142. *The Interaction of Hexamethyldisiloxane with Aluminium Halides and with Iodine.*

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Aluminium chloride and bromide do not form stable adducts with hexamethyldisiloxane, but cleavage of a silicon–oxygen bond occurs with formation of trimethylmonohalogenosilanes and trimethylsiloxyaluminium dihalides. The latter are stable crystalline compounds at room temperature: the dichloride melts at 87—88° and can be distilled *in vacuo*. Both dihalides undergo disproportionation on further heating, into trimethylhalogenosilanes and aluminium oxyhalide.

Iodine forms a purple solution in hexamethyldisiloxane, which behaves as a non-donor solvent.

Emeléus and his co-workers have shown [1] that the electron-donor activity of oxygen and sulphur in dialkyl ethers is absent in their disilyl analogues and that when boron trifluoride or trichloride reacts with 1 : 1′-dimethyl-, 1 : 1′ : 2 : 2′-tetramethyl-, or hexamethyldisiloxane, no stable adduct is formed but cleavage of the Si–O–Si bond occurs, with formation of the methylhalogenosilane and the methylsiloxyboron dihalide. The latter decomposes spontaneously to the methylhalogenosilane, boron trihalide, and boron trioxide.

We have found that a somewhat similar reaction, $(Me_3Si)_2O + \frac{1}{2}Al_2Cl_6 = Me_3SiCl + Me_3Si{\cdot}O{\cdot}AlCl_2$, occurs between hexamethyldisiloxane and aluminium chloride, and correspondingly for the bromide. No stable adduct is formed, but the corresponding trimethylsiloxyaluminium dihalides are much more stable than the boron analogues. The chloride, in particular, forms well-defined crystals and can be distilled in a good vacuum without decomposition: heating under atmospheric pressure, however, leads to decomposition into trimethylchlorosilane and aluminium oxychloride. The bromide is less stable than the chloride: the crystals do not melt, but decompose at 100° into trimethylbromosilane and aluminium oxybromide.

Experimental

A commercial "Silicone Fluid: 0·65 centipoise," which was almost pure hexamethyldisiloxane, was dried (P_2O_5) and fractionated: b. p. 100·3°/768 mm. Aluminium chloride and bromide were prepared from high-purity aluminium wire and hydrogen chloride and bromine, respectively. Both halides were purified by five or six vacuum-sublimations and stored in sealed ampoules.

Reaction of aluminium chloride. An ampoule containing about 15 g. was opened under dry nitrogen and transferred to 50 c.c. of hexamethyldisiloxane. Several hours' shaking at room temperature produced little dissolution. The flask containing the mixture was then immersed in a bath at 40° and shaken occasionally: complete dissolution occurred within $\frac{3}{4}$ hr. On cooling and storage overnight, large (*ca.* several mm.) thin plates were deposited. The mother-liquor was decanted and the crystals were dried *in vacuo* [Found: H, 4·8; C, 19·4; Al, 14·7; Cl, 38·2. $Me_3Si{\cdot}O{\cdot}AlCl_2$ requires H, 4·8; C, 19·3; Al, 14·3; Cl, 38·0%]. Fractionation of the mother-liquor gave, in addition to unchanged hexamethyldisiloxane, a major fraction consisting of trimethylchlorosilane, b. p. 57·2°/764 mm. [Found: H, 8·5; C, 33·1; Cl, 32·9. Calc. for Me_3SiCl: H, 8·4; C, 33·2; Cl, 32·7%].

The crystals of $Me_3Si{\cdot}O{\cdot}AlCl_2$ were quite stable at room temperature and when sealed in an evacuated tube melted at 87—88° and could be distilled from end to end of the tube at about 145—150°. In air, hydrolysis occurred rapidly and the crystals disintegrated to a white powder. When they were heated at atmospheric pressure, decomposition occurred according to the equation

$$Me_3Si{\cdot}O{\cdot}AlCl_2 = Me_3SiCl + AlOCl$$

the trimethylchlorosilane distilling off and leaving a residue which was chiefly amorphous aluminium oxychloride (Found: Al, 31·0; Cl, 42·3. Calc. for AlOCl: Al, 33·9; Cl, 45·3%).

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[1] Emeléus, MacDiarmid, and Maddock, *J. Inorg. Nuclear Chem.*, 1955, **1**, 194; Emeléus and Onyszchuk, *J.*, 1958, 604.

This decomposition into trimethylchlorosilane and aluminium oxychloride rather than into aluminium oxide and chloride is in contrast to the reaction with boron halides.

Reaction of aluminium bromide. About 15 g. of the bromide were added to 50 c.c. of hexamethyldisiloxane. As there was an immediate exothermic reaction, the flask was cooled in ice and shaken until dissolution was complete. On removal of about one third of the liquid under vacuum, a crop of small (*ca.* 1 mm.) white crystals of $Me_3Si{\cdot}O{\cdot}AlBr_2$ was obtained [Found: H, 3·7; C, 11·9; Br, 56·7. $Me_3Si{\cdot}O{\cdot}AlBr_2$ requires H, 3·3; C, 13·0; Br, 57·9%].

The other reaction product was similarly identified as trimethylbromosilane. Failure to cool the mixture during dissolution led to immediate partial decomposition and no crystalline product was obtained.

The $Me_3Si{\cdot}O{\cdot}AlBr_2$ did not melt in an evacuated sealed tube, but decomposed at about 100° with evolution of trimethylbromosilane (b. p. 78°). The solid residue was aluminium oxybromide (Found: Al, 22·3; Br, 64·5. Calc. for AlOBr : Al, 22·0; Br, 65·0%). When the oxybromide was heated at 100° under vacuum for 2 hr., slight decomposition occurred, as indicated by a small white sublimate. At 180° and heating for a further 2 hr. this developed into a crystalline sublimate of aluminium bromide, indicating, as previously suggested,[2] that a disproportionation $6AlOBr \longrightarrow Al_2Br_6 + 2Al_2O_3$ takes place under these conditions. The disproportionation was not complete, much bromine being retained, probably mechanically, in the solid phase.

These reactions between hexamethyldisiloxane and aluminium halides provide a very convenient method for the preparation, from readily available materials and in good yield, of trimethyl-chloro- and -bromo-silanes, and also of nearly pure AlOBr.

The lack of donor activity of the oxygen atom in methyl-siloxanes has been attributed in part to the ability of the silicon atom to use the vacant 3*d* orbitals in the formation of π-type bonds with the oxygen.[1, 5] Further evidence of this lack of donor activity is given by the behaviour of iodine in hexamethyldisiloxane. The colour of iodine solutions can [3] be correlated with the electron-donor character of the solvent, being purple, as in the vapour, in solvents such as carbon tetrachloride and hexane, and brown in donor solvents such as alcohols, ethers, esters, and olefins. We have also examined the absorption spectrum of iodine in hexamethyldisiloxane: the colour is purple, with a maximum $\varepsilon = 850$ at 518 mμ, which is very similar to that in carbon tetrachloride.[4]

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[2] Fairbrother and Frith, *J.*, 1953, 2975.

[3] Fairbrother, *Nature*, 1947, **160**, 87; *J.*, 1948, 1051.

[4] Gmelin, " Handb. d. anorg. Chem.," [8], **8**, 116.

[5] Stone and Seyferth, *J. Inorg. Nuclear Chem.*, 1955, **1**, 112.