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Catalysis of triethoxysilane disproportionation with oligoethylene glycol ethers

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Abstract

Oligoethylene glycol ethers catalyze the disproportionation of triethoxysilane to tetraethoxysilane and silane both at room temperature and upon heating. For comparison, the CsF-catalyzed disproportionation of triethoxysilane has been examined and found more facile. Mechanisms of the reactions involving formation of hypervalent silicon complexes have been discussed.

Keywords: Silane; Triethoxysilane; Tetraethoxysilane; Disproportionation; Oligoethylene glycol ethers; Hypervalent silicon complexes

1. Introduction

Although the disproportionation of trialkoxysilanes in the presence of various homogeneous and heterogeneous catalysts was a subject of many investigations (see Ref. [1]), this reaction keeps being actively studied [2–14] due to its practical value since silane, a disproportionation product, is used for the production of high purity silicon. From the theoretical point of view, this process contributes to a better understanding of hypervalence of silicon [13,14], which has attracted much attention in the last two decades [15–21].

Recently, we have found [22,23] that oligoethylene glycol ethers, including divinyl ethers, catalyze the homodehydrocondensation of poly(methylhydrosiloxane) with the evolution of hydrogen and the formation of Si–Si bonds. The reaction was rationalized via intermediate hexacoordinate complexes formed from siloxane and oligoethylene oxide moieties.

In this work, new data on the catalysis of hydrosilane reactions by oligoethylene glycol ethers, namely, on their ability to catalyze triethoxysilane disproportionation, are presented.

2. Results and discussion

The disproportionation of triethoxysilane to tetraethoxysilane and silane under the action of oligoethylene glycol ethers, such as dimethyl and divinyl ethers of triethylene glycol or divinyl ether of heptaethylene glycol, proceeds at ambient temperature. Thus, in the presence of an equimolar amount of one of the above mentioned divinyl ethers, 50% conversion of triethoxysilane is reached in 85–90 days. In the case of dimethyl ether of triethylene glycol, the same conversion is attainable in 110 days. A two-fold decrease in the ether concentration results in a 30–40% conversion of triethoxysilane for the same period, whereas the use of a two-fold excess of dimethyl or divinyl ether of triethylene glycol allows a 70–75% conversion to be attained.

As observed in [22], at higher temperature, the homodehydrocondensation of poly(methylhydrosiloxane) with oligoethylene glycol ethers was slowing down, which was rationalized in terms of dissociation of weak silane–catalyst complexes. Therefore, the same might be expected in this case. Instead, at 97–100 °C the reaction significantly accelerates. Thus, when equimolar mixtures of triethoxysilane with divinyl ether of triethylene glycol, divinyl ether of heptaethylene glycol or dimethyl ether of triethylene glycol are heated for 11 h, the conversion of triethoxysilane to tetraethoxysilane

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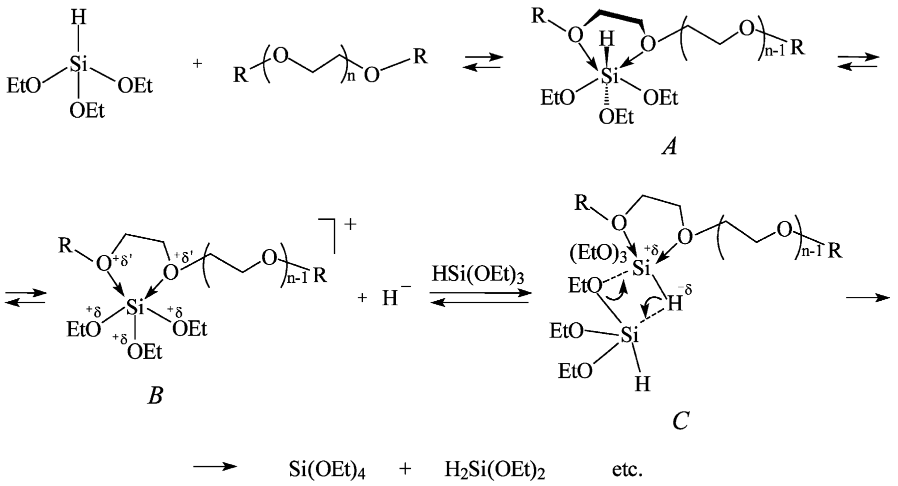
Table 1
Disproportionation of triethoxysilane to tetraethoxysilane with oligoethylene glycol ethers

Ether	$(EtO)_3SiH$:ether (mol)	Temperature (°C)	Time	$(EtO)_3SiH$ conversion (%) [a]
Triethylene glycol dimethyl ether	1:1	Room	110 days	48
	2:1	Room	110 days	30
	1:2	Room	110 days	69
	1:1	97–100	11 h	50
	1:1.8	97–100	11 h	75
Triethylene glycol divinyl ether	1:1	Room	90 days	49
	2:1	Room	90 days	34
	1:2	Room	90 days	75
	1:1	97–100	11 h	43
Heptaethylene glycol divinyl ether	1:1	Room	85 days	51
	2:1	Room	85 days	41
	1:1	97–100	11 h	60

[a] Conversion is the average of those determined by ^{29}Si-NMR and GLC analysis of the reaction mixture.

and silane is 43, 60 and 50%, respectively. When the molar portion of triethylene glycol dimethyl ether is 1.8 (for 1 mol of triethoxysilane), the conversion increases to 75%. Some other representative results are given in Table 1.



R = Me, n = 3; R = CH_2=CH, n = 3; R = CH_2=CH, n = ~7.

It is likely that the first reaction stage, as in the case of poly(methylhydrosiloxane) homodehydrocondensation under the action of oligoethylene glycol ethers [22,23], is the formation of intermolecular complex *A* with the participation of silicon and oxygen atoms of the ethylene glycol unit, in which the silicon atom is hexacoordinated [15–21]. This makes the Si–H bond weaker and thus more prone to dissociation. Due to the possibility of positive charge redistribution over the five oxygen atoms, a dissociation leading to siliconium cation *B* and, correspondingly, hydride ion, seems probable. Further, these two ions can take part in disproportionation: hydride ion replaces the ethoxy group in the next triethoxysilane molecule, whereas siliconium cation *B* accepts the ethoxide ion to afford tetraethoxysilane. It is more likely that these are concerted processes occurring as a bimolecular reaction via transition state of type *C*. The diethoxysilane thus formed participates further in a similar exchange with triethoxysilane to convert to ethoxysilane, which, likewise, finally is transformed to silane.

$$HSi(OEt)_3 + H_2Si(OEt)_2 \rightarrow Si(OEt)_4 + H_3SiOEt$$

$$HSi(OEt)_3 + H_3SiOEt \rightarrow Si(OEt)_4 + SiH_4$$

This mechanism is also supported by the fact that alkoxide ions coordinate readily to organyloxysilanes to give stable derivatives [19–21], such as $K^+[HSi(OR)_4]^-$

(R = Et, *i*-Pr, Ph) [24,25], $K^+[H_2Si(OR)_3]^-$ (R = Et, *i*-Pr) [25], $[K, 18\text{-crown-6}]^+[PhSi(OCH_2CF_3)_4]^-$ [26], for example.

For comparison, the triethoxysilane disproportionation was carried out in the presence of CsF. As known, fluoride anion exhibits a strong silicon atom affinity [19,21], which seems to be responsible for the catalytic effect of potassium fluoride in the triethoxysilane disproportionation [14]. At the same time to our knowledge, CsF has been never used in this reaction, though the triethoxysilane–CsF system was often employed for the reduction of carbonyl compounds as a hydride ion donor [19,21]. Despite the fact that pentacoordinate hydridosilicates were also assumed to be intermediates in such a reduction [19,21], the authors reported no disproportionation of triethoxysilane.

Since cesium fluoride is insoluble in triethoxysilane, the disproportionation rate of the latter strongly depends on stirring. Thus, at room temperature in the presence of 2 mass% of CsF, the full conversion of triethoxysilane to tetraethoxysilane is reached within a week without and for 24 h with stirring. Heating of the reaction mixture to 63–65 °C upon stirring reduces the reaction time to 9 h, the evolved silane being often exploded even with small amounts of triethoxysilane (1 mmol) and under argon blanket.

As far as pentacoordinate monofluorosilicates do not tend to give hexacoordinate species with the second fluoride anion [21], the pentacoordinated complex *D* might be considered as a first probable intermediate for the CsF-catalyzed disproportionation of triethoxysilane. The catalytic exchange with the ethoxy group and hydride ion between two triethoxysilane molecules may occur in dimeric hexacoordinate intermediate *E*.

To conclude, oligoethylene glycol ethers are weaker catalysts of triethoxysilane disproportionation compared with CsF, that indicates their lower activity as ligands in the formation of hypercoordinate silicon complexes.

3. Experimental

3.1. General

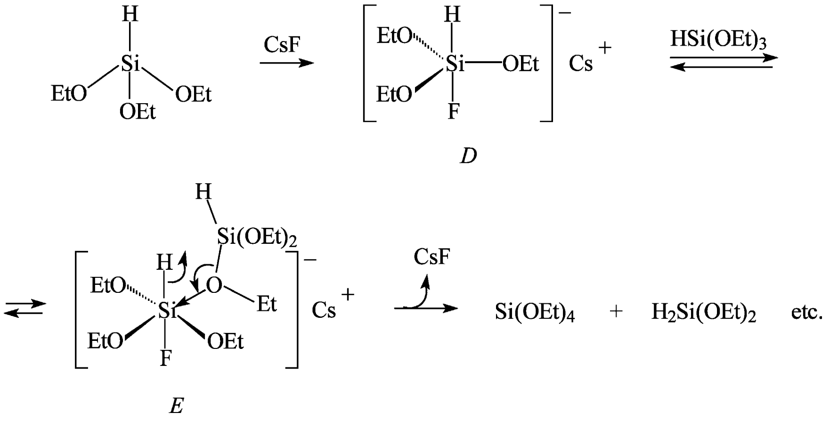
IR spectra were recorded on a Specord IR-75 spectrometer in thin film. ^1H- and ^{29}Si-NMR spectra were measured on a Bruker DPX 400 instrument (400.1 and 79.5 MHz, respectively) in $CDCl_3$ solutions, HMDS as an internal standard. Analyses of the reaction mixtures were performed using GLC on a LCM-80 instrument (thermal conductivity detector, carrier gas: helium (2 l h^{-1} consumption), 3000 × 3 mm column, liquid phase: Siloxane DS-550, 5% on Chromaton N-AW-HMDS, analysis temperature: 90 °C).

All experiments were carried out under argon atmosphere.

Oligoethylene glycol divinyl ethers were prepared by vinylation of the corresponding glycols with acetylene in the superbase system KOH–DMSO [27]. Triethoxysilane and dimethyl ether of triethylene glycol are commercial products (Aldrich and Merck, respectively).

3.2. Disproportionation of triethoxysilane in the presence of triethylene glycol divinyl ether

A mixture of 1.64 g (10 mmol) of triethoxysilane and 2.02 g (10 mmol) of triethylene glycol divinyl ether (reactants are soluble in each other) was placed in a glass flask, filled with argon and sealed with a rubber septum. The evolving silane volume was periodically measured by pushing-out of a 2-ml syringe piston. The reaction was also controlled by GLC, IR and ^{29}Si-NMR spectroscopy. A total of 28 ml of the gas was collected after 90



days. The mixture of tri- and tetraethoxysilane (ca. 1:1, 1.08 g total) was separated from triethylene glycol divinyl ether by distillation under reduced pressure (10 mmHg). The ratio of silanes was determined using GLC and also by ratio of signals at −58 (triethoxysilane) and −82 ppm (tetraethoxysilane) in the ^{29}Si-NMR spectrum. Formation of any side products was not observed.

The runs with different quantities of this divinyl ether at room temperature, as well as experiments in the presence of other ethers of oligoethylene glycol, including those upon heating, were carried out in an analogous way.

3.3. Disproportionation of triethoxysilane in the presence of cesium fluoride

In a typical procedure, triethoxysilane (1.64 g, 10 mmol) and CsF powder (0.03 g, 2 mass%) were placed under Ar into a glass vial equipped with a small Teflon stirring bar and a rubber septum. The evolution of silane from the stirred mixture was monitored analogous as above. In these runs, during measurements of the evolved gas volume, it often exploded in the syringe or inflamed at the needle tip. After 24 h, the evolution of gas stopped (total amount 55 ml, 98%). In the ^{29}Si-NMR spectrum of the reaction mixture there was no signal of triethoxysilane at −58 ppm, though, according to GLC, 3% of this silane remained unreacted (conversion 97%).

The experiments at 63–65 °C were carried out analogously (when the procedure was altered and an attempt was made to collect the gas over the water layer, the securing flask blew up even though the whole system was filled with argon). Evolution of the gas thus stopped after 9 h (triethoxysilane conversion 95%).

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