.57	37.57 33.67
				Calc. Metal/Cl=0.225. Metal/Cl=0.225.		

(d) denotes decomposition.

tin to remove free chlorine. The colorless liquid was fractionated in nitrogen atmosphere and the product coming at 113-14°/742 mm was collected (yield 175 g.)

Antimony pentachloride (Riedel-Dehaen Ag. Sulze Hanover) was used as such since there were chances of its being dissociated into trichloride during distillation.

Quinoline (35 g.) was dissolved in 200 ml of dilute hydrochloric acid (1:4) and the solution heated to 60°. A solution of zinc chloride (23 g.) in hydrochloric acid (125ml) was then added dropwise when a white complex separated. The reaction mixture was cooled to room temperature and crushed ice was added. The mixture was thoroughly stirred. The precipitate was filtered and washed with dilute hydrochloric acid.

The complex was then suspended in a small quantity of water and 10% NaOH solution was added dropwise till the solid was completely dissolved. A layer of quinoline separated which was extracted with ether. The ethereal layer was separated and the ether distilled. The residue was fractionated over KOH and the distillate coming at 227-30°/734 mm was collected. It was then kept over KOH beads and was freshly distilled in an all-glass apparatus in an atmosphere of dry nitrogen. The fraction boiling at 228-29°/734 mm was collected for use.

Pyridine, α - and β -picolines, dimethylaniline, and isoquinoline were purified by refluxing over KOH beads for about 2 hours. These were then distilled in an atmosphere of dry nitrogen and fractions boiling at the following temperatures were collected in glass-stoppered bottles.

	B.P.		B.P.
Pyridine	112.5°/737 mm	Quinoline	228-29°/734 mm
α -Picoline	125.5-26°/735	Isoquinoline	232°/737
β -Picoline	143°/742	Dimethylaniline	192.5-93°/732

Triethylbenzylammonium chloride was purified by crystallisation in a dry atmosphere from absolute ethanol at about 60°.

The complexes were prepared by dissolving the acids and bases in sulphuryl chloride in fixed molar proportions and cooling the mixture in an ice-bath for some time for completion of the reaction. The filtration was carried out in a dry atmosphere in a sintered glass funnel. The complex was washed with pure dry benzene and dried in vacuum. The sample was analysed for chlorine by Volhard's method, antimony estimated iodometrically, and nitrogen was estimated by Jackson and Smith's method⁶. Tin and titanium were estimated as their dioxides.

In the case of complexes No. 7, 14, 15, and 20, there seems to be an admixture with the inert solvent which could not be removed. In consequence, the analytical results are low, but the ratio metal/Cl is correct in these cases. Complex No. 18 (diquinolino-titanium tetrachloride) has been obtained by subjecting complex No. 17 to vacuum.

6. *J. Amer. Chem. Soc.*, 1940, 62, 544.