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Alcoholysis Equilibria of Dialkoxydimethylsilanes Catalyzed by Iodine or Iodine Monobromide

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Iodine or iodine monobromide was found to be an especially favorable catalyst for the study of the alcoholysis equilibria of dialkoxydimethylsilanes by gas chromatography. Iodine monobromide was employed to promote the reactions associated with tertiary alcohols, and iodine was used for the other reactions. Eight alcohols were allowed to react with diethoxydimethylsilane, and successive equilibrium constants, K_1 and K_2, were determined at 20 °C. $K_1=2.36$—2.75 and $K_2=0.66$—0.69 (by the use of primary alcohols), $K_1=1.34$—1.38 and $K_2=0.28$—0.30 (secondary alcohols), and $K_1=0.15$—0.16 (tertiary alcohols) were observed. These values express precisely the difference of reactivities of the three groups of alcohols with diethoxydimethylsilane. Out of the dialkoxydimethylsilanes used in this study, eight unreported compounds were isolated and characterized.

For alcoholysis or disproportionation of alkoxysilanes, iodine and interhalogen compounds such as iodine monobromide exhibit excellent catalytic action.[1,2] These catalysts lead such reaction systems readily to equilibrium even at ordinary temperature; the reaction mixtures with the catalyst can be satisfactorily analyzed by gas chromatography.

Alcoholysis of diethoxydimethylsilane[3–6] and the other alkoxysilanes has been well studied. However, the equilibrium constants of these reactions can not be found in the literature, although a few quantitative studies of disproportionation equilibria of alkoxysilanes have been reported.[7–9]

Thus, the alcoholysis equilibria of alkylalkoxysilanes catalyzed by iodine or iodine monobromide were investigated, and the equilibrium constants of these reactions were determined. This paper presents the alcoholysis equilibrium data of dialkoxydimethylsilanes at 20 °C, following the previous report on the alcoholyses of alkoxytriethylsilanes.[2]

The reactivities of alcohols to alkoxysilanes are considered in the order of primary>secondary>tertiary,[10,11] and the alcoholysis equilibrium constants of alkoxytriethylsilanes have been found to follow this order.[2] The difference in alcohol reactivities may be revealed more distinctly by the data of dialkoxydimethylsilanes, as the two alkoxyl groups should be exchanged in these cases.

Experimental

General Procedure. Given amounts of dialkoxydimethylsilane and alcohol were placed in a 5-cm^3 reaction vessel. Molar ratios of alcohols to alkoxysilanes in the reaction mixtures were in the range of about 0.7 to 5.1. Iodine or iodine monobromide was added to the reaction mixtures as the solution in each alcohol.

Each reaction associated with primary and secondary alkoxyl groups was promoted by iodine. Three directions were investigated:

A-series: $\mathrm{Me_2Si(OEt)_2 + ROH \longrightarrow}$

B-series: $\mathrm{Me_2Si(OEt)(OR) + ROH\ or\ EtOH \longrightarrow}$

C-series: $\mathrm{Me_2Si(OR)_2 + EtOH \longrightarrow}$

Equilibrium compositions were ascertained by GLPC, from which data K_1 and K_2 values were estimated.

As the pure di-*t*-butoxydimethylsilane and dimethyldi-*t*-pentyloxysilane could not be isolated, the reactions associated with *t*-alkoxyl groups were examined for A- and B-series, and only K_1 values were determined. In this case, iodine monobromide was employed to accelerate the reactions. Each reaction mixture was divided into two or three parts and maintained in a thermostat setting at (20.0± 0.1) °C. One of them was used to monitor the time course of the reaction until the composition became constant, and then the others were used to determine the equilibrium compositions.

Analysis. Analyses were performed by GLPC using a Shimadzu model GC-4B gas chromatograph with a thermal conductivity detector. The packings with the following stationary phases were used. PEG 4000+PEG 6000 (ROH: $\mathrm{Bu^nOH}$), PEG 1000+SPAN 80 ($\mathrm{Bu^iOH}$, $\mathrm{Bu^sOH}$), SPAN 80 ($\mathrm{Bu^tOH}$), PEG 1000 ($\mathrm{C_5H_{11}{}^nOH}$, $\mathrm{C_5H_{11}{}^tOH}$), PEG 4000 ($\mathrm{MePr^nCHOH}$, $\mathrm{Et_2CHOH}$).

Reagents. Diethoxydimethylsilane was prepared by the reaction of octamethylcyclotetrasiloxane with tetraethoxysilane in the presence of potassium hydroxide.[14] The other alkoxysilanes were prepared by iodine or iodine monobromide-catalyzed alcoholysis of diethoxydimethylsilane. After the resulting ethanol and excess alcohol were removed by distillation, each alkoxysilane was obtained by fractional distillation.

Ethoxydimethyl-*t*-pentyloxysilane was purified by means of GLPC fractional elution, employing a Shimadzu model GC-5A gas chromatograph, equipped with a model APP-5 autofraction collector. A stainless column (6 mm $\phi\times4.5$ m) containing 25% PEG 1000 on Chromosorb P was used. The other dialkoxydimethylsilanes were purified by repeated fractional distillation.

The fifteen dialkoxydimethylsilanes mentioned below were prepared and characterized by ^{13}C NMR, MS, and elemental analyses. As eight of these were unreported compounds, their boiling points, refractive indices, and analytical data are added. Di-*t*-alkoxydimethylsilanes were detected by GC-MS in the reaction mixtures, but the contents were too small to isolate.

$\mathrm{Me_2Si(OEt)_2}$, $\mathrm{Me_2Si(OBu^n)_2}$, $\mathrm{Me_2Si(OBu^s)_2}$, $\mathrm{Me_2Si(OBu^i)_2}$, $\mathrm{Me_2Si(OC_5H_{11}{}^n)_2}$, $\mathrm{Me_2Si(OEt)(OBu^n)}$, $\mathrm{Me_2Si(OEt)(OBu^s)}$.

$\mathrm{Me_2Si(OEt)(OBu^i)}$: bp 146.5 °C; n_D^{20} 1.3923; ^{13}C NMR (neat) $\delta=-3.83$(q, 2C), 17.92(q), 18.46(q, 2C), 30.38(d), 57.35(t), 68.58(t). Found: C, 54.49%; H, 11.57%. Calcd for $\mathrm{C_8H_{20}O_2Si}$: C, 54.52%; H, 11.44%. $\mathrm{Me_2Si(OEt)(OBu^t)}$: 135.0 °C; 1.3905; $\delta=1.05$ (q, 2C), 17.85(q), 31.35(q, 3C), 57.00(t), 71.51(s). Found: C, 54.49%; H, 11.47%. Calcd: C, 54.52%; H, 11.44%. $\mathrm{Me_2Si(OEt)(OC_5H_{11}{}^n)}$: 175.2 °C; 1.4016; $\delta=3.75$(q, 2C), 13.58(q), 17.97(q), 22.21(t), 27.82

TABLE 1. ALCOHOLYSIS EQUILIBRIUM CONSTANTS OF DIALKOXYDIMETHYLSILANES AT 20 °C

$$Me_2Si(OEt)_2 + ROH \rightleftharpoons Me_2Si(OEt)(OR) + EtOH$$
$$K_1 = \{[Me_2Si(OEt)(OR)][EtOH]\}/\{[Me_2Si(OEt)_2][ROH]\}$$
$$Me_2Si(OEt)(OR) + ROH \rightleftharpoons Me_2Si(OR)_2 + EtOH$$
$$K_2 = \{[Me_2Si(OR)_2][EtOH]\}/\{[Me_2Si(OEt)(OR][ROH]\}$$

ROH		Equilibrium constants K_1 and K_2			
		Reaction system^a)			Mean value of all kinds
		A-series	B-series	C-series	
Bu^nOH	K_1:	2.48±0.05	2.48±0.04	2.51±0.04	2.49±0.04
	K_2:	0.68±0.01	0.68±0.01	0.70±0.02	0.68±0.02
Bu^iOH	K_1:	2.76±0.03	2.75±0.03	2.74±0.02	2.75±0.03
	K_2:	0.69±0.01	0.69±0.01	0.70±0.01	0.69±0.01
Bu^sOH	K_1:	1.34±0.02	1.34±0.03	1.34±0.05	1.34±0.03
	K_2:	0.28±0.01	0.28±0.02	0.29±0.01	0.28±0.01
Bu^tOH	K_1:	0.150±0.008	0.146±0.005		0.148±0.006
$C_5H_{11}{}^nOH$	K_1:	2.34±0.05	2.37±0.02	2.38±0.03	2.36±0.04
	K_2:	0.67±0.02	0.66±0.02	0.66±0.01	0.66±0.02
$MePr^nCHOH$	K_1:	1.43±0.04	1.44±0.04	1.43±0.04	1.43±0.04
	K_2:	0.30±0.01	0.30±0.01	0.30±0.02	0.30±0.01
Et_2CHOH	K_1:	1.37±0.04	1.38±0.02	1.38±0.04	1.38±0.03
	K_2:	0.29±0.01	0.29±0.01	0.29±0.01	0.29±0.01
$C_5H_{11}{}^tOH$	K_1:	0.157±0.008	0.154±0.007		0.156±0.007

a) Equilibrium constants were determined for the reaction systems with one of three different starting dimethyldialkoxysilanes: A: $Me_2Si(OEt)_2$ B: $Me_2Si(OEt)(OR)$ C: $Me_2Si(OR)_2$

(t), 32.11(t), 57.39(t), 61.93(t). Found: C, 56.75%; H, 11.83%. Calcd for $C_9H_{22}O_2Si$: C, 56.79%; H, 11.65%. $Me_2Si(OEt)(OCHMePr^n)$: 166.4 °C; 1.3990; $\delta=-3.02$(q, 2C), 13.63(q), 17.97(q), 18.60(q), 23.31(q), 41.64(t), 57.35 (t), 67.71(d). Found: C, 56.71%; H, 11.85%. Calcd: C, 56.79%; H, 11.65%. $Me_2Si(OEt)(OCHEt_2)$: 165.8 °C; 1.4012; $\delta=3.24$(q, 2C), 9.09(q, 2C), 17.82(q), 28.96(t), 57.22(t), 74.36(d). Found: C, 56.60%; H, 11.80%. Calcd: C, 56.79%; H, 11.65%. $Me_2Si(OEt)(OC_5H_{11}{}^t)$: 156 °C; 1.3998; $\delta=-0.80$(q, 2C), 8.26(q), 18.07(q), 28.84(q, 2C), 37.03(t), 57.32(t), 73.99(s). Found: C, 56.45%; H, 11.85%. Calcd: C, 56.79%; H, 11.65%. $Me_2Si(OCHMePr^n)_2$: 206.5 °C; 1.4092; $\delta=2.19$(q, 2C), 13.73(q, 2C), 18.60(t, 2C), 23.36(q, 2C), 41.69(t, 2C), 67.71(d, 2C). Found: C, 61.62 %; H, 12.33%. Calcd for $C_{12}H_{28}O_2Si$: C, 62.01%; H, 12.14%. $Me_2Si(OCHEt_2)_2$: 205.2 °C; 1.4139; $\delta=-1.97$(q, 2C), 9.36(q, 4C), 29.14(t, 4C), 74.56(d, 2C). Found: C, 61.66%; H, 12.36%. Calcd: C, 62.01%; H, 12.14%.

Alcohols, iodine, and iodine monobromide were purified by methods similar to those previously reported.[1,2]

Results and Discussion

The following successive equilibrium constants were determined at 20 °C.

$$Me_2Si(OEt)_2 + ROH \rightleftharpoons Me_2Si(OEt)(OR) + EtOH$$
$$K_1 = \{[Me_2Si(OEt)(OR)][EtOH]\}/\{[Me_2Si(OEt)_2][ROH]\}$$
$$Me_2Si(OEt)(OR) + ROH \rightleftharpoons Me_2Si(OR)_2 + EtOH$$
$$K_2 = \{[Me_2Si(OR)_2][EtOH]\}/\{[Me_2Si(OEt)(OR)][ROH]\}$$

The following alcohols were examined in this study:

ROH: Bu^nOH, Bu^iOH, Bu^sOH, Bu^tOH, $C_5H_{11}{}^nOH$, $MePr^nCHOH$, Et_2CHOH, $C_5H_{11}{}^tOH$.

The reactions were well-promoted in the presence of about 0.1 mol% catalyst (iodine or iodine monobromide), and in most cases the reactions attained equilibrium within several hours.

To make sure that the equilibrium compositions can be determined by means of GLPC even in the presence of the catalyst, a test similar to the previous study[1] was attempted. A reaction mixture, $Me_2Si(OEt)_2$–Bu^nOH (I_2), was divided into two parts, one of which was treated with silver powder to remove the catalyst from the reaction system,[15] while the other was left untreated; the compositions of both samples were determined by GLPC at about one hour intervals. In the latter case, the reaction proceeded to equilibrium, and $K_1=2.45$, $K_2=0.69$ were observed. In the former case, $\{[Me_2Si(OEt)(OBu^n)][EtOH]\}/\{[Me_2Si(OEt)_2][Bu^nOH]\}=1.27$, 1.33, 1.31, and $\{[Me_2Si(OBu^n)_2][EtOH]\}/\{[Me_2Si(OEt)(OBu^n)][Bu^nOH]\}=0.31$, 0.33, 0.30, proving that the reaction practically stopped due to silver-treatment. Moreover, a similar test was undertaken for the equilibrium mixture, and it was confirmed that the equilibrium did not shift during GLPC analysis even in the presence of the catalyst.

Each reaction was carried out from two or three directions as mentioned above, but the resulting equilibrium constants agreed very well with each other; the data are summarized in Table 1.

The K_1 and K_2 values are close to 2 and 0.5, when both alkoxyl groups have about the same binding ability to silicon and both alcohols have similar reactivity.

In case ROH are primary alcohols, *i.e.* Bu^nOH, Bu^iOH, $C_5H_{11}{}^nOH$, $K_1=2.36$—2.75 and $K_2=0.66$—0.69; these values are somewhat larger than those described above.

However, in the case of the reaction systems associated with secondary alkoxyl groups, K_1 and K_2

are smaller than the above values. $K_1=1.34$, $K_2=0.28$ (ROH:Bu^sOH); $K_1=1.43$, $K_2=0.30$ ($MePr^nCHOH$); $K_1=1.38$, $K_2=0.29$ (Et_2CHOH). Therefore, secondary alcohols seem to be less reactive to diethoxydimethylsilane than primary alcohols.

Tertiary alcohols are still more inactive than secondary alcohols,[10–13] and so the observed K_1 values of the reactions involving tertiary alcohols are fairly small, *i.e.* 0.148 (ROH:Bu^tOH) and 0.156 ($C_5H_{11}{}^tOH$).

As it was impossible to obtain the GLPC calibration curves of the di-*t*-alkoxydimethylsilanes, because of the inaccessibility of the pure sample, the accurate K_2 values could not be evaluated. But these values are estimated to be about 0.005 or below, when the slope of the calibration curves are inferred from analogy with the other alkoxysilanes. Such small values suggest that the di-*t*-alkoxysilanes are especially unstable, based on the steric repulsion between the two *t*-alkoxyl groups.

As described above, the K_1 and K_2 values of the reaction systems associated with primary, secondary, and tertiary alkoxyl groups decrease in this order, and these values reflect clearly the extent of the binding abilities of alkoxyl groups to silicon.

The catalytic function of iodine or iodine monobromide may also be illustrated by a mechanism *via* a four-centered transition state analogous to that previouly proposed.[1,2] Iodine or iodine monobromide forms charge transfer complexes with alcohols, and also with alkoxysilanes, and the dative forms of these complexes, *e.g.* $[ROH\cdots I]^+I^-$ or $[Me_2Si(OR)_2\cdots I]^+I^-$, seem to make up the above transition state.

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