

NOTE

THE EQUILIBRIUM OF FLUORINE AND HYDROGEN REDISTRIBUTION ON SILICON

LOUIS G. MAHONE AND DONALD R. WEYENBERG

Organometallic Laboratory, Dow Corning Corporation, Midland, Mich. (U.S.A.)

(Received October 16th, 1967)

Presently there is available a rather large amount of information^{1,2} pertaining to ligand redistribution on silicon which might be useful in determining the effect of structure upon the stability of silicon compounds. The direct comparison of these data, however, is difficult since no common reaction medium was generally used. In fact, most equilibrations were carried out in multivariant solvents, the neat liquids themselves.

While it seems reasonable to attribute the larger deviations from random distributions primarily to an enthalpy effect, relatively few calorimetric or equilibrium-temperature studies have been done to support this view. Less clear is the dependence of unusually large deviations from random distributions on the reaction medium. Hence, it is not certain that these previous studies truly reflect bond reorganization energies. For this reason we have undertaken a comparison of equilibrium constants for a redistribution reaction in the neat liquid, in benzene solution, and in the gas phase.

The strong tendency towards accumulation of like ligands in the redistribution of fluorine and hydrogen on the phenylmethylsilicon moiety has been demonstrated by an equilibrium study as well as a calorimetric measurement³ to be larger than any previous case for silicon. Our results (Table 1) for the equilibration of PhMeSiHF (0.145 mole fraction) in benzene solution give the following thermodynamic values*:



$$\Delta H = -3.47 \pm 0.06 \text{ kcal/mole}$$

$$\Delta G_{\text{chem.}} = -3.79 \pm 0.04 \text{ kcal/mole (25.1}^\circ\text{)}$$

$$\Delta S_{\text{chem.}} = +1.1 \pm 0.2 \text{ eu/mole}$$

These values compare favorably with those from previous work without solvent³.

$$\Delta H_{40} = -3.2 \text{ kcal/mole (calorimetry)}$$

$$\Delta G_{\text{chem.}} = -3.8 \pm 0.2 \text{ kcal/mole (100}^\circ\text{)}$$

* The subscript "chem." indicates a value corrected for symmetry effects and is equivalent to the subscript "dev." used in the papers of Moedritzer and Van Wazer².

TABLE I
EQUILIBRATION RESULTS IN BENZENE SOLUTION

Relative moles			T	K
PhMeSiF ₂	PhMeSiHF	PhMeSiH ₂		
1.000 ^a	0.0816 ± 0.0003	1.00 ± 0.01 ^b	25.1	150 ± 1 ^c
1.000 ^a	0.1155 ± 0.0004		65.3	75 ± 0.4 ^c

^a Defined. ^b Based on GLC area. ^c Based on the assumption [PhMeSiH₂] = [PhMeSiF₂] due to stoichiometry.

While this result suggests no unusual medium effect, a better test can be made by comparing the gas phase equilibrium constant.

Rather than attempting a gas phase equilibration, we chose to relate the gas phase and solution equilibria by means of phase equilibrium data. The gas phase equilibrium constant, K_p , is related to the solution equilibrium constant, K , by the relation

$$K_p = \pi \cdot \left(\frac{p_i}{\chi_i} \right)^{v_i} \cdot K$$

where $\pi \cdot (p_i/\chi_i)^{v_i}$ is a dimensionless parameter determined by phase equilibria⁴. For the reaction of interest, this factor was found to be 1.254 ± 0.05 at 84.7° for a benzene solution 0.145 mole fraction in silicon compounds. At this temperature the calculated values for $\Delta G_{\text{chem.}}$ are as follows:

$$\text{Gas Phase: } \Delta G_{\text{chem.}} = -4.01 \pm 0.06 \text{ kcal/mole}$$

$$\text{Solution: } \Delta G_{\text{chem.}} = -3.86 \pm 0.05 \text{ kcal/mole}$$

Thus, the initial results in the neat liquid correspond quite closely to the gas phase result. The correspondence between the gas phase value of $\Delta G_{\text{chem.}}$ and ΔH was not determined, but according to the first-order approximation of Benson and Buss⁵, $\Delta S_{\text{chem.}}$ for such reactions in the gas phase are usually within ± 0.7 eu/mole and rarely in excess of ± 1.5 eu/mole.

The close correspondence in this case between the thermodynamic parameters of redistribution in the neat liquid, in benzene solution, and in the gas phase cannot necessarily form a basis for broader generalizations. However, it would seem imprudent to attribute other large deviations from random redistributions to entropy and/or medium effects.

EXPERIMENTAL

Materials

The phenylmethylsilane used in this study had n_D^{25} 1.5039 and b.p. $91^\circ/155$ mm. Phenylmethyldifluorosilane had n_D^{25} 1.4443 and b.p. 142.5° . Phenylmethylfluorosilane was prepared from phenylmethylchlorosilane⁶ (b.p. 143° , n_D^{25} 1.4730).

Analyses

Analyses were performed by GLC using a 6 ft. \times 0.25 in. column held at 90° and packed with Dow Corning[®] FS 1265 fluid. Standard solutions were analyzed using both area and peak height ratios.

Equilibrations

All equilibrated solutions were formed from PhMeSiHF in order to obtain equal molar concentrations of PhMeSiH₂ and PhMeSiF₂. The solutions were 0.85 mole fraction in benzene and contained 0.75 wt. % of tetrabutylammonium fluoride as catalyst. The equilibrations were followed kinetically after creating small displacements from equilibrium via temperature change or small additions of PhMeSiHF. The resulting pseudo-first-order kinetics readily demonstrated catalyst activity and attainment of equilibrium. The observed half-lives at 25.1 and 65.3° were about 16 and 0.9 min respectively. It was necessary to quench the catalyst with a 100% excess of BF₃·Et₂O in order to stabilize these solutions to the GLC injector temperatures.

Vapor-liquid equilibrations were carried out in a conventional Othmer still⁷ without catalyst. The liquid phase was 0.85 mole fraction in benzene.

REFERENCES

- 1 D. R. WEYENBERG, L. G. MAHONE AND W. H. ATWELL, *Ann. N.Y. Acad. Sci.*, in press.
- 2 K. MOEDRITZER, *Organometal. Chem. Rev.*, 1 (1966) 179.
- 3 D. R. WEYENBERG, A. E. BEY, H. F. STEWART AND W. H. ATWELL, *J. Organometal. Chem.*, 6 (1966) 583.
- 4 K. DENBIGH, *The Principles of Chemical Equilibrium*. University Press, Cambridge, 1961. p. 299.
- 5 S. W. BENSON AND J. H. BUSS, *J. Chem. Phys.*, 29 (1958) 546.
- 6 *French Patent* 1,303,018; *Chem. Abstr.*, 58 (1963) 9137.
- 7 E. HALA, J. PICK, V. FRIED AND O. VILIM, *Vapor-Liquid Equilibrium*, Pergamon Press, New York, 1958, p. 256.

J. Organometal. Chem., 12 (1968) 231-233