STABILITY OF DIMETHYL(ETHOXY)ALKOXYSILANES*

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Dimethyl(ethoxy)alkoxysilanes of the type $(CH_3)_2Si(OC_2H_5)OR$ ($R = CH_3$, n-C_4H_9, $(CH_3)_3C$, $(CH_3)_3CCH_2$, $Cl(CH_2)_2$, Cl_3CCH_2) were synthesized and their stability in neutral, acidic and basic media was determined by means of gas chromatography. It was found that redistribution reactions of these compounds are thermoneutral and acid-base catalysed, and their rate is controlled by steric effects of alkyl groups R.

The stability of organosilicon compounds of the type $R_nSiX_xY_y$ (R = alkyl, X, Y = electronegative substituent) depends strongly not only on the nature of groups X and Y but also on their mutual ratio[1] x/y. The stability of the compounds $R_2Si(OR)X$ can be estimated from the equilibrium constants of such redistribution reactions of the substances $(CH_3)Si(OCH_3)X$ which do not correspond to random distribution of reactants (the compounds $(CH_3)_2Si(OCH_3)X$ with $X = Cl$, Br are more stable than the products of their redistribution and the derivatives with $X = H$, SCH_3 are less stable, cf.[2] and references therein). Until now, the experience with storage of the compounds $R_2Si(OR)X$ is consistent with this estimation.

Data about stability of the compounds $R_2Si(OR)OR'$ are not available in literature and the use of the above mentioned estimation is not possible due to the fact that redistribution of OR groups on the silicon has been studied thus far only for the alkoxy groups with short alkyl chain, in which case it proceeds as random distribution[3-5].

A study of the stability of compounds $(CH_3)_2Si(OC_2H_5)OR$ ($R = CH_3$, n-C_4H_9, $(CH_3)_3C$, $(CH_3)_3CCH_2$, $Cl(CH_2)_2$, Cl_3CCH_2) and determination of the equilibrium constants of their redistribution reactions is therefore of interest especially with regard to what extent the electronic and steric effects of groups R affect the stability of these compounds and deviations from equilibrium random distribution.

EXPERIMENTAL AND RESULTS

Compounds $(CH_3)_2Si(OC_2H_5)OR$ were prepared by reaction of dimethyl(ethoxy)chlorosilane[6] with an appropriate alcohol. A solution of 0·2—0·3 mol of an alcohol and pyridine was rapidly added to a solution of 0·2—03 mol of $(CH_3)_2Si(OC_2H_5)Cl$ in 500—700 ml of dry diethyl ether. The reaction mixture was then stirred and refluxed for 2—5 h. Pyridine hydrochloride was

filtered off and extracted with the ether. Dimethyl(ethoxy)alkoxysilanes were obtained by distillation of the filtrate combined with extract on a column with glass packing.

$(CH_3)_2Si(OC_2H_5)OR/R$, yield (%), n_D^{20}, b.p. (°C/Torr)): CH_3, 61, 1·3750, 93; n-C_4H_9, 73, 1·3943, 78/75, (lit.[7]: b.p. 155°C, n_D^{20} 1·3949); $Cl(CH_2)_2$, 65, 1·4116, 95/55; $(CH_3)_3C$, 53, 1·3889, 52/62; $(CH_3)_3CCH_2$, 64, 1·3924, 64/42; Cl_3CCH_2, 57, 1·4379, 85/25.

The purity of all compounds was checked by gas chromatography and their structure was verified by elemental analysis and by ^{1}H-NMR spectroscopy. Redistribution reactions of the compounds $(CH_3)_2Si(OC_2H_5)OR$ were followed on a chromatograph equipped with a thermal conductivity detector and programmed temperature, using the column filled with 8·8% Sil E elastomer on Chromaton N and hydrogen as the carrier gas. The ratio of concentrations $P = [(CH_3)_2Si(OR)_2].[(CH_3)_2Si(OC_2H_5)_2]/[(CH_3)_2Si(OC_2H_5)OR]^2$ was determined such that 1% pyridine was added to individual samples of $(CH_3)_2Si(OC_2H_5)(OR)$ and changes in the composition of the reaction mixture with time were followed by gas chromatography. In the time when the redistribution of the two most reactive derivatives (R = CH_3 and n-C_4H_9) reached equilibrium state ($P \approx 0·29$ and 0·27, respectively) the values of P for the other derivatives (R, P) were following: $Cl(CH_2)_2$, 0·18; $(CH_3)_3CCH_2$, 0·042; Cl_3CCH_2, 0·045; $(CH_3)_3C$, 0.

The ratio of concentrations of a dimethyl(ethoxy)alkoxysilane to dimethyldiethoxysilane was determined with a maximum error of 6 per cent.

DISCUSSION

It was found that all the compounds prepared can be stored over several months in sealed ampoules without their decomposition. The necessary condition for their longer storage is, however, the exclusion of traces of acids or bases. Already 0·5% solutions of an acid (p-toluensulphonic acid, sulphuric acid) or a base (pyridine, sodium ethylate) causes that redistribution reactions (1) of all the compounds but $(CH_3)_2Si(C_2H_5)OC(CH_3)_3$ reach equilibrium state in several days to several weeks. A similar result is achieved by heating the compounds at 150°C for several days. Dimethyl(ethoxy)tert. butoxysilane is stable under

$$(CH_3)_2Si(OC_2H_5)OR \quad \rightleftharpoons \quad (CH_3)_2Si(OC_2H_5)_2 + (CH_3)_2Si(OR)_2 \qquad (1)$$
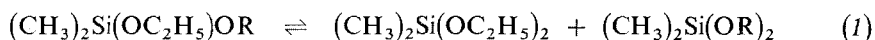
the conditions mentioned — its decomposition has not been observed to take place even during its standing over a period of several months. Its decomposition does not proceed also on heating the sample at 150°C for ten days.

The equilibrium constants of the redistribution taking place at 150°C and of the acid–base catalysed redistribution at room temperature had always essentially the same value for a given compound and corresponded within experimental errors to random distribution of reaction components ($K = 0·25$). The rate of the redistribution reaction of the compounds $(CH_3)_2Si(OC_2H_5)OR$ depends, however, on the substituent R. The same dependence is observed for the base-, acid-catalysed, and thermal redistribution. From the parallelity of $P(R)$ with Taft $E_s(R)$ constants[8] it follows that the rate is not influenced by electronic effects of groups R but solely by their steric effect. The mechanism of redistribution reactions on the silicon is

usually discussed in terms of synchronous formation of a four-centre transition state $-S_F(2)$, and the acceleration of disproportionation by a catalyst is accounted for by the occurrence of different reaction mechanism[9]. The parallelity of $P(R)$ with E_s in the thermal disproportionation speaks for the $S_F(2)$ state, since in such a case one can expect compensation of the electronic effect of group R. Group R affects both centres in the molecule of dimethyl(ethoxy)alkoxysilanes in the opposite way, *i.e.* one centre (*e.g.* silicon) is more favoured for an interaction leading to the $S_F(2)$ transition state, while the other, oxygen, unfavoured. The independence of redistribution rate on the electronic effect of group R in the acid-base disproportionation indicates that the rate determining step of this reaction is probably again formation of a cyclic transition state, here likely as a result of interaction of the complex formed from dimethyl(ethoxy)alkoxysilane molecule and the catalyst with additional molecule of dimethyl(ethoxy)alkoxysilane.

REFERENCES

1. Moedritzer K.: Organometal. Chem. Rev. *1*, 179 (1966).
2. Moedritzer K., vanWazer J. R.: Inorg. Chem. *7*, 2105 (1968).
3. Peppard D. F., Brown W. G., Johnson W. C.: J. Amer. Chem. Soc. *68*, 77 (1946).
4. Moedritzer K., vanWazer J. R.: Inorg. Chem. *3*, 268 (1964).
5. vanWazer J. R., Moedritzer K.: J. Inorg. Nucl. Chem. *26*, 737 (1964).
6. Sokolov N. N., Andrianov K. A.: Izv. Akad. Nauk SSSR *1957*, 806.
7. Krieble R. H., Burkhard C. A.: J. Amer. Chem. Soc. *69*, 2689 (1947).
8. Taft R. W. in the book: *Steric Effects in Organic Chemistry* (M. S. Newman, Ed.). Wiley, New York 1956.
9. Lockhart J. C.: *Redistribution Reactions*. Academic Press, New York 1970.

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