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Abstract

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THE DISPROPORTIONATION REACTION—A NEW METHOD FOR THE SYNTHESIS OF ORGANOSILICON POLYMERS. SYNTHESIS OF POLYPHENYLENESILANES

In organoelement chemistry, the disproportionation reaction is widely used in syntheses of various monomers (1-3). Meanwhile, this interesting reaction can be used for the synthesis of high-molecular-weight compounds.

Our experiments showed that, on heating bis-(dimethylethoxysilyl)benzene with catalytic amounts of certain nucleophilic reagents, evolution of dimethyldiethoxysilane and formation of polydimethylphenylenesilane are observed.

The reaction proceeds according to the scheme:

$$C_2H_5O{-}Si(CH_3)_2\,C_6H_4\,Si(CH_3)_2{-}OC_2H_5 \xrightarrow[230^\circ]{KOH} (CH_3)_2Si(OC_2H_5)_2 + [-Si(CH_3)_2\,C_6H_4-]_n\,.$$

Depending on the extent to which the reaction has proceeded, it is possible to isolate oligomers with different numbers of units. Thus, upon disproportionation of bis-(dimethylethoxysilyl)benzene with cleavage of 0.5 mole of dimethyldiethoxysilane per mole of starting substance, after hydrolysis in a weakly acidic medium the dimer was isolated

$$HO{-}Si(CH_3)_2\,C_6H_4\,Si(CH_3)_2\,C_6H_4\,Si(CH_3)_2{-}OH$$

—a crystalline substance with m.p. 132°. This indicates the stepwise character of polymer formation.

If the reaction is carried out so that the amount of dimethyldiethoxysilane evolved is close to the theoretical amount, polymers are obtained which are readily soluble in organic solvents and have reduced viscosity up to 0.4.

The disproportionation reaction proceeds not only in the presence of KOH, but also under the action of alkali-metal alcoholates, amines, etc. The interaction of nucleophilic reagents with bis-(alkylalkoxysilyl)benzenes probably proceeds by an ionic mechanism:

$$RO{-}Si(CH_3)_2{-}C_6H_4{-}Si(CH_3)_2{-}OR + (OR)^- \rightleftharpoons [RO{-}Si(CH_3)_2{-}C_6H_4\,:]^- + (CH_3)_2Si(OR)_2$$

$$[ROSi(CH_3)_2{-}C_6H_4\,:]^- + ROSi(CH_3)_2{-}C_6H_4{-}Si(CH_3)_2{-}OR \rightleftharpoons RO{-}$$

$$-\left[Si(CH_3)_2{-}C_6H_4\right]_2{-}Si(CH_3)_2{-}OR + (OR)^- \quad \text{etc.}$$

Such a reaction mechanism is consistent with the fact that the use of tri-, tetra-, and hexaalkoxy derivatives of disilylbenzenes ultimately leads to the formation of spatial polymers.

The disproportionation reaction, with the aim of using it for the synthesis of polymers, as well as its mechanism, is being studied by us using other examples.

Experimental Part

Disproportionation of 1,4-bis-(dimethylethoxysilyl)benzene. Into a four-necked 100-ml flask equipped with a stirrer, thermometer, straight condenser, and tube for the introduction of nitrogen were placed 28.2 g (0.1 mole) of 1,4-bis-(dimethylethoxysilyl)benzene and 0.28 g (1%) of powdered KOH. The reaction mixture was heated at 230° with stirring and with a stream of dry nitrogen freed from oxygen until the required amount of condensate had separated; the condensate was collected in a weighed graduated receiver. A total of 14.25 g (96.3%) of condensate was obtained with n_D^{20} 1.3858; content of C_2H_5O groups, 57.4%; Si 18.52%. (For $(CH_3)_2Si(OC_2H_5)_2$, n_D^{20} 1.3860; Si 18.7%.) The residue in the flask was dissolved in 20 ml of benzene, neutralized with concentrated acetic acid, then filtered, the solvent was distilled off, and the material was dried at 70° and a residual pressure of 2-3 mm Hg to constant weight. A total of 13.9 g (99.8%) of a brown resin with a softening temperature of 43° was obtained. The reduced viscosity of the solution was η_{red} 0.32. The polymer is soluble in aromatic hydrocarbons and insoluble in petroleum ether and alcohols. Elemental composition:

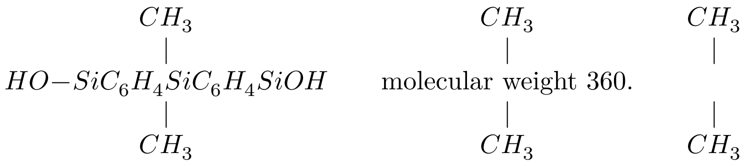
$\vert(CH_3)_2SiC_6H_4\vert$	Found, %:	C 69.05; 69.30; H 7.98; 8.2; Si 19.84; 20.11
	Calculated, %:	C 71.6; H 7.46; Si 20.9

On cleavage of 0.495 mole of $(CH_3)_2Si(OC_2H_5)_2$ per mole of starting monomer, a light-yellow viscous liquid was obtained. On hydrolysis of its ether solution with 5% aqueous acetic acid at 30°, a partially crystalline mass formed; after recrystallization from a fivefold amount of hot benzene, crystals with m.p. 132°

were isolated (yield 42%). Molecular weight (ebullioscopically in benzene) 322; elemental composition:

Found, %: C 58.82; 59.12; H 8.18; 8.43; Si 23.25; 22.94

For the dimer



$HO-\underset{CH_3}{\overset{CH_3}{Si}}C_6H_4\underset{CH_3}{\overset{CH_3}{Si}}C_6H_4\underset{CH_3}{\overset{CH_3}{Si}}OH$

molecular weight 360.

Calculated, %: C 60; H 7.77; Si 23.3

Disproportionation of $(CH_3)_2(OC_2H_5)SiC_6H_4Si(OC_2H_5)_3$. The reaction was carried out by the method described, at a temperature of 200°. A total of 34.2 g (0.1 mole) of monomer and 0.5 g of powdered KOH were taken. A total of 14.49 g of condensate distilled off, with n_D^{20} 1.3846. On distillation of the condensate with a 200-mm-high dephlegmator, the following fractions were isolated: I. 74-80°; weight 0.78 g; n_D^{20} 1.3794. II. 98-115°; weight 10.11 g; n_D^{20} 1.3830; C_2H_5O 59.57; 59.97%; Si 18.01; 17.85%. III. 115-160°; weight 2.94 g; n_D^{20} 1.3830; C_2H_5O 79.48; 79.80%; Si 14.09; 13.99%. On the basis of the analytical data it may be assumed that fraction III contains ~70% dimethyldiethoxysilane. The total amount of $(CH_3)_2Si(OC_2H_5)_2$ separated was thus 12.16 g, i.e., 82% of theory. The resin obtained was partially (~10%) insoluble in benzene. After neutralization and removal of the solvent, η_{red} 0.19. Yield of polymer, 27.1 g (98.7%). Elemental analysis of the polymer:

Found, %: C 59.79; 59.85; H 7.80; 7.71; Si 16.82; 17.05

For a polymer of composition $[(CH_3)SiC_6H_4]_{0.2}\,[(C_2H_5O)_2SiC_6H_4]_{0.8}$ $(C_{9.6}H_{13.2}SiO_{1.6})$. Calculated, %: C 63.2; H 7.25; Si 15.38.

Disproportionation of $(CH_3)(OC_2H_5)_2SiC_6H_4Si(OC_2H_5)_2CH_3$.

1. For the reaction, 25.7 g (0.075 mole) of the starting monomer was taken. The reaction was carried out as indicated above, in the presence of 1.5% freshly prepared sodium ethylate. The reaction began at 195°. A total of 13.29 g (74.7%) of condensate was distilled off, with n_D^{20} 1.3868; d_4^{20} 0.8950. Ethoxy-group content, 73.2%; Si 15.45%. (For $(CH_3)Si(OC_2H_5)_3$: n_D^{20} 1.3861; d_4^{20} 0.8955; Si 15.75%.) In the flask there remained 12.4 g of a brown, infusible and insoluble mass, which swells strongly in benzene. Elemental analysis, %: C 58.14; H 5.59; 6.16; Si 17.79; 16.88.

Fig. 1. Kinetics of the disproportionation reaction. **I** $-(CH_3)_2(OC_2H_5)SiC_6H_4Si(CH_3)_2OC_2H_5$, 200°, 1% KOH; **II** $-C_2H_5O(CH_3)_2SiC_6H_4Si\cdot(CH_3)_2OC_2H_5$, 230°, 1% KOH;

Fig. 1. Kinetics of the disproportionation reaction. I – $(CH_3)_2(OC_2H_5)SiC_6H_4Si(CH_3)_2OC_2H_5$, 200°, 1% KOH; II – $C_2H_5O(CH_3)_2SiC_6H_4Si \cdot (CH_3)_2OC_2H_5$, 230°, 1% KOH; III – $(C_2H_5O)_2 \cdot CH_3SiC_6H_4SiCH_3(OC_2H_5)_2$, 230°, 1.5% C_2H_5ONa; IV – $(C_2H_5O)_3SiC_6H_4Si(OC_2H_5)_3$, 240°, 1% KOH

Figure 1: Fig. 1. Kinetics of the disproportionation reaction. I –$(CH_3)_2(OC_2H_5)SiC_6H_4Si(CH_3)_2OC_2H_5$, 200°, 1% KOH; II –$C_2H_5O(CH_3)_2SiC_6H_4Si \cdot (CH_3)_2OC_2H_5$, 230°, 1% KOH; III – $(C_2H_5O)_2 \cdot CH_3SiC_6H_4SiCH_3(OC_2H_5)_2$, 230°, 1.5% C_2H_5ONa; IV – $(C_2H_5O)_3SiC_6H_4Si(OC_2H_5)_3$, 240°, 1% KOH

III –$(C_2H_5O)_2 \cdot CH_3SiC_6H_4SiCH_3(OC_2H_5)_2$, 230°, 1.5% C_2H_5ONa; **IV** – $(C_2H_5O)_3SiC_6H_4Si(OC_2H_5)_3$, 240°, 1% KOH.

2. A total of 25.7 g (0.075 mole) of the starting compound was charged. The reaction temperature was 220°. A total of 8.63 g (0.483 mole) of condensate was distilled off, with n_D^{20} 1.3872; d_4^{20} 0.895. A resin with η_{sp} 0.12 was obtained. Upon hydrolysis with 5% acetic acid in ether solution, an infusible and insoluble product was formed. Elemental analysis of the polymer:

Found, %: C 60.35; 59.86; H 7.09; 6.73; Si 17.29; 17.97
For the elemental unit $|(C_2H_5O)CH_3SiC_6H_4|$.
Calculated, %: C 64.7; H 7.32; Si 17.07

Disproportionation of $(C_2H_5O)_3SiC_6H_4Si(OC_2H_5)_3$. To 20.1 g (0.05 mole) of $(C_2H_5O)_3SiC_6H_4Si(OC_2H_5)_3$, 2% sodium ethylate was added, and the mixture was heated at 230°. A total of 9.4 g of condensate distilled off, with n_D^{20} 1.3835; content of C_2H_5O groups 85.53%; Si 13.4%. (For $(C_2H_5O)_4Si$: n_D^{20} 1.3830; C_2H_5O 86%; Si 13.4%.) A total of 10.53 g of brown, infusible and insoluble resin was obtained.

The kinetics of the disproportionation reaction is presented in Fig. 1.

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REFERENCES

1. H. Wagner, D. L. Bailey et al., *Ind. and Eng. Chem.*, **45**, 367 (1953).
2. D. L. Bailey, U. S. Pat., 2 723 983, 2 723 984, 2 723 985, 1955.
3. A. N. Pines, R. E. Godlewsky, U. S. Pat., 2 851 474, 1958; *Chem. Abstr.*, **53**, 13056 (1959).

Note: Figure translations are in progress. See original paper for figures.