491. *Salt-like Behaviour of Trichloromethanesulphenyl Chloride.*

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Trichloromethanesulphenyl chloride forms a weakly conducting solution in glacial acetic acid. It behaves as a salt with silver nitrate, giving silver chloride and trichloromethanesulphenyl nitrate, $CCl_3{\cdot}S{\cdot}NO_3$, in the acetic acid solution. Its reaction with potassium iodide has been reinvestigated and extended to acetic acid solution; the probable course is discussed. Two new solid addition complexes, $SbCl_5,CCl_3{\cdot}SCl$ and $SbCl_5,2CCl_3{\cdot}SCl$, have been prepared; they decompose above room temperatures, in ways which have been studied in detail.

Arenesulphenyl chlorides have been shown to form cations, ArS^+, in acid solution.[1] This property is responsible for exchange reactions of the chlorides with many salt-like compounds.[2] These sulphenyl chlorides also form complex salts with Lewis acids such as aluminium chloride, and antimony chloride and fluoride, *e.g.*, $ArS^+AlCl_4^-$ (Ar = 1,4-dinitrophenyl).[1] The existence of a univalent sulphur cation is interesting in view of the electronic configuration of the sulphur atom which has two of its 3*p*-electrons unpaired. No similar studies have been reported for the perhalogenoalkanesulphenyl chlorides, $CF_3{\cdot}S{\cdot}Cl$ or $CCl_3{\cdot}S{\cdot}Cl$, and no information is recorded on the ionic dissociation of the S–Cl linkage in these compounds. The main object of the present investigation was to evaluate trichloromethanesulphenyl chloride as a source of the sulphenium ion.

Trichloromethanesulphenyl chloride forms a weakly conducting solution in glacial acetic acid; the specific conductance for a 0·2M-solution is 2×10^{-7} ohm^{-1} cm.$^{-1}$ at 25° (cf. 4×10^{-9} ohm^{-1} cm.$^{-1}$ for the pure solvent). Silver nitrate, which is sparingly soluble in glacial acetic acid (0·21 g. per 100 g. at 30°), reacts readily with trichloromethanesulphenyl chloride in this medium, yielding a precipitate of silver chloride, and trichloromethanesulphenyl nitrate, $CCl_3{\cdot}S{\cdot}NO_3$, remains in solution.

Conductivity measurements show that the compound is to be formulated as $CCl_3{\cdot}S^+Cl^-$ in glacial acetic acid, for titration of silver nitrate (0·1M) by trichloromethanesulphenyl chloride, both in glacial acetic acid, resulted in a fall of specific conductance from $8{\cdot}05 \times 10^{-6}$ to $2{\cdot}35 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$ and there was a sharp break in the conductivity curve (see Figure) at a molar ratio of 1 : 1, implying that precipitation of the chloride was complete at this stage.

Trichloromethanesulphenyl nitrate is stable only in the glacial acetic acid solution; attempts to isolate it failed. Sulphenyl nitrates, in general, appear to exist in organic solvents.[3a] The direct reaction between trichloromethanesulphenyl chloride and powdered silver nitrate was too vigorous and led to an explosion after an induction period. Trichloromethanesulphenyl nitrate has oxidising properties, liberating iodine from potassium iodide.

In line with the arenesulphenyl chlorides, dissociation of trichloromethanesulphenyl chloride is dependent on solvent polarity. The reversible equilibrium between it and potassium iodide in carbon tetrachloride is slow compared with that in acetic acid. The end products, in both cases, however, contained iodine, presumably formed by the decomposition of trichloromethanesulphenyl iodide (II), generated as intermediate[3b] as the result of the ionic equilibrium (i):

$$CCl_3{\cdot}SCl\ (I) + KI \rightleftharpoons CCl_3{\cdot}SI\ (II) + KCl \quad \dots\dots\dots \quad (i)$$

$$2CCl_3{\cdot}SI \longrightarrow (CCl_3)_2S_2 + I_2 \quad \dots\dots\dots\dots \quad (ii)$$

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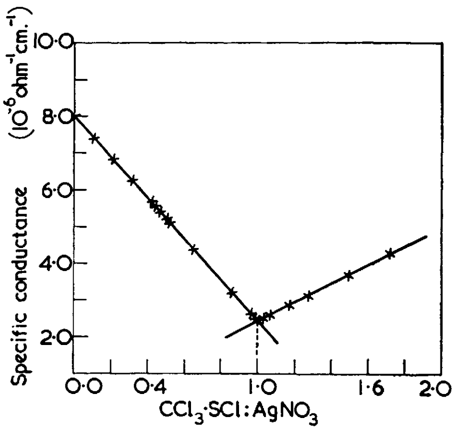
[1] Kharasch, Buess, and King, *J. Amer. Chem. Soc.*, 1953, **75**, 6035; Kharasch and Assony, *ibid.*, p. 1081.

[2] Kharasch, Potempa, and Wehrmeister, *Chem. Rev.*, 1946, **39**, 299.

[3] Kharasch, "Organic Sulphur Compounds," Pergamon Press, Oxford, Vol. I, (*a*) p. 377, (*b*) pp. 364, 387.

Further evidence in favour of the ionic dissociation of the chloride is obtained by conductometric measurement of its titration with potassium iodide in glacial acetic acid: there was first a gradual rise in conductance, followed by a decrease as reaction (ii) occurred. A comparable reaction is known between benzenesulphenyl chloride and potassium iodide, but conductance results are not available.[4]

Earlier investigations[3b,5] left doubts whether the other product of the reaction was bistrichloromethyl disulphide $(CCl_3)_2S_2$ or thiocarbonyl chloride. It appears that the former is formed but, being unstable, decomposes slowly into thiocarbonyl chloride and trichloromethanesulphenyl chloride: $(CCl_3)_2S_2 \longrightarrow CCl_3{\cdot}SCl + CSCl_2$. Bistrichloromethyl disulphide is, however, considered[6] to be an intermediate in the preparation of thiocarbonyl chloride from trichloromethanesulphenyl chloride. The re-formation of trichloromethanesulphenyl chloride in this decomposition explains the higher yields of iodine in experiments carried over extended periods and in presence of an excess of iodide ions; but, contrary to Perret and Perrot's observation[5] with aqueous iodide, the yield of iodine in the present case never corresponded to 2 atoms of chlorine per mole of sulphenyl chloride, and this precludes the direct or complete reduction of the latter to thiocarbonyl chloride.[6]



Conductometric titration of silver nitrate with trichloromethanesulphenyl chloride, both in glacial acetic acid.

The reaction of trichloromethanesulphenyl nitrate with potassium iodide in acetic acid solution appear anomalous; only 0·5 atom of iodine is liberated per mole of sulphenyl nitrate reacting. The reason for this is not understood.

At slightly below room temperature trichloromethanesulphenyl chloride and antimony pentachloride gave two new solid addition compounds, $SbCl_5,CCl_3{\cdot}SCl$ and $SbCl_5,2CCl_3{\cdot}SCl$. Although these unstable adducts have not been fully characterised, they appear to be analogous in composition to those of the arenesulphenium salts.[1] If electrophilic attack by antimony pentachloride operates, the adducts may be formulated as complex salts, $[CCl_3{\cdot}S]^+[SbCl_6]^-$ and $2[CCl_3{\cdot}S]^+[SbCl_7]^{2-}$. In view of the polar nature of $CCl_3{\cdot}\overset{\delta+}{S}{-}\overset{\delta-}{Cl}$, bonding through chlorine seems likely, effecting the fission of the S–Cl linkage. Both the compounds were highly hygroscopic and melted above room temperatures to brown liquids which decomposed subsequently into antimony trichloride, disulphur dichloride, and carbon tetrachloride: $SbCl_5 + 2CCl_3{\cdot}SCl \longrightarrow SbCl_3 + S_2Cl_2 + 2CCl_4$. If, however, the proportion of antimony pentachloride was increased, further reaction took place and the

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[4] (*a*) Böhme and Schneider, *Ber.*, 1943, **76**, 483; (*b*) Stamm and Goehring, *ibid.*, p. 737.

[5] Perret and Perrot, *Bull. Soc. chim. France*, 1934, **1**, 1531.

[6] Sosnovsky, *Chem. Rev.*, 1958, **58**, 509.

addition complex, $SbCl_5,SCl_4$ was produced instead of disulphur dichloride: $3SbCl_5 + CCl_3{\cdot}SCl \longrightarrow 2SbCl_3 + CCl_4 + SbCl_5,SCl_4$. The reaction of disulphur dichloride with antimony pentachloride has been investigated by Partington.[7]

Conductometric titration of antimony pentachloride with trichloromethanesulphenyl chloride in glacial acetic acid gave no definite information on the formation of these complexes because of their instability.

EXPERIMENTAL

Trichloromethanesulphenyl chloride was prepared by treatment of carbon disulphide with chlorine in the presence of iodine.[6,8] It was separated by washing the reaction mixture with water, followed by distillation, dried ($CaCl_2$), and redistilled under reduced pressure.

Merck's glacial acetic acid was further dried by mixing it with 2—3% of acetic anhydride, refluxing for some time, and distillation in an all-glass apparatus. Other solvents and materials used were dried and purified by standard procedures.

For conductance measurements, use was made of a small dipping-electrode type of cell; the electrodes were of smooth platinum (cell constant 1·45 cm.$^{-1}$). Conductance was measured by a specially designed Wheatstone bridge or, when a portable bridge was more suitable, a Mullard conductance bridge of type E7566.

Reaction of Trichloromethanesulphenyl Chloride with Silver Nitrate.—Trichloromethanesulphenyl chloride (87·5 mg.) in glacial acetic acid was added to a saturated solution (100 ml.) of silver nitrate (79·1 mg.) in the same solvent. A white solid separated. The mixture was then stirred vigorously in subdued light, set aside for 1 hr., and filtered out of contact with the atmosphere. The white solid was silver chloride (66·0 mg., 99%) (Found: Cl, 23·8. Calc. for AgCl: Cl, 24·7%). The filtrate contained NO_3^- as the only significant anion. For analysis the mixture was decomposed by 15% sodium hydroxide solution. Sulphur was oxidised to sulphate by treatment with hydrogen peroxide and weighed as barium sulphate, chlorine was estimated volumetrically by Volhard's method, and nitrogen by the Kjeldahl semimicromethod after reduction with Devarda's alloy (Found: Cl, 49·3; S, 14·4; N, 6·5. Calc. for $CCl_3{\cdot}S{\cdot}NO_3$: Cl, 50·1; S, 15·1; N, 6·6%).

Conductometric Titration.—A saturated solution (100 ml.) of silver nitrate (79·1 mg.) in glacial acetic acid was titrated conductometrically with a glacial acetic acid solution (0·1M) of trichloromethanesulphenyl chloride. Addition of the titrant was continued until present in excess, *i.e.*, until the conductivity changed only very slowly. The conductivity curve (Figure) shows sharp break at a 1 : 1 molar ratio (Found: AgCl, 65·0 mg., 97·5%).

Reaction of Trichloromethanesulphenyl Nitrate with Potassium Iodide.—Trichloromethanesulphenyl nitrate (8·2 mg., 2 mol., in glacial acetic acid) was allowed to react with potassium iodide (3·2 mg., 1 mol., in the same solvent); there was immediate reaction with the liberation of iodine which was estimated (2·36 mg., 97·8%). When the same reaction was performed with a 1 : 1 proportion of the reactants the yield of iodine was only about 50%. Increase in the proportion of potassium iodide above 2 mol. did not influence the course of the reaction substantially.

Reaction of Trichloromethanesulphenyl Chloride with Potassium Iodide.—(i) *In carbon tetrachloride.* Trichloromethanesulphenyl chloride (18·13 mg.) in dry carbon tetrachloride was allowed to react with potassium iodide (1 g.) in a closed tube. When the mixture was shaken for 10—15 min. there was slow liberation of iodine (12·1 mg., 96%). When the reaction time was extended to 15 hr. the yield of iodine was somewhat higher (17·5 mg.). Reaction of equimolar amounts of the reactants led to equilibrium at an intermediate position (yield of iodine 44%).

(ii) *In glacial acetic acid.* Trichloromethanesulphenyl chloride (18·27 mg.) was treated with an equimolecular amount of potassium iodide (16·30 mg.) in acetic acid. Iodine was at once liberated (12·2 mg.; 98%). With an excess of potassium iodide (10—15 min.) there was some rise in the yield of iodine; for KI : $CCl_3{\cdot}S{\cdot}Cl$ molar ratios of 2, 3, 4, and 6, yields of iodine were equivalent to 1·12, 1·13, 1·14, and 1·16 atoms, respectively.

On addition of an acetic acid solution (0·1M) of trichloromethanesulphenyl chloride to an

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[7] Partington, *J.*, 1929, 2573.

[8] Rathke, *Annalen*, 1873, **167**, 195.

acetic acid solution of potassium iodide there was a gradual rise in specific conductivity of the solution from $2{\cdot}90 \times 10^{-5}$ to $4{\cdot}61 \times 10^{-5}$ ohm^{-1} cm.$^{-1}$, and thereafter a steep fall to $2{\cdot}32 \times 10^{-5}$ ohm^{-1} cm.$^{-1}$ and subsequently a rise again. Iodine was liberated, and this obscured the nature of the changes.

Reaction of Trichloromethanesulphenyl Chloride with Antimony Pentachloride.—(i) *Reaction in equimolar ratio.* Antimony pentachloride (1·4 g., 4·67 mmoles), in a trap connected to a vacuum-system, was kept slightly below room temperature (20°). Trichloromethanesulphenyl chloride (0·87 g., 4·67 mmoles) was added. The mixture became solid at once. Volatile matter was pumped off and the solid product was analysed by decomposition with 15% potassium hydroxide solution and was the 1 : 1 *complex*, $SbCl_5,CCl_3{\cdot}SCl$ (Found: Sb^{5+}, 25·6; S, 6·1; Cl, 65·0. CCl_9SSb requires Sb^{5+}, 25·1; S, 6·6; Cl, 65·8%). On warming to the room temperature the solid slowly melted to a brown liquid which gradually decomposed to a complex mixture.

(ii) *Reaction in the molar ratio* 1 : 2.—Antimony pentachloride (4·33 g., 14·4 mmoles) and trichloromethanesulphenyl chloride (5·37 g., 28·8 mmoles), when allowed to react as above, formed a solid product. This, on removal of volatile matters, was the 1 : 2 *complex*, $SbCl_5,2CCl_3{\cdot}SCl$ (Found: Sb^{5+}, 18·8; S, 8·8; Cl, 67·7. $C_2Cl_{13}SSb_2$ requires Sb^{5+}, 18·2; S, 9·5; Cl, 68·7%). The solid melted to a brown liquid above room temperature; this liquid soon deposited white crystals which, when filtered off out of contact with air and washed with a little dry carbon tetrachloride, were highly hygroscopic and were identified as antimony trichloride (3·85 g., 93%) (Found: Sb^{3+}, 53·3; Cl, 46·7. Calc. for $SbCl_3$: Sb^{3+}, 53·5; Cl, 46·5%). The liquid product was distilled, giving carbon tetrachloride (4·02 g., 91%) (Found: Cl, 91·8. Calc. for CCl_4: Cl, 92·0%). Another yellow liquid fraction distilling at 120—140° was disulphur dichloride (1·1 g., 97%) (Found: Cl, 52·3; S, 47·6. Calc. for S_2Cl_2: Cl, 52·25; S, 47·75%).

(iii) *Reaction in the molar ratio* 3 : 1. Antimony pentachloride (1·96 g., 5·2 mmoles) was allowed to react with trichloromethanesulphenyl chloride (0·313 g., 1·73 mmoles) as above. A reaction was again apparent by the liberation of heat. A semi-solid yellow mass was formed which soon melted to a brown liquid. From this, a light yellow solid gradually separated and the supernatant liquid became colourless. This liquid was then separated and identified as carbon tetrachloride (0·245 g., 94%) (Found: Cl, 91·7. Calc: Cl. 92·2%). The solid product was a mixture which was extracted with sulphuryl chloride. The insoluble component was antimony trichloride (0·95 g., 95·5%) (Found: Sb^{3+}, 53·1; Cl, 46·6%). The soluble component was crystallised under a partial vacuum as needles and was the complex, $SbCl_5,SCl_4$ (0·875 g., 88%) (Found: Sb^{5+}, 24·5; Cl, 65·75; S, 8·75. Calc. for $SbCl_9S$: Sb^{5+}, 24·8; Cl, 66·3; S, 8·9%).

(iv) *Conductometric experiment.* When a solution (30 ml.) of antimony pentachloride (0·299 g.) in glacial acetic acid was titrated conductometrically with a 0·1M-solution of trichloromethanesulphenyl chloride in the same solvent at 25°, the conductance decreased asymptotically without any sharp change.

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