

The Disproportionation of Dimethyldialkoxysilanes Catalyzed by Iodine Monobromide

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Synopsis. Iodine monobromide is an extremely effective catalyst for the redistribution of alkoxy groups on silicon atoms in dimethyldialkoxysilanes. The equilibrium constants of these reactions were determined at 40 °C by means of gas chromatography. Assuming that the reaction intermediate is the dative form of a dimethyldialkoxysilane-iodine monobromide complex, a mechanism of the reaction was proposed.

Although numerous examples of redistribution reactions in organosilicon compounds have been reported,^{1–3)} only a few studies concerning alkoxy-alkoxy exchange are found in the literature.^{4–8)} In these studies, the quantitative determination of the equilibria of the following reaction systems has been made by means of GLPC:

Tetramethoxysilane–Tetraethoxysilane^{6,8)}

Methyltrimethoxysilane–Methyltriethoxysilane⁷⁾

Dimethyldimethoxysilane–Dimethyldiethoxysilane⁷⁾

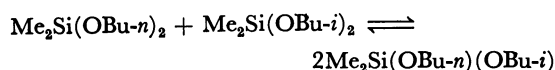
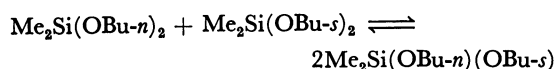
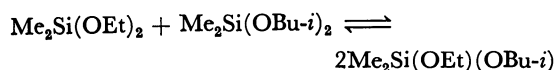
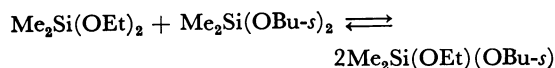
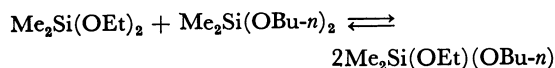
These reactions were carried out under rather severe conditions in the absence of a catalyst. Thus, to reach equilibrium the reaction mixtures were heated for 4 d at 150 °C,⁶⁾ 2 d at 120 °C,⁸⁾ or 7 d at 150 °C.⁷⁾ Consequently, the equilibrium data of such reactions at ordinary temperatures have not been available.

In the course of our studies of alkoxy-silane-iodine complexing, we noticed that iodine or interhalogen compounds catalyzed alkoxy-alkoxy exchange, and that iodine monobromide was an especially favorable catalyst for the disproportionation of alkylalkoxysilanes. In the presence of iodine monobromide, the redistribution equilibrium was readily attained at the ambient temperature, and the equilibrium constants were determined by means of gas chromatography.

Results and Discussion

Redistribution Equilibria in Dimethyldialkoxysilanes.

The following dimethyldialkoxysilane-systems were investigated at (40.0 ± 0.1) °C:



Both forward and reverse reactions proceeded in the

presence of iodine monobromide. In most cases, the composition of the reaction mixture became constant within a few hours; the equilibrium constant was then evaluated from the composition. The values thus obtained for reactions from both sides agreed very well with each other; the results are summarized in Table 1.

TABLE 1. EQUILIBRIUM CONSTANTS OF THE DISPROPORTIONATION OF DIMETHYLDIALKOXY-SILANES CATALYZED BY IODINE MONOBROMIDE AT (40.0 ± 0.1) °C

$$\text{Me}_2\text{Si}(\text{OR})_2 + \text{Me}_2\text{Si}(\text{OR}')_2 \rightleftharpoons 2 \text{Me}_2\text{Si}(\text{OR})(\text{OR}')$$

$$K = [\text{Me}_2\text{Si}(\text{OR})(\text{OR}')]^2 / \{[\text{Me}_2\text{Si}(\text{OR})_2][\text{Me}_2\text{Si}(\text{OR}')_2]\}$$

Substituent		K (Forward reaction)	K (Reverse reaction)	K (Mean)
OR	OR'			
OEt	OBu- <i>n</i>	4.17 ± 0.04	4.18 ± 0.02	4.17 ± 0.03
OEt	OBu- <i>s</i>	4.91 ± 0.03	4.88 ± 0.05	4.90 ± 0.04
OEt	OBu- <i>i</i>	4.17 ± 0.07	4.18 ± 0.05	4.17 ± 0.05
OBu- <i>n</i>	OBu- <i>s</i>	4.65 ± 0.06	4.72 ± 0.01	4.67 ± 0.06
OBu- <i>n</i>	OBu- <i>i</i>	3.98 ± 0.04	3.98 ± 0.04	3.98 ± 0.04

The K values of the reaction systems with ethoxy-butoxy, ethoxy-isobutoxy and butoxy-isobutoxy pairs are 4.17, 4.17, and 3.98, respectively, suggesting that these equilibria are close to the random distribution, where $K=4$. However, in the cases associated with the *s*-butoxy group, $K=4.90$ and $K=4.67$, some deviation from random distribution is indicated.

Iodine monobromide was added to the reaction system as a piece of crystal, or solution in hexane, *o*- or *p*-xylene. The same equilibrium constant was obtained in each case; therefore, the influence of these solvents on the equilibrium state appeared to be negligible. The reaction was well-promoted in the presence of about 0.001 (mole fraction) of iodine monobromide.

It is noted that GLPC may be employed for the study of the disproportionation equilibria of alkyl-alkoxysilanes in which the rate of reaction is slow compared to the retention times of the reactants and products.¹⁾ Hence, the following attempt was made to see if the GLPC technique could be employed for the study of the catalyzed reactions presented here.

The equilibrium mixture of the ethoxy-butoxy system was divided into two parts, one of which was treated with silver powder in order to allow it to react with iodine monobromide to remove the catalyst from the reaction system,⁹⁾ while the other was left untreated. The GLPC analysis of each sample gave virtually identical results, *i.e.*, $K=4.16$ was the mean value from the former case, and $K=4.15$, from the latter. (The mean value in the table is 4.17) This means that equilibrium does not shift during GLPC analysis even in the presence of iodine monobromide, and it was concluded that the composition of the equilibrium

