Thermal Decomposition of Di-t-butyl Sulphide–Mercury(II) Chloride

By **P. Biscarini** * and **L. Fusina**, Istituto di Chimica Fisica e Spettroscopia dell'Università, Viale Risorgimento 4, 40136 Bologna
G. D. Nivellini, Laboratorio di Spettroscopia Molecolare del C.N.R., Via Castagnoli 1, 40126 Bologna, Italy

Thermal decomposition of the 1 : 1 adduct of di-t-butyl sulphide and mercury(II) chloride has been investigated. The following products of decomposition were identified: mercury sulphide chloride, chloro-t-butylthiomercury(II), 2-methylpropene, hydrochloric acid, and t-butyl chloride. The reaction is first order in the adduct and a mechanism of intramolecular decomposition, involving interactions between aliphatic chains and the halogen atoms of mercury(II) chloride, has been hypothesized. The reactions of formation of chloro-t-butylthiomercury(II) and of its decomposition in the presence of mercury(II) chloride are also identified.

PREVIOUS investigations[1] showed the instability of the addition compounds between mercury(II) chloride and organic sulphides, or sulphoxides. Complexes of highly sterically hindered sulphides were found to be thermally unstable and the existence of a steric repulsion between the aliphatic chains of the ligand and the halogens bridging two mercury atoms was suggested.[1c] McAllan *et al.*[2] observed that on crystallization from ethanol, the mercury(II) chloride–ethyl t-butyl sulphide complex, $EtBu^tS,HgCl_2$, is decomposed partially to form t-butyl chloride and chloroethylthiomercury(II).

The behaviour of the complex between mercury(II) chloride and a highly sterically hindered sulphide, $[Bu^t_2S,HgCl_2]_2$, is here investigated in order to identify the mechanism of interaction between the aliphatic chains of the ligands and the halogens of mercury(II) chloride and also to ascertain how mercury(II) chloride can contribute to the cleavage of the carbon–sulphur bond. This should help to explain why, with mercury(II) chloride, organic sulphides do not give substitution compounds but only unstable addition compounds.

EXPERIMENTAL

Preparation.—The di-t-butyl sulphide–mercury(II) chloride 1 : 1 adduct, was prepared as described.[1c]

Chloro-t-butylthiomercury(II), Bu^tSHgCl.—$[Bu^t_2S,HgCl_2]_2$ (6·6 g) was suspended in ethanol (60 ml), brought to the boil and quickly filtered. The residual solid was treated several times with new portions of ethanol. From the filtered solutions a white product separates slowly, which does not melt below 260 °C and is slightly soluble in ethanol, identified as chloro-t-butylthiomercury(II) (0·5 g, 9·7%) (Found: C, 14·3; H, 2·2; S, 9·7; Hg, 63·0; C_4H_9SHgCl requires, C, 14·7; H, 2·8; S, 9·83; Hg, 61·7%). The i.r. spectrum in Nujol mulls in the range 600—200 cm^{-1} shows many bands: 557vs, 435m, 379m, 360s, 337m, 323m, 275vs, and 237m cm^{-1}.

From the treatments with ethanol a pale yellow solid identified as the mercury sulphide chloride, $Hg_3S_2Cl_2$ (2·7 g, 45·6%), was obtained as residue.[1c] The i.r. spectrum in Nujol mulls in the range 3500—200 cm^{-1} shows an intense and broad band at 319 cm^{-1} with two shoulders at 340 and 288 cm^{-1}.

When decomposition of $[Bu^t_2S,HgCl_2]_2$ is carried out in the presence of mercury(II) chloride (10 mol of $HgCl_2$ for 1 mol of the complex), only mercury sulphide chloride was obtained. By heating the complex for 2—3 h it is impossible to isolate chloro-t-butylthiomercury(II).

Decomposition of Chloro-t-butylthiomercury(II).—Bu^tSHgCl (0·1 g, 0·3 mmol) dissolved in ethanol (60 ml) and boiled for 2 h remained unchanged. Addition to the boiling solution of mercury(II) chloride (0·08 g, 0·3 mmol) causes immediate separation of $Hg_3S_2Cl_2$ (0·08 g, 71%). The reaction is complete in 3 h. During the reaction both conductivity and acidity of the solution increase strongly.

Decomposition of Di-t-butyl Sulphide–Mercury(II) *Chloride 1 : 1 Adduct.*—Decomposition of $[Bu^t_2S,HgCl_2]_2$ was performed by warming (a), the solution during the complex formation; (b), an ethanol solution of the complex; (c), the complex in presence of an excess of $HgCl_2$; (d), the complex suspended in carbon tetrachloride; (e), the complex in the absence of solvent. The same products, in different amounts, were obtained.

(a) Di-t-butyl sulphide (9·0 g, 0·06 mol) was added to a boiling ethanol solution of mercury(II) chloride, (16·6 g, 0·06 mol in 150 ml). A pale yellow precipitate forms immediately. After 10 h of heating and stirring, insoluble $Hg_3S_2Cl_2$ (12·85 g; S, 56·7; Hg, 85·1; Cl, 28·4%) was obtained. The volatile products were removed during the reaction by means of a weak nitrogen stream. The gases, passing through two traps cooled to 0 and −70 °C respectively, separate ethanol, di-t-butyl sulphide (0·7 g, 7·8%), and t-butyl chloride, (1·06 g, 9·0% on initial chlorine), b.p. 760 mmHg 52—53 °C, identified by g.l.c. and n.m.r. spectrum (CCl_4,Me_4Si, $\delta = 1·59$ p.p.m.). The residual gases were bubbled through a solution of bromine in acetic acid and trapped finally in liquid air. The contents of the last traps were collected and the acetic acid solution, diluted with water, was neutralized with solid sodium carbonate. The oil which separated was extracted with ether, washed with sodium thiosulphate (10%) and dried over sodium sulphate. From distillation 1,2-di-bromo-2-methylpropane, (3·1 g, 11·7%), b.p. 20 mmHg 62—64 °C, was obtained. The n.m.r. spectrum (CCl_4,Me_4Si) shows two signals at $\delta = 1·9$ p.p.m. (6H, $2CH_3$) and $\delta = 3·9$ p.p.m. (2H, s, CH_2).

The presence of 2-methylpropene and t-butyl chloride was confirmed by cooling at liquid nitrogen temperature all the gases developed from the decomposition reaction. The n.m.r. spectrum (CCl_4,Me_4Si) of the condensed products shows the characteristic signals[3] of 2-methylpropene, $\delta = 1·68$ p.p.m. (6H, $2CH_3$) and $\delta = 4·58$ p.p.m. (2H, CH_2) and of t-butyl chloride, $\delta = 1·59$ p.p.m.

During the decomposition the acidity of the solution increases strongly as well as the conductivity. This can be ascribed to the formation of hydrochloric acid. The

---

[1] (*a*) P. Biscarini and G. D. Nivellini, *J. Chem. Soc.* (*A*), 1969, 2206; (*b*) P. Biscarini, L. Fusini, and G. D. Nivellini, *ibid.*, 1971, 1128; (*c*) P. Biscarini, L. Fusina, and G. D. Nivellini, *Inorg. Chem.*, 1971, **10**, 2564.

[2] D. T. McAllan, T. V. Cullum, R. A. Dean, and F. A. Fidler, *J. Amer. Chem. Soc.*, 1951, **73**, 3627.

[3] E. B. Whipple, I. H. Goldstein, and L. Mandell, *J. Amer. Chem. Soc.*, 1960, **80**, 3010.

reaction solution, after the separation of $Hg_3S_2Cl_2$, was diluted with water. The oil which separated was extracted with n-pentane and a small quantity of white solid chloro-t-butylthiomercury(II) (0·22, 1% on sulphide) was filtered off. The extracts were dried over Na_2SO_4 and distilled give di-t-butyl sulphide undecomposed (2·4 g, 26·7%), b.p. 151—153 °C.

Evaporation of a small portion of the residual aqueous solution showed the presence of undecomposed adduct (1·22 g, 4·7% of the initial sulphide). In a second portion the presence of unreacted $HgCl_2$ was shown by titration[4] (2·35 g, 14·1% of the initial mercury salt).

A third portion of the same solution showed the presence of $5·2 \times 10^{-2}$ hydrogen ions, by titration (NaOH, methyl orange), and the presence of $6·9 \times 10^{-2}$ halogen ions (56·2% of initial chlorine), by precipitation as AgCl with HNO_3 and $AgNO_3$.

The products of reactions (b), (c), and (e) were separated and identified as described for reaction (a). In reaction (c), an excess of mercury(II) chloride (33·3 g, 0·12 mol), 22·46 g of $Hg_3S_2Cl_2$, were obtained (S, 99·2; Hg, 74·6; Cl, 24·8%). In the solution were found the residue (7·85 g, 23·85%) of $HgCl_2$ and 0·079 mol of HCl, 32·4% on initial chlorine. From the gases developed during the reaction t-butyl chloride (3·56 g, 15·22% on initial chlorine), and 1,2 dibromo-2-methylpropane (3·7 g, 14·2%) were isolated. In this reaction chloro-t-butylthiomercury(II) was not found.

Kinetic Measurements.—The reaction was investigated conductometrically in absolute ethanol at 80·0 ± 0·1 °C (concn. of complex in the range $0·4—1·0 \times 10^{-2}$M). $[Bu^t_2S,HgCl_2]_2$, freshly prepared, was dissolved in cold ethanol in a volumetric flask and an aliquot of the solution was transferred to a glass tube, containing the conductivity cell (constant 0·55 cm^{-1}). At zero time the closed tube was plunged into a thermostat at 80 °C and the conductivity was noted at various times.

Spectra.—I.r. spectra were recorded as described previously.[1a]

RESULTS AND DISCUSSION

Unlike all other complexes between organic sulphides and mercury(II) chloride, which are prepared using boiling ethanol solutions, the di-t-butyl sulphide–mercury(II) chloride 1:1 adduct can be obtained only at room temperature, owing to its easy decomposition. In fact this occurs slowly in the air, or quickly on warming the adduct and its solutions. As products of decomposition 2-methylpropene, t-butyl chloride, hydrochloric acid, chloro-t-butylthiomercury(II) and mercury sulphide chloride together with unreacted di-t-butyl sulphide and mercury(II) chloride were identified. The following mechanism for the decomposition, based on the products obtained and on the conditions used, is suggested:

$$[Bu^t_2S,HgCl_2]_2 \overset{\text{EtOH}}{\rightleftharpoons} 2Bu^t_2S + 2HgCl_2 \qquad (1)$$

$$[Bu^t_2S,HgCl_2]_2 \longrightarrow 2(CH_3)_2C{:}CH_2 + 2HCl + 2Bu^tSHgCl \qquad (2)$$

$$2Bu^tSHgCl + HgCl_2 \longrightarrow Hg_3S_2Cl_2 + 2(CH_3)_2C{:}CH_2 + 2HCl \qquad (3)$$

$$(CH_3)_2CH{:}CH_2 + HCl \longrightarrow (CH_3)_3CCl \qquad (4)$$

The di-t-butyl sulphide–mercury(II) chloride adduct dissociates in ethanol solution after equation (1). The existence of this equilibrium was noticed always in solutions of complexes between organic sulphides and mercury(II) chloride.[1c] Osmotic measurements in absolute ethanol at 37 °C provided a value of molecular weight of the adduct, **338 ± 2** (theoretical for a complete molecular dissociation **208·9**), which agrees with values obtained for other complexes with mole ratio 1 : 1.[1c] Therefore this complex exists in ethanol solution as a partially dissociated dimer. The degree of dissociation, $\alpha = 0·48$, is constant within the experimental errors in the concentration range used for measurements ($0·4—1·1 \times 10^{-2}$M).

The participation in the decomposition reaction of the undissociated adduct [equation (2)], is demonstrated by the identification of the reaction products. The formation of 2-methylpropene from decomposition of di-t-butyl sulphoxide is known,[5] but a reaction involving a breaking of a C–S bond in t-butyl sulphide has never been reported previously. In the present reaction, mercury(II) chloride is the agent favouring the cleavage of the carbon–sulphur bond.

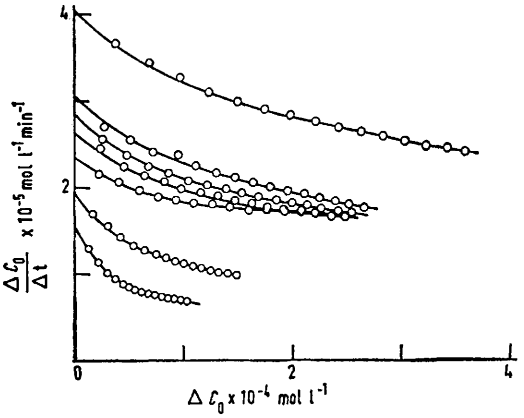

FIGURE 1 Determination of initial rates for decomposition of $[Bu^t_2S,HgCl_2]_2$ by extrapolation. Initial concentration of the adduct in the range $0·4—1·0 \times 10^{-2}$M

The progressive formation of hydrochloric acid was evidenced by means of acidity and conductivity measurements, which allowed reaction (2) to be followed kinetically. However, hydrochloric acid develops also from reaction (3), and reacts with 2-methylpropene to form t-butyl chloride [equation (4)]. To avoid interference by consecutive reactions (3) and (4), initial reaction rates were measured to investigate the order in the complex. For each run, from the measured conductivity values, the changes of concentration of hydrochloric acid and hence of complex (ΔC_0) at various times were determined graphically. Plotting the rates of disappearance of the complex, ($\Delta C_0/\Delta t$), versus ΔC_0, and, extrapolating to $\Delta C_0 = 0$, the initial reaction rates of runs with various initial concentrations of complex were deter-

---

[4] M. Vecera, J. Gasparic, D. Snobl, and M. Jurecek, *Coll. Czech. Chem. Comm.*, 1956, **21**, 1284.

[5] L. Bateman, M. Cain, T. Colclough, and J. I. Cunneen, *J. Chem. Soc.*, 1962, 3570; T. Colclough and J. I. Cunneen, *Chem. and Ind.*, 1960, 626.

mined (see Figure 1). A plot of $-\log (\Delta C_0/\Delta t)_0$ *vs.* $-\log C_0$, yields a straight line (correlation coefficient 0·996), with slope 1·01 ± 0·04 (see Figure 2). C_0 is the actual initial concentration of undissociated complex, calculated from the initial concentration C_i by using the degree of dissociation at 37 °C. It is impossible to determine α at 80 °C, owing to fast decomposition of the complex by warming. A different value of α_{80° does not affect the slope of the straight line of Figure 2 because all the values of $\log C_0 = \log C_i + \log (1 - \alpha_{37^\circ})$ will be shifted by the constant amount $\log (1 - \alpha_{37^\circ})/(1 - \alpha_{80^\circ})$ if α_{80° is approximately constant in the range of concentrations considered. Reaction (2) is thus first order in the adduct.

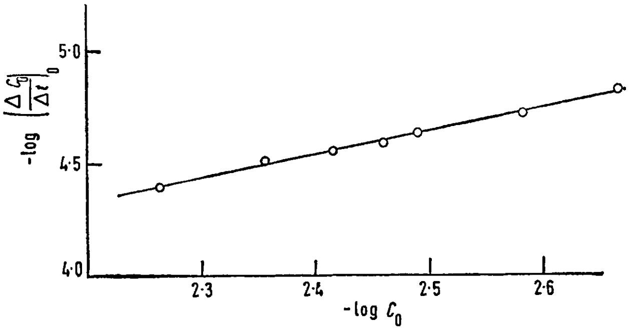

FIGURE 2 Plot of —log of initial rate versus —log of initial concentration of adduct: correlation coefficient 0·996, slope 1·01 ± 0·04

From these results it is reasonable to suppose that the reaction involves an intramolecular mechanism, with a six-membered cyclic transition state (see Figure 3), followed by a breaking of a C–S bond, the elimination of hydrochloric acid, and the formation of 2-methylpropene and chloro-t-butylthiomercury(II).

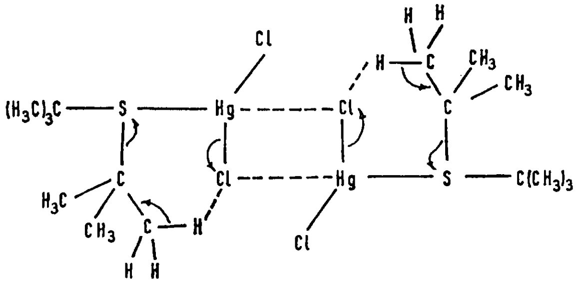

FIGURE 3 Scheme of decomposition of $[\mathrm{Bu^t}_2\mathrm{S,HgCl_2}]_2$

The interaction between the alkyl chains of the sulphide and the halogen atoms of mercury(II) chloride, suggested from these results, is also supported by the value, 288 $\mathrm{cm^{-1}}$, of the i.r. stretching frequency of $\mathrm{HgCl_2}$ group bonded to di-t-butyl sulphide. The frequency shift, $\Delta\nu = 84\ \mathrm{cm^{-1}}$, from the ν_3 of free mercury(II) chloride, if correlated to the basicity of the sulphide, $\sigma^* = -0{\cdot}600$, is very low compared to those observed for the other 1 : 1 adducts.[1a] This indicates that the attack of di-t-butyl sulphide on mercury(II) chloride induces a modification on the hybridization of mercury and hence a weakening of Hg–Cl bonds smaller than that expected on the basis of the high Lewis basicity.

Chloro-t-butylthiomercury(II) was isolated by carefully controlling the heating times, and separating it before the decomposition proceeds to mercury sulphide chloride (equation 3). In fact this compound also is thermally unstable, however its decomposition occurs only in presence of mercury(II) chloride. If chloro-t-butylthiomercury(II) is warmed without mercury(II) chloride it remains unchanged, while it cannot be isolated when di-t-butyl sulphide–mercury(II) chloride adduct is decomposed in presence of an excess of mercury(II) chloride. Therefore we may hypothesize that reaction (3) occurs through the formation of an addition compound with mercury(II) chloride: the high Lewis basicity of sulphur atom in chloro-t-butylthiomercury(II) should allow the formation of this compound. Compounds of the type $m\mathrm{RSHgCl,HgCl_2}$ with $m = 1, 2,$ and 3 have been isolated and identified.[6,7] The nucleophilic attack of thiol on mercury(II) chloride should give rise to an interaction between the alkyl groups and the halogen atom of mercury(II) chloride. At the same time the formation of the new S–Hg bond causes a lowering of basicity on the sulphur atom, thus favouring the cleavage of C–S bond, the elimination of hydrochloric acid, and the formation of 2-methylpropene and mercury sulphide chloride. The presence, between the products of decomposition, of t-butyl chloride and the low yield in 2-methylpropene support the existence of a reaction (equation 4), between hydrochloric acid and the olefin formed from reactions (2) and (3).

These results indicate that, under particular conditions, when the steric hindrance of alkyl chains is so remarkable as to determine an electrostatic interaction between hydrogens of alkyl group and the bridging chlorine atom, decomposition of complex may take place. In any case a repulsive interaction between the alkyl groups and the halogen atoms will prevent the stabilization of the sulphide in a transitional position such as to allow it to replace the halogen atom on mercury. Moreover the halogen atom, being at the same time bonded to two mercury atoms is not sufficiently displaced to determine its removal. Owing to this situation the charge density on mercury remains high and the S–Hg bond becomes very weak.

It is clear that the formation of a substitution compound with a stable metal–sulphur bond and *sp* hybridization on mercury is prevented both for sterical and electronic reasons, and from these the high instability of the adducts between mercury(II) chloride and organic sulphides originates.

We wish to thank Prof. C. Zauli for helpful comments.

[1/1719 *Received, 20th September,* 1971]

---

[6] F. Challenger and A. A. Rawlings, *J. Chem. Soc.*, 1937, 868.
[7] S. Blackburn and F. Challenger, *J. Chem. Soc.*, 1938, 1872.