165. *Some Addition Compounds of Bis(trifluoromethylthio)mercury.*

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1 : 1 Addition compounds of bis(trifluoromethylthio)mercury $Hg(SCF_3)_2$ with tetramethylammonium chloride and iodide have been prepared. Conductivity measurements in acetone solution show that the compounds are to be formulated as $Me_4N^+[Hg(SCF_3)_2Cl]^-$ and $Me_4N^+[Hg(SCF_3)_2I]^-$ respectively. The thermal behaviour of the compounds and some of their reactions have been studied. Conductometric titrations of bis(trifluoromethylthio)mercury in acetone with potassium iodide indicate the formation of $K^+[Hg(SCF_3)_2I]^-$ in solution. The titration is complicated by irreversible chemical reactions occurring as soon as the ratio KI : $Hg(SCF_3)_2$ exceeds one.

Replacement of the hydrogen atoms in an alkyl group by fluorine produces a radical with substantial inductive character, and as a result the electronic environment of the mercury atom in bis(trifluoromethyl)mercury permits the formation of anions of the type $[Hg(CF_3)_2X_2]^{2-}$ (X = Cl, Br, I).[1] Neither dialkylmercurys nor alkylmercuric salts have been reported to undergo similar complex formation. In view of these results and since mercury sulphides have not been reported to form complex ions, the interaction of bis(trifluoromethylthio)mercury and ionic halides was investigated.

Solid bis(trifluoromethylthio)mercury and tetramethylammonium chloride or iodide react at room temperature to give white non-hygroscopic solids. The *X*-ray powder patterns of these products and their chemical behaviour are different from those of the starting material and also from that of trifluoromethylthiomercuric chloride. Indirect chemical analysis shows the reaction products to be 1 : 1 addition compounds $Hg(SCF_3)_2,Me_4NX$ (X = Cl or I). As we did not succeed in recrystallizing the addition compounds without partial decomposition, no direct chemical analysis was practicable. An *X*-ray phase study of the systems $Hg(SCF_3)_2$–Me_4NCl and $Hg(SCF_3)_2$–Me_4NI indicates that only the 1 : 1 compounds exist. The 1 : 1 addition compounds in the two systems are isomorphous.

Solutions of $Hg(SCF_3)_2,Me_4NI$

Concn. (10^{-4}M)	Molar conductivity obs.	Molar conductivity calc.
43·60	131·4	131·8
38·29	135·2	134·7
19·14	145·5	147·7
9·572	155·8	156·3
4·786	163·8	162·8
2·393	166·7	167·2
1·197	171·6	170·4
0·598	174·9	172·6
0·299	174·7	174·2

Solutions of $Hg(SCF_3)_2,Me_4NCl$

Concn. (10^{-4}M)	Molar conductivity obs.	Molar conductivity calc.
31·31	128·3	128·1
20·87	138·1	136·6
10·43	147·1	147·5
5·217	155·2	155·3
2·609	157·9	160·8
1·304	165·4	164·6
0·652	168·9	167·4
0·326	171·5	169·3

The compounds $Hg(SCF_3)_2,Me_4NCl$ and $Hg(SCF_3)_2,Me_4NI$ are readily soluble in acetone, yielding stable solutions which are strong electrolytes. The molar conductivites of dilute solutions ($4·4 \times 10^{-3}$ to 3×10^{-5}M) of $Hg(SCF_3)_2,Me_4NI$ in acetone at 22° can be expressed by $\lambda = 178 - 700\sqrt{c}$ (where c = molarity) within experimental accuracy (~1%) (see Table). The conductivities of solutions of mercuric iodide or bis(trifluoromethylthio)mercury of corresponding concentrations are much lower. On the other hand, the extrapolated molar conductivity at infinite dilution, $\lambda_0 = 178$, is significantly different from that for tetramethylammonium iodide, $\lambda_0 = 213·2$, at 22°. The latter value has been calculated from data given by Walden, Ulich, and Busch [2] by application of Stokes's

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[1] Emeléus and Lagowski, *J.*, 1959, 1497.

[2] Walden, Ulich, and Busch, *Z. phys. Chem.*, 1926, **123**, 429.

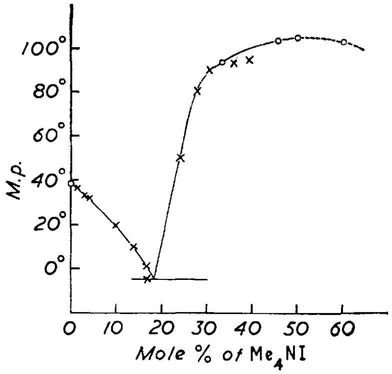
law which has been shown to be valid in this case.[2] These observations indicate that even in very dilute solutions $Hg(SCF_3)_2,Me_4NI$ is not dissociated into its components to an appreciable extent.

According to Onsager [3] the molar conductivities of completely ionized 1–1 electrolytes can be expressed by:

$$\lambda = \lambda_0 - \left(\frac{0{\cdot}821 \times 10^6}{(D_0T)^{3/2}} \cdot \lambda_0 + \frac{82{\cdot}394}{(D_0T)^{1/2}\eta_0}\right)\sqrt{c} \quad . \quad . \quad . \quad . \quad (1)$$

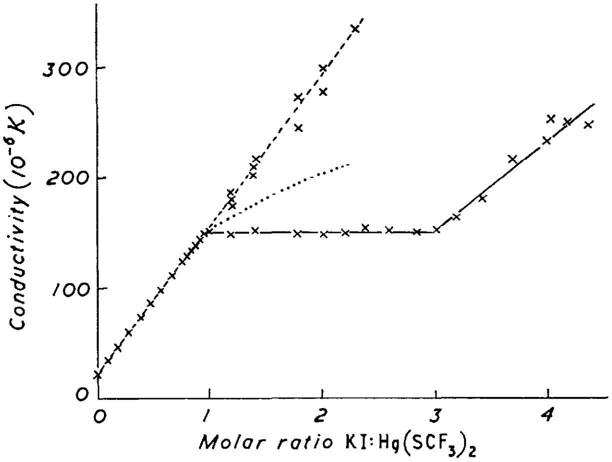
For other types of strong electrolytes the slope of the plot of λ as a function $\sqrt{c}$ should be several times larger, and it should also be larger if ion-pair formation is of importance. Substituting $\lambda_0 = 178$, $T = 295°$ K, $D_0 = 19{\cdot}37$ (interpolated from refs. 4 and 5), $\eta_0 = 0{\cdot}00324$ (interpolated from ref. 2) into equation (1), we get $\lambda = 178 - 675\sqrt{c}$, in good agreement with the observed function. Therefore, solutions of $Hg(SCF_3)_2,Me_4NI$ in acetone behave as strong 1–1 electrolytes. This observation, together with the fact that very similar results have been obtained for trialkylanilinium tri-iodomercurates(II),[6] indicates that the compound is to be regarded as tetramethylammonium iodobis(trifluoromethylthio)mercurate(II), $Me_4N^+[Hg(SCF_3)_2I]^-$.

FIG. 1. *M. p. curve of the system* $Hg(SCF_3)_2$–Me_4NI.



×, *By the " cumulative method "*; ○, *by the " preparative method."*

FIG. 2. *Conductometric titration of a* $Hg(SCF_3)_2$ *solution in acetone with* KI.



—— *Slow titration.* ---- *Fast titration.* . . . . *Constant speed.*

From data by Walden *et al.*[2] it is calculated that the equivalent conductivity of Me_4N^+ at 22°, $l_0 = 100{\cdot}2$; thus, we find $l_0 = 78$ for the $[Hg(SCF_3)_2I]^-$ ion. From these values the Stokes radii of Me_4N^+ and $[Hg(SCF_3)_2I]^-$ are computed as 2·52 Å and 3·25 Å respectively, which seem to be reasonable values.

Very much the same reasoning holds for dilute solutions of $Hg(SCF_3)_2,Me_4NCl$ in acetone. The observed molar conductivities at 22° can be expressed by $\lambda = 174 - 820\sqrt{c}$ (see Table). The conductivities of solutions of mercuric chloride, bis(trifluoromethylthio)-mercury and trifluoromethylthiomercuric chloride in acetone again are much lower, while for tetramethylammonium chloride $\lambda_0 = 202{\cdot}5$ is calculated from data by ref. 2. Substitution of $\lambda_0 = 174$, $T = 295°$ K, $D_0 = 19{\cdot}37$, $\eta_0 = 0{\cdot}00324$ in equation (1) yields: $\lambda = 174 - 667\sqrt{c}$. The fact that the observed slope of the plot of λ against $\sqrt{c}$ is somewhat greater than the theoretical might indicate that ion-pair formation is of some (though

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[3] Onsager, *Physik. Z.*, 1926, **27**, 388; 1927, **28**, 277.
[4] Åkerlöf, *J. Amer. Chem. Soc.*, 1932, **54**, 4125.
[5] Le Fèvre, *Trans. Faraday Soc.*, 1938, **34**, 1127.
[6] Cavell and Sugden, *J.*, 1930 2572.

minor) importance in this case. It appears, therefore, that the addition compound can be formulated as tetramethylammonium chlorobis(trifluoromethylthio)mercurate(II), $Me_4N^+[Hg(SCF_3)_2Cl]^-$. The observed value of $l_0 = 74$ at 22° C for the $[Hg(SCF_3)_2Cl]^-$ ion is equivalent to a Stokes radius of 3·4 Å.

Solid $Me_4N^+[Hg(SCF_3)_2Cl]^-$ decomposes at 131°, forming mercuric chloride and a liquid which decomposes slowly on further heating to form mercuric sulphide, tetramethylammonium fluoride, and volatile C–F–S compounds. The volatile products react with the glass walls of the reaction vessel, forming mainly carbonyl sulphide (*M*, 60·08), carbon disulphide (*M*, 76·14), and fluoroform (*M*, 70·02); among the minor constituents of the final volatile mixture bistrifluoromethyl sulphide (*M*, 170·09) or disulphide (*M*, 202·15) and silicon tetrafluoride (*M*, 104·09) were identified. The apparent molecular weight of the mixture was found to be 64. Pyrolysis of bis(trifluoromethylthio)mercury has been reported to yield mercuric fluoride and carbonyl sulphide, together with smaller amounts of carbon dioxide, bistrifluoromethyl sulphide, and silicon tetrafluoride; the volatile products are regarded as secondary products formed by reaction of thiocarbonyl fluoride with the reaction vessel.[7]

$Me_4N^+[Hg(SCF_3)_2I]^-$ melts sharply at 105°. On further heating, mercuric iodide separates from the melt which in turn decomposes slowly in the same way as described for the chloro-compound. Mixtures of bis(trifluoromethylthio)mercury and tetramethylammonium iodide containing up to 50 mole-% of the latter melt reversibly, but the shape of the melting point curve (Fig. 1) indicates that the 1 : 1 compound dissociates reversibly to some extent on melting. From melts containing about 25 mole-% of the iodide the 1 : 1 addition compound separates in long needles. Again, there is no indication of the existence of a second addition compound. Mixtures of bis(trifluoromethylthio)mercury and tetramethylammonium iodide containing more than 50 mole-% of the latter undergo irreversible chemical reactions before melting. By analogy with the course of the reactions between $[Hg(SCF_3)_2I]^-$ and I^- in acetone solution [8] the following reactions may be assumed to take place:

$$Me_4N^+[Hg(SCF_3)_2I]^- + Me_4NI \longrightarrow Me_4N^+[Hg(SCF_3)I_2]^- + Me_4NF + CSF_2$$
$$Me_4N^+[Hg(SCF_3)I_2]^- + Me_4NI \longrightarrow Me_4N^+HgI_3^- + Me_4NF + CSF_2$$

Indeed, tetramethylammonium fluoride has been identified in the product; the thiocarbonyl fluoride formed is unstable and attacks glass.[7]

The addition compounds $Me_4N^+[Hg(SCF_3)_2X]^-$ are soluble in water, but these solutions decompose with the formation of fluoride, carbonate, and sulphide; bis(trifluoromethylthio)mercury has been found to be hydrolysed in a similar manner.[9] Tetramethylammonium chloro- and iodo-bis(trifluoromethylthio)mercurate(II) are insoluble in ether, but they are partly decomposed by prolonged treatment with the boiling solvent. The decomposition products of the chloro-compound have been identified as trifluoromethylthiomercuric chloride and tetramethylammonium fluoride, so the reaction can probably be represented by

$$Me_4N^+[Hg(SCF_3)_2Cl]^- \longrightarrow HgCl{\cdot}SCF_3 + Me_4NF + CSF_2$$

Results of conductometric titrations of bis(trifluoromethylthio)mercury with potassium iodide in acetone solution are shown in Fig. 2. The electrical conductivity of the solution increases sharply on the addition of potassium iodide until a value of one is reached for the molar ratio KI : $Hg(SCF_3)_2$. Further addition of potassium iodide, however, gives rise to irreversible chemical reactions and the shape of the plot of conductivity against molar ratio KI : $Hg(SCF_3)_2$ is highly dependent on the speed of the titration. On slow titration the graph shows very pronounced breaks at molar ratios 1 : 1 and 3 : 1; between these limits the final conductivity is virtually independent of the ratio. The fast-titration plot is rather inaccurate because of extrapolation uncertainties; there may be a break at ratio 1 : 1,

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[7] Haszeldine and Kidd, *J.*, 1955, 3871.
[8] Jellinek, *Proc. Chem. Soc.*, 1959, 319.
[9] Pugh, personal communication.

but it certainly is not pronounced. When the titration is done at a constant speed, the plot is a slightly curved line lying between the two extremes; again, a sharp break is observed at molar ratio 1 : 1. This is taken to indicate the formation of $K^+[Hg(SCF_3)_2I]^-$ in solution.

The specific conductivity of a solution with a 1 : 1 ratio of potassium iodide and bis(trifluoromethylthio)mercury which is 10^{-3}M with respect to the mercury compound is found to be 146 × 10^{-6} at 22°. Applying Onsager's relation[1] to the data by Walden *et al.*[2] combined with our observations gives the conductivity of a 10^{-3}M-solution of $K^+[Hg(SCF_3)_2I]^-$ as 126·3 × 10^{-6} and that of a mixed solution of the two components of corresponding concentration as 181·2 × 10^{-6} at 22°. The reason for the discrepancy is not evident. In view of our observations on $Me_4N^+[Hg(SCF_3)_2I]^-$ solutions, partial dissociation of the iodobis(trifluoromethylthio)mercurate(II) ion in the potassium salt solution is hardly probable, as this would mean that the stability constant on the complex anion in acetone solution would be dependent on the cation present. The possibility that the break in the titration curve at molar ratio 1 : 1 does not indicate complex formation, but rather the completion of a substitution of the type $Hg(SCF_3)_2 + I^- \longrightarrow Hg(SCF_3)I + [SCF_3]^-$, can also be excluded because the trifluoromethyl sulphide ion has been found to be unstable under the experimental conditions and to disintegrate[8] into thiocarbonyl fluoride and fluoride ion with a half-life of the order of 0·5 hr. The fast titration curve mentioned above closely resembles that of mercuric iodide with potassium iodide in acetone; in the latter case an equilibrium $2HgI_3^- = HgI_2 + HgI_4^{2-}$ can be expected to take place in solution. A similar equilibrium, however, cannot be assumed in solutions of $[Hg(SCF_3)_2I]^-$, since the irreversible reactions which occur as soon as the molar ratio $KI : Hg(SCF_3)_2$ exceeds one show that the $[Hg(SCF_3)_2I_2]^{2-}$ ion is very unstable, if it exists at all, in acetone solution. A kinetic study of these reactions will be reported elsewhere.

EXPERIMENTAL

Preparation of $Me_4N^+[Hg(SCF_3)_2X]^-$ (X = Cl *or* I).—Bis(trifluoromethyl) disulphide was prepared by a slight modification[9] of the method described by Haszeldine and Kidd[10] and bis(trifluoromethylthio)mercury was prepared by the interaction of bis(trifluoromethyl) disulphide and mercury under the influence of ultraviolet light.[11] Finely powdered bis(trifluoromethylthio)mercury and tetramethylammonium chloride or iodide were mixed in molar proportions of 1·1 : 1·0. The mixture initially formed a paste which was homogenized. After some time the mixture solidified; it was heated at 50°, crushed, and homogenized several times. The product was cooled to room temperature, quickly washed three times with cold ether [which removes the excess of bis(trifluoromethylthio)mercury], and dried at 50°. For the chloro-compound the preparation was carried out in dry nitrogen, because of the hygroscopicity of the starting material.

The product was completely soluble in a small volume of acetone (tetramethylammonium chloride and iodide are only sparingly soluble in this solvent). From the weight of bis(trifluoromethylthio)mercury in the ether filtrate the composition of the product was found to be $Hg(SCF_3)_2,Me_4NX$; the yield was quantitative within 0·5%. When the preparation is carried out with an excess of tetramethylammonium halide, side reactions occur and the yield of the 1 : 1 addition compounds is considerably less.

X-Ray Powder Photographs.—These were taken in a Unicam camera of the Bradley–Bragg type with a radius of 19 cm.; nickel-filtered Cu-*K* radiation was employed.

Conductivity Measurements.—These were at 22° in cells of 5 and 10 ml. capacity. Resistances were measured with a Philips bridge (alternating current of 1000 Hz). The specific conductivity of the acetone used as a solvent was about 10^{-6}. (Specific conductivities are expressed in ohm^{-1} $cm.^{-1}$, molar conductivities in ohm^{-1} $cm.^2$ $mole^{-1}$.) For the conductometric titrations a 15·98 × 10^{-3}M-solution of potassium iodide in acetone was added by means of a calibrated Agla micrometer syringe to a 1·056 × 10^{-3}M-solution of bis(trifluoromethylthio)-mercury. Thus, the concentration of the mercury compound is almost exactly 10^{-3}M when the solute has the 1 : 1 ratio $Hg(SCF_3)_2 : KI$. The experimental points of the slow titration curve

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[10] Haszeldine and Kidd, *J.*, 1953, 3219.

[11] Brandt, Emeléus, and Haszeldine, *J.*, 1952, 2198.

were measured after the conductivity of the solution had become constant within experimental accuracy. When the final I : Hg ratio in the solution was smaller than 3 : 1, the measurements were performed about 20 hr. after addition of potassium iodide solution; when the ratio was larger than 3 : 1, not until about 80 hr. after the addition. Points of the fast titration plot were extrapolated from conductivity measurements shortly (1½, 2, 3, 4, and 5 min.) after addition of potassium iodide solution. The curves of the "titrations at constant speed" were determined by adding 0·05 ml. of potassium iodide solution to the previously mixed solution, measuring the conductivity after 2 min., adding another 0·05 ml. after a fixed time, etc. All conductivities are corrected for dilution to a standard concentration of 10^{-3}M with respect to the mercury compound, and for the conductivity of the pure solvent.

Melting-point Curve.—For the system $Hg(SCF_3)_2$–Me_4NI this was determined by the "cumulative method": a weighed quantity of the iodide was added to a solid mixture of the mercury compound and the iodide of known composition; the new mixture was completely melted, frozen again, and melted again. This last m. p. was plotted against composition. The cumulative method became less reliable for mixtures containing more than 30 mole-% of iodide; when more than 40 mole-% was present, overheating appeared to be unavoidable when homogenizing the mixture, and mercuric iodide was deposited. Therefore, in this range the "preparative method" was employed: for every m. p. determination a fresh mixture was used.

Decompositions.—Solid decomposition products were identified by qualitative microchemical tests, mercuric chloride and iodide also by their m. p., trifluoromethylthiomercuric chloride by its decomposition reaction at 128°, and mercuric sulphide also by the transformation of the brownish-black into the red modification. Thermal decomposition of the 1 : 1 addition compounds was studied under atmospheric pressure and *in vacuo*; both conditions gave the same solid products. Volatile products were identified only in the case for the vacuum-pyrolysis, by means of infrared absorption diagrams. The diagrams were recorded by a Perkin–Elmer Model 21 double-beam spectrometer and a Perkin–Elmer "Infracord" spectrometer with sodium chloride prisms.

We gratefully acknowledge encouragement and suggestions from Professor H. J. Emeléus, and support of the Netherlands Organization for Pure Research "Z.W.O." (F. J.) and a Marshall Scholarship (J. J. L.).

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[*Received, August* 21*st*, 1959.]