  Bull. Chem. Soc. Jpn., 55, 2973—2975 (1982)

Alcoholysis Equilibria of Triethylalkoxysilanes Catalyzed by Iodine or Iodine Monobromide

Katsuko Ito and Takeshi Ibaraki*

Department of Natural Science, Osaka Women's University, Daisen-cho, Sakai, Osaka 590

(Received January 23, 1982)

The equilibrium constants K of alcoholysis of triethylalkoxysilanes were determined at 20 °C and 40 °C. Iodine monobromide was used to promote the reactions associated with the tertiary alkoxyl groups, while the other reactions proceeded in the presence of iodine. The K values of the reaction systems with ethoxyl or propoxyl—primary, secondary, and tertiary alkoxyl pairs were 1 or above, about 0.5, and about 0.05, respectively. These values reflect the extent of the binding abilities of the alkoxyl groups to silicon, which is in the expected order of primary>secondary>tertiary alkoxyl groups. A mechanism is postulated for the reaction which involves participation by the iodine or iodine monobromide.

Alcoholysis of alkoxysilanes had been carried out previously in the absence of catalyst,[1] but it was noted that under anhydrous conditions alkoxysilanes were generally quite stable and that non-catalytic alcoholysis proceeded only slowly.[2,7] Various acids and bases have been employed to catalyze such reactions,[2–11] as well as alkali metals.[2–4,9,10] Reaction mechanisms have been proposed in some of these cases,[2,7–9] but quantitative data concerning the equilibria of such reactions cannot be found in the literature, although a few kinetic studies have been reported.[8,11]

Alkoxyl-alkoxyl exchange reactions are promoted by iodine or interhalogen compounds such as iodine monobromide, and the equilibrium compositions of such systems can be ascertained by gas chromatography as described in the previous paper.[12] Thus, the iodine- or iodine monobromide-catalyzed reactions of triethylalkoxysilanes with various alcohols were examined, and the equilibrium constants at two different temperatures were determined. For reactions with tertiary alcohols, iodine monobromide was employed because of its superior catalytic activity, while iodine was used in the other cases.

Results and Discussion

Alcoholysis Equilibria of Triethylalkoxysilanes. Thirteen reaction systems with different OR–OR′ pairs were studied at 20.0 °C and 40.0 °C in the presence of iodine or iodine monobromide.

$$Et_3SiOR + R'OH \rightleftharpoons Et_3SiOR' + ROH$$

The equilibria were established from both forward and reverse directions. In most cases the compositions of the reaction mixtures became constant within a few hours. Equilibrium constants, K, for these reactions are summarized in Table 1. The K values are close to unity when both alkoxyl groups have about the same binding ability to silicon and both alcohols have similar reactivity. The reaction systems with ethoxyl–methoxyl, propoxyl and butoxyl, and propoxyl–butoxyl pairs seem to correspond to such cases, as the K values are 1.00—1.12. (entries 1—3,13 in Table 1)

In the reaction systems with ethoxyl–isobutoxyl, pentyloxyl, and isopentyloxyl pairs, K values somewhat larger than unity were observed. (entries 4,7,8) Corresponding free-energy changes for these reactions are −0.62——1.02 kJ, which suggest that the products are slightly more stable than reactants.

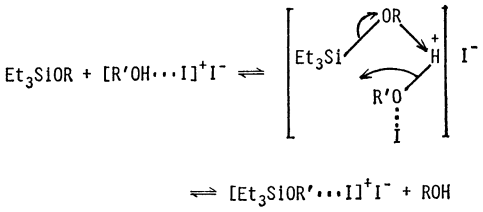
The K values of reaction systems associated with secondary alkoxyl groups are considerably less than unity (entries 5,9,10,12), so that the reverse reactions are spontaneous. Therefore, the alkoxyl groups with a side chain in the α-carbon appear to be attached more loosely to silicon than are the primary alkoxyl groups.

Since tertiary alcohols react slowly with triethylethoxysilane, iodine monobromide was used to accelerate the reactions. The K values observed for these reactions were small, about 0.05. (entries 6,11) These small values may be attributed to the steric hindrance of tertiary alkoxyl groups in the triethylalkoxysilanes.

The equilibrium constants determined at 20 °C and 40 °C were virtually the same, as shown in Table 1, so that the enthalpy changes in these reactions appear to be very small.

Proposed Reaction Mechanism. For the base-catalyzed alcoholysis of alkoxysilanes, some mechanisms with five- or six-coordinate intermediates have been proposed.[2,8,9] However, in the case of iodine- or iodine monobromide-catalyzed alcoholysis, a mechanism *via* a four-centered transition state as given below seems to be most suitable.

Iodine or iodine monobromide forms charge transfer complexes with alcohols,[13] and also with alkoxysilanes,[12] and hence the dative form of the complexes, *e.g.* $[R'OH\cdots I]^+I^-$ or $[Et_3SiOR\cdots I]^+I^-$, may be regarded as the reaction intermediate. In addition, alkoxysilane–alcohol complexing has been suggested,[14] so that the four-centered transition states are still more readily formed. The following mechanism may be derived.



or

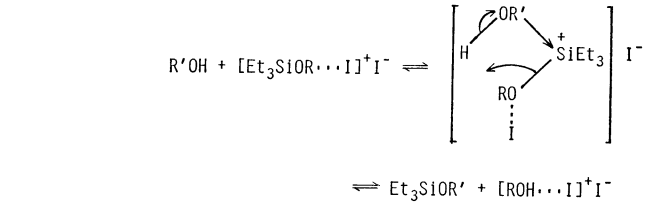
Table 1. Alcoholysis equilibrium constants of triethylalkoxysilanes

$Et_3SiOR + R'OH \rightleftharpoons Et_3SiOR' + ROH$

$K = \{[Et_3SiOR'][ROH]\}/\{[Et_3SiOR][R'OH]\}$

Entry	Substituent		Temp °C	Equilibrium constant K		
	OR	OR'		Forward reaction	Reverse reaction	Mean value[a]
1	OEt	OMe	20	1.08±0.03	1.08±0.02	1.08±0.03
			40	1.06±0.03	1.06±0.01	1.06±0.02
2	OEt	OPr^n	20	1.11±0.02	1.11±0.02	1.11±0.02
			40	1.09±0.02	1.10±0.02	1.09±0.02
3	OEt	OBu^n	20	1.12±0.03	1.13±0.03	1.12±0.03
			40	1.09±0.04	1.08±0.04	1.09±0.04
4	OEt	OBu^i	20	1.52±0.03	1.52±0.02	1.52±0.03
			40	1.48±0.03	1.48±0.04	1.48±0.03
5	OEt	OBu^s	20	0.51±0.01	0.50±0.01	0.51±0.01
			40	0.55±0.02	0.54±0.02	0.54±0.02
6	OEt	OBu^t	20	0.050±0.003	0.049±0.003	0.050±0.003
			40	0.053±0.002	0.052±0.003	0.053±0.002
7	OEt	$OC_5H_{11}^n$	20	1.31±0.02	1.32±0.03	1.32±0.03
			40	1.28±0.03	1.29±0.02	1.29±0.03
8	OEt	$OC_5H_{11}^i$	20	1.29±0.03	1.30±0.03	1.30±0.03
			40	1.27±0.04	1.27±0.03	1.27±0.03
9	OEt	$OCHMePr^n$	20	0.52±0.02	0.50±0.03	0.51±0.03
			40	0.53±0.01	0.53±0.03	0.53±0.02
10	OEt	$OCHEt_2$	20	0.43±0.03	0.42±0.01	0.43±0.02
			40	0.45±0.01	0.44±0.02	0.45±0.02
11	OEt	$OC_5H_{11}^t$	20	0.047±0.003	0.047±0.004	0.047±0.004
			40	0.050±0.002	0.050±0.005	0.050±0.003
12	OPr^n	OPr^i	20	0.40±0.01	0.40±0.01	0.40±0.01
13	OPr^n	OBu^n	20	0.99±0.01	1.00±0.02	1.00±0.03

a) Mean value of equilibrium constants of both forward and reverse reactions.



Experimental

General Procedure. In a reaction vessel (volume about 5 cm^3) with a sealing-cap, measured amounts of triethylalkoxysilane and alcohol were placed. Molar ratios of alkoxysilanes to alcohols in the reaction mixtures were in the range of 1:0.5 to 1:6. I_2 or IBr was added to the reaction mixtures as the solution in each alcohol. The reaction was promoted using about 0.001 (mole fraction) of catalyst.

Each reaction mixture thus prepared was divided into two or three parts and maintained in a thermostat set at (20.0±0.1) °C or (40.0±0.1) °C. One of them was used to monitor the time course of the reaction until the composition became constant. The others were then used to determine the equilibrium composition.

Analysis. Analyses were performed by means of GLPC using a Shimadzu model GC-4B gas chromatograph with a thermal conductivity detector. The stationary phases of the packings used in this investigation were as follows:

PEG 4000+SPAN 80 (entries 1,8 in Table 1), SPAN 80 (entries 2,4,5,7,13), PEG 1000+DOP-B (entry 3), PEG 4000 (entry 6), PEG 6000 (entries 9,10), PEG 1000 (entry 11), SPAN 80+PEG 6000 (entry 12).

Reagents. Triethylmethoxysilane and triethylethoxysilane were prepared by the reaction of tetramethoxysilane or tetraethoxysilane with ethylmagnesium bromide. The other triethylalkoxysilanes were prepared by iodine or iodine monobromide-catalyzed alcoholysis of triethylethoxysilane. After the resulting ethanol and excess alcohol had been removed by distillation, each triethylalkoxysilane was obtained by fractional distillation. These triethylalkoxysilanes were purified by repeated fractional distillation, and the following compounds were prepared.

Et_3SiOMe, Et_3SiOEt, Et_3SiOPr^n, Et_3SiOPr^i, Et_3SiOBu^n, Et_3SiOBu^i, Et_3SiOBu^s, Et_3SiOBu^t, $Et_3SiOC_5H_{11}^n$, $Et_3SiOC_5H_{11}^i$, $Et_3SiOC_5H_{11}^t$, $Et_3SiOCHMePr^n$: bp 205.1 °C; n_D^{20} 1.4243; ^{13}C NMR (neat) δ=4.78 (t, 3C), 6.22 (q, 3C), 13.58 (q), 18.48 (t), 23.31 (q), 41.96 (t), 67.63 (d). Found: C, 65.04; H, 13.25%. Calcd for $C_{11}H_{26}SiO$: C, 65.27; H, 12.95%. $Et_3SiOCHEt_2$: bp 206.2 °C; n_D^{20} 1.4272; ^{13}C NMR (neat) δ=4.88 (t, 3C), 6.27 (q, 3C), 8.83 (q, 2C), 28.94 (t, 2C), 74.12 (d). Found: C, 65.08; H, 13.25%. Calcd: C, 65.27; H, 12.95%.

The last two alkoxysilanes are unreported compounds, while the boiling points and refractive indices of the others were virtually identical with the reported values.[4]

The alcohols were purified by fractional distillation. Methanol, ethanol, 1- and 2-propanol were previously freed from water by refluxing with magnesium or magnesium activated with iodine. *t*-Butyl alcohol was repeatedly recrystallized after distillation.[15]

Iodine was purified by repeated sublimation with calcium oxide and potassium iodide. Iodine monobromide was prepared and purified by recrystallization.[12]

The authors wish to thank professor Makoto Kumada of Kyoto University and Dr. Kenzo Hirayama for their kind advice and encouragement. We also would

like to thank professor Toshiyuki Shono of Osaka University and his co-workers for the elemental analyses and for the NMR spectral data.

References

1) E. W. Abrahamson, I. Joffe, and H. W. Post, *J. Org. Chem.*, **13**, 275 (1948).
2) B. Helferich und W. Reimann, *Chem. Ber.*, **80**, 163 (1947).
3) E. Larsson, *Acta Chem. Scand.*, **8**, 898 (1954).
4) B. N. Dolgov, N. P. Kharitonov, and M. G. Voronkov, *J. Gen. Chem. USSR.*, **24**, 1169 (1954).
5) H. Gilman and G. N. R. Smart, *J. Org. Chem.*, **19**, 441 (1954).
6) M. G. Voronkov and B. N. Dolgov, *Bull. Acad. Sci. USSR., Div. Chem. Sci.*, **1957**, 1153.
7) M. G. Voronkov and L. A. Zhagata, *J. Gen. Chem. USSR.*, **37**, 2630 (1967).
8) R. L. Schowen and K. S. Latham, Jr., *J. Am. Chem. Soc.*, **89**, 4677 (1967).
9) L. H. Sommer and H. Fujimoto, *J. Am. Chem. Soc.*, **90**, 982 (1968).
10) H. G. Emblem and K. Hargreaves, *J. Inorg. Nucl. Chem.*, **30**, 721 (1968).
11) G. Tschernko und H. Hamann, *Z. Chem. (DDR)*, **18**, 64 (1978).
12) T. Ibaraki and K. Ito, *Bull. Chem. Soc. Jpn.*, **54**, 3235 (1981).
13) L. J. Andrews and R. M. Keefer, *Adv. Inorg. Chem. Radiochem.*, **3**, 91 (1961).
14) J. Nagy, S. Ferenczi-Gresz, R. Farkas, und T. Gábor, *Z. Anorg. Allg. Chem.*, **377**, 328 (1970).
15) J. A. Riddick and W. B. Bunger, "Organic Solvents, Techniques of Chemistry," 3rd ed, Wiley-Interscience, New York (1970), Vol. II, pp. 638—664.