

The initial step of the reaction between aluminium chloride and siloxanes involves coordination of aluminium chloride to oxygen of the siloxanes, to give a complex:



This type of adduct has been isolated from the reaction of boron trifluoride or trichloride with hexamethyldisiloxane at low temperature.⁵ During the reaction between aluminium chloride and siloxanes, in the conditions of the present work, adducts of this type may undergo rapid decomposition by cleavage of Si-O-Si bonds.

According to Andrianov the compound of formula $\text{C}_8\text{H}_{24}\text{Al}_3\text{Cl}_5\text{O}_6\text{Si}_4$, first prepared by Hyde,⁶ is obtained by intramolecular cyclisation of the product of reaction of aluminium chloride with siloxanes. Further cleavage of Si-O-Si bonds in this compound by aluminium chloride may give dichloro(chlorodimethylsiloxy)aluminium, in agreement with our finding that aluminium chloride reacts with Andrianov's compound to form siloxyaluminium dichloride. However, the compound $\text{C}_8\text{H}_{24}\text{Al}_3\text{Cl}_5\text{O}_6\text{Si}_4$ is not necessarily an intermediate when an excess of aluminium chloride reacts with siloxanes.

Reaction of $\alpha\omega$ -dichlorosiloxanes with aluminium chloride proceeds similarly:



The reaction between dichloro(chlorodimethylsiloxy)aluminium and octamethylcyclotetrasiloxane is analogous to that of dichlorotrimethylsiloxyaluminium and cyclic siloxanes.¹ Both reactions lead to the compound $\text{C}_8\text{H}_{24}\text{Al}_3\text{Cl}_5\text{O}_6\text{Si}_4$, showing that $\text{O}\cdot\text{AlCl}_2$ groups also are reactive towards Si-O-Si bonds, although to a smaller extent than is aluminium chloride. In fact, reactions with siloxyaluminium dichlorides proceed at a temperature of 170–180°, but with aluminium chloride at ~120°.

It is known⁷ that in the presence of strong bases and acids, Lewis acids, and Friedel-Crafts catalysts, Si-O-Si bonds of siloxanes may be broken and re-formed continually, until the system reaches equilibrium of cyclic and linear siloxanes. Thus in the reaction between aluminium chlorides and siloxanes a continuous cleavage and re-formation of Si-O-Si bonds, together with the formation of new Si-O-Al bonds, would be expected. As a consequence intermediates are likely to be more numerous than usual.

Thermal decomposition of the product $\text{C}_8\text{H}_{24}\text{Al}_3\text{Cl}_5\text{O}_6\text{Si}_4$ may be interpreted by this mechanism. The aluminium chloride present in the Andrianov's complex may provoke further cleavage of Si-O-Si bonds, leading to a structure of alternating silicon and aluminium atoms and to the formation of chlorosilanes.

Chlorotrimethyl- and dichlorodimethyl-silane on thermal decomposition of the compound $\text{C}_8\text{H}_{24}\text{Al}_3\text{Cl}_5\text{O}_6\text{Si}_4$ may be formed either in a condensation or in a disproportion of the dichlorodimethylsilanes.⁸

The product $[\text{Me}_2\text{Si}\cdot\text{O}\cdot\text{AlClO}]_n$ is not a polymer of high molecular weight: viscosity measurements and cryoscopic determination indicate a molecular weight of only about 1000.

EXPERIMENTAL

Reaction (A): Aluminium Chloride with Octamethylcyclotetrasiloxane; AlCl_3 : Me_2SiO = 1 : 3.—This reaction was carried out by the method of Zhdanov *et al.*² The purified product had m. p. 153–154°, d^{20} 1.45 ± 0.03 (Found: Al, 13.5, 13.9, 13.2; Cl, 29.3, 29.3. Calc. for $\text{C}_8\text{H}_{24}\text{Al}_3\text{Cl}_5\text{O}_6\text{Si}_4$: Al, 13.8; Cl, 30.2%).

Reaction (B): Aluminium Chloride with Polydimethylsiloxanes; AlCl_3 : Me_2SiO = 1 : 3.—Polydimethylsiloxanes were prepared by hydrolysis of dichlorodimethylsilane. The volatile products were eliminated by vacuum distillation. The reaction with aluminium chloride was carried out as in (A) above, *i.e.*, at 120° for 20 hr. Polydimethylsiloxane (24.34 g.) and

⁵ H. J. Emeléus and M. Onyszchuk, *J.*, 1958, 604; E. Wiberg and U. Krueker, *Z. Naturforsch.*, 1953, 8b, 610.

⁶ J. F. Hyde, U.S.P. 2,645,654/1953 (*Chem. Abs.*, 1954, 48, 7050).

⁷ D. T. Hurd, *J. Amer. Chem. Soc.*, 1955, 77, 2998.

⁸ R. O. Sauer and E. M. Hadsell, *J. Amer. Chem. Soc.*, 1948, 70, 3590.

aluminium chloride (15.07 g.) gave, after purification, 16.31 g. of a crystalline compound $C_8H_{24}Al_3Cl_5O_6Si_4$ (Found: Al, 12.6; Cl, 29.1%), having the m. p. and X-ray diffraction spectrum of the powder obtained in reaction (A).

Reaction (C): Aluminium Chloride with Octamethylcyclotetrasiloxane; $AlCl_3 : Me_2SiO = 1 : 1$.—Octamethylcyclotetrasiloxane (24.75 g.) and aluminium chloride (44.71 g.) were heated under reflux for 20 hr. at 120° , after which the mixture was distilled. Dichlorodimethylsilane (7.50 g.) was obtained as a first fraction (identified by its infrared spectrum and Cl analysis). A second fraction (29.5 g.) which solidified on the walls of the condenser was distilled under a vacuum; it crystallized from benzene as white needles, m. p. $54-56^\circ$ which were dried under a vacuum (the compound was extremely unstable to moisture and when kept in a desiccator became yellow) (Found: C, 11.8; H, 4.2; Al, 12.9; Cl, 50.0; Si, 12.9. $C_2H_6AlCl_3OSi$ requires C, 11.6; H, 2.9; Al, 13.0; Cl, 51.3; Si, 13.5%). A molecular-weight determination by cryoscopic method in benzene gave M 383 (calc. for dimer, 415). A glassy distillation residue resembled the amorphous product obtained in reaction (H).

Reaction (D): Aluminium Chloride and the Compound $C_8H_{24}Al_3Cl_5O_6Si_4$.—Aluminium chloride (2.06 g.) was placed in a break-seal ampoule with the compound $C_8H_{24}Al_3Cl_5O_6Si_4$ (3.16 g.). The ampoule was sealed under a vacuum and kept in a thermostat at 120° for 40 hr. After this the ampoule was connected with a trap, the system evacuated, the seal was broken, and the volatile fractions were distilled by heating the ampoule at 170° . A glassy amorphous residue remained. Two fractions were recovered: (a) 0.420 g. of a volatile liquid which was condensed in the trap (cooled by liquid nitrogen); this was identified as dichlorodimethylsilane by infrared spectrum and Cl analysis; (b) 2.00 g. of a solid substance sublimed on the walls as white needles, identified as $C_2H_6AlCl_3OSi$ by Cl analysis and m. p.

Reaction (E): Aluminium Chloride with 1,5-Dichlorohexamethyltrisiloxane; $AlCl_3 : Me_2SiO = 1 : 1$.—1,5-Dichlorohexamethyltrisiloxane was obtained by distillation of the $\alpha\omega$ -dichloromethylsiloxanes formed as in reaction (A) (Found: Cl, 28.2. Calc. for $C_6H_{12}Cl_2O_2Si_3Cl$, 25.6%). This compound (17.08 g.) and aluminium chloride (15.21 g.) were heated at 120° for 20 hr. After fractionation, as in experiment (C), dichlorodimethylsilane (7.61 g.) and a crystalline compound (ca. 20 g.) were formed. The latter compound, when recrystallized from benzene, had m. p. $54-55^\circ$ (Found: Cl, 49.9%).

Reaction (F): $ClMe_2Si \cdot O \cdot AlCl_2$ and $(Me_2SiO)_4$.—The compound $ClMe_2SiOAlCl_2$ (3.88 g.), obtained as in (C), and octamethylcyclotetrasiloxane (2.96 g.) were heated at 170° for 20 hr. Afterwards the following products were obtained by distillation: (a) Me_2SiCl_2 (0.54 g.); (b) $\alpha\omega$ -dichlorosiloxanes and unchanged octamethylcyclotetrasiloxanes (1.02 g. together); (c) a crystalline material (3.89 g.) which sublimed on the cold walls of the apparatus; crystallized on cooling, from benzene it had m. p. $153-154^\circ$. The X-ray diffraction spectrum of the powder was identical with that of $C_8H_{24}Al_3Cl_5O_6Si_4$ as prepared in (A).

Reaction (G): Thermal Decomposition of Compound $C_2H_6AlCl_3OSi$.—The compound $ClMe_2Si \cdot O \cdot AlCl_2$ (2.06 g.), obtained as in reaction (C), was heated at 170° for 20 hr. The products were fractionated and gave (a) Me_2SiCl_2 (0.64 g.); (b) $AlCl_3$ (0.56 g.); (c) a glassy residue (0.86 g.); its composition, calculated by difference, is close to that of the glassy product of reaction (H).

Reaction (H): Thermal Decomposition of Compound $C_8H_{24}Al_3Cl_5O_6Si_4$.—Various break-seal ampoules were filled with the compound $C_8H_{24}O_6Si_4Al_3Cl_5$ (2-3 g.), sealed under a vacuum, placed in a thermostat at 225° for up to 120 hr., and then connected to a vacuum and evacuated, the seals being broken. Three fractions were obtained by heating the ampoules at 170° : a volatile fraction, mainly Me_2SiCl_2 and Me_3SiCl ; undecomposed product, sublimed on the cold walls; and a glassy, transparent, colourless residue.

The decomposition increases with heating time, and after 120 hr. is nearly complete. The glassy residue is soluble in benzene, insoluble in cyclohexane, and easily hydrolysed in moist air. The ratio Si : Al : Cl approaches 1 : 1 : 1. Viscosimetric measurement in benzene of various samples gave a low values of the intrinsic viscosity ($[\eta]$ 0.02). *M* ca. was ~ 1000 (cryoscopic method in benzene).

We thank Professors V. Caglioti and G. Sartori for suggestions and discussions. One of us (A. S.) received an A.I.E.A. Fellowship.

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[Received, February 17th, 1964.]