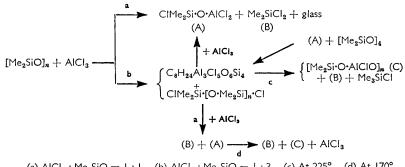
1012. Reactions of Aluminium Chloride with Dimethylsiloxanes.

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Aluminium chloride reacts with an excess of cyclic and linear dimethylsiloxanes to give a compound C₈H₂₄Al₃Cl₅O₆Si₄ (I); with an excess of aluminium chloride, a product CIMe₂Si·O·AlCl₂ (II) is formed. Compound (I) is also formed in the reaction of (II) with octamethylcyclotetrasiloxane. Thermal decomposition of compounds (I) and (II) gives dichlorodimethylsilane and a glassy compound $(Me_2Si \cdot O \cdot AlCl \cdot O -)_n$, where n < 10. Compound (II) is also formed when aluminium chloride reacts with compound (I) or αω-dichlorodimethylsiloxanes.

During a study of silicon-aluminium compounds we re-examined some reactions between aluminium chloride and dimethylsiloxanes. Andrianov and his co-workers 2 showed that aluminium chloride reacts with dimethylcyclosiloxanes to give a crystalline substance, $C_8H_{24}Al_3Cl_5O_6Si_4$, and $\alpha\omega$ -dichlorodimethylsiloxanes.

We have found that altering the ratio of the reactants may lead to different products. Aluminium chloride and an excess of dimethylsiloxanes give a crystalline compound C₈H₂₄Al₃Cl₅O₆Si₄ (I), in agreement with the statement of Andrianov et al. From an excess of aluminium chloride, dichloro(chlorodimethylsiloxy)aluminium, ClMe₂Si·O·AlCl₂ (II), dichlorodimethylsilane, and a glassy residue (Me₂Si•O•AlCl•O)_n, are obtained. Compound (II) is also obtained on reaction of aluminium chloride with the product $C_8H_{24}Al_3Cl_5O_6Si_4$ and with $\alpha\omega$ -dichlorodimethylsiloxanes. The compound $ClMe_2Si \cdot O \cdot AlCl_2$ may in turn react with octamethylcyclotetrasiloxane to form a material, C₈H₂₄Al₃Cl₅O₆Si₄. This last, when heated at 225°, gives dichlorodimethylsilane, chlorotrimethylsilane, and the glassy residue (Me₂Si·O·AlCl·O)_n. The reactions are summarised in the annexed scheme.



(a) $AICI_3 : Me_2SiO = I : I$. (b) $AICI_3 : Me_2SiO = I : 3$. (c) At 225°. (d) At 170°.

Analyses and molecular weights suggested that the crystalline compound from aluminium chloride and siloxanes was dichloro(chlorodimethylsiloxy)aluminium. From cryoscopic measurements in benzene a molecular weight corresponding to a dimer was found. Analogous results indicating association of two molecules through chlorine atoms has been found for aluminium chloride in benzene.3 This product has not been prepared before but analogous chlorides, R₃Si·O·AlCl₂ where R = Me and Et have been described.⁴ They are crystalline, melt at <100°, are soluble in ether, benzene, carbon tetrachloride and hexane, and are easily hydrolysed. They may be prepared by reaction of aluminium chloride with silyl ethers R₃Si·O·SiR₃.

¹ C. Ercolani, A. Camilli, and L. De Luca, preceding Paper.

² A. A. Zhdanov, K. A. Andrianov, and A. A. Bogdanov, Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk, 1961, 1261.

³ F. Nagy, O. Dobis, G. Litvan, and J. Toth, Magyar Kém. Folybirat, 1960, 66, 134 (Chem. Abs., 1961, 55, 15,086).
N. F. Orlov, Doklady Akad. Nauk S.S.S.R., 1957, 114, 1033.

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:

$$A|C|_3 + (R_2Si)_2O \longrightarrow \begin{array}{c} C1 \cdots A|C|_2 \\ \vdots \\ -R_2Si \cdots O \cdot SiR_2 - \end{array}$$

This type of adduct has been isolated from the reaction of boron trifluoride or trichloride with hexamethyldisiloxane at low temperature. 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 C₈H₂₄Al₃Cl₅O₆Si₄, first prepared by Hyde, 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 $C_8H_{24}Al_3Cl_5O_6Si_4$ is not necessarily an intermediate when an excess of aluminium chloride reacts with siloxanes.

Reaction of aw-dichlorisiloxanes with aluminium chloride proceeds similarly:

The reaction between dichloro(chlorodimethylsiloxy)aluminium and octamethylcyclotetrasiloxane is analogous to that of dichlorotrimethylsiloxy) aluminium and cyclic siloxanes.1 Both reactions lead to the compound C₈H₂₄Al₃Cl₅O₆Si₄, showing that O·AlCl₂ 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 \sim 120°.

It is known 7 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 C₈H₂₄Al₃Cl₅O₆Si₄ 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 $C_8H_{24}Al_3Cl_5O_6Si_4$ may be formed either in a condensation or in a disproportion of the dichlorodimethylsilanes.8

The product $[Me_2Si \cdot O \cdot AlClO]_n$ 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. $153-154^{\circ}$, d^{20} 1.45 ± 0.03 (Found: Al, 13.5, 13.9, 13.2; Cl, 29.3, 29.3. Calc. for $C_8H_{24}Al_3Cl_5O_6Si_4$: 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. Kruerke, Z. Naturforsch, 1953, **8**b, 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.

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aluminium chloride (15·07 g.) gave, after purification, $16\cdot31$ g. of a crystalline compound $C_8H_{24}Al_3Cl_5O_6Si_4$ (Found: Al, $12\cdot6$; Cl, $29\cdot1\%$), having the m. p. and X-ray diffraction spectrum of the powder obtained in reaction (A).

Reaction (C): Aluminium Chloride with Octamethylcyclotetrasiloxane; AlCl₃: Me₂SiO = 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 dessicator 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 fraction were recovered: (a) 0·420 g. of a volatile liquid 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; AlCl₃: Me₂SiO = 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 C₆H₁₂Cl₂O₂Si₃:Cl, 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° (Found: Cl, 49·9%).

Reaction (F): ClMe₂Si·O·AlCl₂ and (Me₂SiO)₄.—The compound ClMe₂SiOAlCl₂ (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) Me₂SiCl₂ (0·54 g.); (b) αω-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°. 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 C₂H₆AlCl₃OSi.—The compound ClMe₂Si·O·AlCl₂ (2·06 g.), obtained as in reaction (C), was heated at 170° for 20 hr. The products were fractionated and gave (a) Me₂SiCl₂ (0·64 g.); (b) AlCl₃ (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 Me₂SiCl₂ and Me₃SiCl; 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 intrisic viscosity ($[\eta] 0.02$). $M ca. was \sim 1000$ (cryoscopic method in benzene).

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