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The Disproportionation of Dimethyldialkoxysilanes Catalyzed by Iodine Monobromide

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Synopsis. Iodine monobromide is an extremely effective catalyst for the redistribution of alkoxyl groups on silicon atoms in dimethyldiakoxysilanes. 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 alkoxyl-alkoxyl 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–Methyltriethoxysilane[7]

Dimethyldimethoxysilane–Dimethyldiethoxysilane[7]

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 alkoxysilane–iodine complexing, we noticed that iodine or interhalogen compounds catalyzed alkoxyl-alkoxyl 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:

$$\mathrm{Me_2Si(OEt)_2 + Me_2Si(OBu\text{-}}n\mathrm{)_2 \rightleftharpoons 2Me_2Si(OEt)(OBu\text{-}}n\mathrm{)}$$

$$\mathrm{Me_2Si(OEt)_2 + Me_2Si(OBu\text{-}}s\mathrm{)_2 \rightleftharpoons 2Me_2Si(OEt)(OBu\text{-}}s\mathrm{)}$$

$$\mathrm{Me_2Si(OEt)_2 + Me_2Si(OBu\text{-}}i\mathrm{)_2 \rightleftharpoons 2Me_2Si(OEt)(OBu\text{-}}i\mathrm{)}$$

$$\mathrm{Me_2Si(OBu\text{-}}n\mathrm{)_2 + Me_2Si(OBu\text{-}}s\mathrm{)_2 \rightleftharpoons 2Me_2Si(OBu\text{-}}n\mathrm{)(OBu\text{-}}s\mathrm{)}$$

$$\mathrm{Me_2Si(OBu\text{-}}n\mathrm{)_2 + Me_2Si(OBu\text{-}}i\mathrm{)_2 \rightleftharpoons 2Me_2Si(OBu\text{-}}n\mathrm{)(OBu\text{-}}i\mathrm{)}$$

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 DISPRONPORTIONATIO OF DIMETHYLDIALKOXYSILANES CATALYZED BY IODINE MONOBROMIDE AT (40.0±0.1) °C

$$\mathrm{Me_2Si(OR)_2 + Me_2Si(OR')_2 \rightleftharpoons 2\ Me_2Si(OR)(OR')}$$

$$K = [\mathrm{Me_2Si(OR)(OR')}]^2/\{[\mathrm{Me_2Si(OR)_2}][\mathrm{Me_2Si(OR')_2}]\}$$

Substituent OR	 OR′	K (Forward reaction)	K (Reverse reaction)	K (Mean)
OEt	OBu-*n*	4.17±0.04	4.18±0.02	4.17±0.03
OEt	OBu-*s*	4.91±0.03	4.88±0.05	4.90±0.04
OEt	OBu-*i*	4.17±0.07	4.18±0.05	4.17±0.05
OBu-*n*	OBu-*s*	4.65±0.06	4.72±0.01	4.67±0.06
OBu-*n*	OBu-*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*-butoxyl 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.

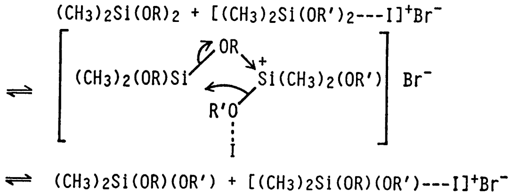
It is noted that GLPC may be employed for the study of the disproportionation equilibria of alkylalkoxysilanes in which the rate of reaction is slow compared to the retention times of the reactants and products.[1] Hence, the following attempt was made to see if the GLPC technique could be employed for 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 mixture could be directly analyzed by GLPC.

Iodine Monobromide–Dimethyldialkoxysilane Complexes. The absorption spectra of iodine monobromide solutions in dimethyldialkoxysilanes were examined with a Shimadzu model UV-200 double-beam spectrophotometer, using stoppered silica cells with a path length of 10.0 mm. The visible and ultraviolet absorption peaks were observed at 428—436 nm and 218—234 nm respectively, indicating the formation of charge-transfer complexes,[10] similarly to the iodine–tetraethoxysilane system.[11]

A CT complex is usually represented as a resonance hybrid of a no-bond form and a dative form, and the dative form of a iodine monobromide–dimethyldialkoxysilane complex is regarded as $[(CH_3)_2Si(OR)_2{\cdots}I]^+Br^-$.

Proposed Reaction Mechanism. In the study of the disproportionation of ethyltrimethylsilane catalyzed by aluminum bromide, Russell postulated a reaction mechanism *via* a four-centered transition state.[12] An iodine monobromide–alkoxysilane complex is apparently of an ionic character, while an alkoxyl group also has considerable polarity. Consequently, in this case, a reaction intermediate with an ionic structure can be readily deduced, leading to the following mechanism, similar to that proposed by Russell:



Experimental

General Procedure. In an about 10-cm³ reaction vessel with a sealing-cap, a certain amount of each alkoxysilane was placed; iodine monobromide was then added as a piece of crystal or a proper quantity of the solution in hexane, *o*- or *p*-xylene. Each reaction mixture thus prepared was divided into two or three parts and maintained in a thermostat setting of (40.0±0.1) °C. One of them was used to follow the time course of the reaction until the composition came to a constant, and then the others were used to determine the equillbrium composition.

Analysis. Analyses were performed by GLPC using a Shimadzu model GC-4B gas chromatograph with a thermal conductivity detector and equipped with a printing integrator.

In the case of the ethoxy–butoxy system, a 3 mm $\phi\times5$ m glass column with Neopak 1A (diatomaceous earth) supporting 25% PEG 4000 was employed at a column temp of 120 °C, the relative retention times being: $Me_2Si(OEt)_2$: 1, $Me_2(OEt)(OBu\text{-}n)$: 2.46, $Me_2Si(OBu\text{-}n)_2$: 5.85.

In the other cases, a 4 mm $\phi\times6$ m glass column with 5% Silicone OV-17 on Chromosorb W (diatomaceous earth) was used at a column temp of 110 °C. The relative retention times under these conditions were as follows: $Me_2Si(OEt)_2$: 1, $Me_2Si(OEt)(OBu\text{-}s)$: 2.30, $Me_2Si(OBu\text{-}s)_2$: 4.93, $Me_2Si(OEt)(OBu\text{-}i)$: 2.40, $Me_2Si(OBu\text{-}i)_2$: 4.95, $Me_2Si(OEt)(OBu\text{-}n)$: 3.30, $Me_2Si(OBu\text{-}n)(OBu\text{-}s)$: 6.67, $Me_2Si(OBu\text{-}n)(OBu\text{-}i)$: 6.68, $Me_2Si(OBu\text{-}n)_2$: 9.78.

Reagents. The dimethyldiethoxysilane was prepared by the reaction of octamethylcyclotetrasiloxane with tetraethoxysilane in the presence of potassium hydroxide.[13] The dimethyldibutoxysilanes and dimethylethoxybutoxysilanes were prepared by the iodine-catalyzed reaction of dimethyldiethoxysilane with butyl, *s*-butyl, or isobutyl alcohol. After the resulting ethanol and excess alcohol had been removed by distillation, each alkoxysilane was obtained by fractional distillation.

The dimethyldiethoxysilane was purified by repeated fractional distillation under ordinary pressure, while the dibutoxy-, di-*s*-butoxy-, and diisobutoxy-silanes were distilled under reduced pressure. The dialkoxysilanes with different alkoxyl groups were purified by means of GLPC fractional elution, employing a Shimadzu model GC-5A gas chromatograph, equipped with a model 4APP-5 autofraction collecteor. Stainless columns (8 mm $\phi\times2.8$—3.5 m) containing 25% Ucon oil on Chromosorb W or 35% PEG 6000 on Shimalite NAW were used at a column temp of 120—180 °C.

The iodine used in the alcoholysis of dimethyldiethoxysilane was purified by repeated sublimation with calcium oxide and potassium iodide. The iodine monobromide was prepared and purified by recrystallization as reported in the literature.[14]

References

1) K. Moedritzer, *Adv. Organomet. Chem.*, **6**, 171 (1968).

2) K. Moedritzer, *Organomet. Chem. Rev.*, **1**, 179 (1966).

3) J. C. Lockhart, *Chem. Rev.*, **65**, 131 (1965).

4) R. H. Krieble and C. A. Burkhard, *J. Am. Chem. Soc.*, **69**, 2689 (1947).

5) F. C. Boye and H. W. Post, *J. Org. Chem.*, **17**, 1389 (1952).

6) K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, **3**, 268 (1964).

7) J. R. Van Wazer and K. Moedritzer, *J. Inorg. Nucl. Chem.*, **26**, 737 (1964).

8) D. N. Dolan and G. Nickless, *J. Chromatogr.*, **37**, 1 (1968).

9) W. T. Grubb and R. C. Osthoff, *J. Am. Chem. Soc.*, **77**, 1405 (1955).

10) L. J. Andrews and R. M. Keefer, *Adv. Inorg. Chem. Radiochem.*, **3**, 91 (1961).

11) K. Shinoda and J. H. Hildebrand, *J. Phys. Chem.*, **62**, 789 (1957).

12) G. A. Russell, *J. Am. Chem. Soc.*, **81**, 4815 (1959).

13) M. G. Voronkov, *J. Gen. Chem. USSR.*, **29**, 890 (1959).

14) A. I. Popov and N. E. Skelly, *J. Am. Chem. Soc.*, **77**, 3722 (1955).