

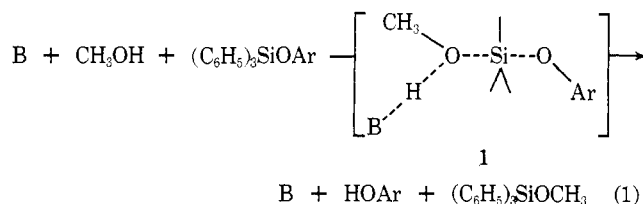
# General-Base Catalysis of Silicon-Oxygen Bond Cleavage. Hidden Isotope Effects<sup>1,2</sup>

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**Abstract:** The methoxide-catalyzed methanolyses of *p*-chlorophenoxytriphenylsilane and of *p*-methoxyphenoxytriphenylsilane, reactions previously shown to occur with general-base catalysis, proceed in mixtures of CH<sub>3</sub>OD (mole fraction *n*) and CH<sub>3</sub>OH (mole fraction 1 - *n*) at 25° with second-order rate constants described by  $k_n = k_0(1 - n + n\phi^*)(1 - n + n\phi_m)^2/(1 - n + 0.74n)^3$ , where  $k_0 = 13,600 M^{-1} \text{ min}^{-1}$  (*p*-Cl) and  $2710 M^{-1} \text{ min}^{-1}$  (*p*-CH<sub>3</sub>O). Values of  $\phi^* = 0.25-0.50$  and  $\phi_m = 0.8-1.2$  are consistent with the data for both compounds. These relations show that one proton in each transition state is generating a considerable isotope effect ( $k_H/k_D = 2-4$ ), which is being nearly cancelled by inverse isotope effects from reactant and possibly transition-state solvation shells. Thus the observed net solvent isotope effects are only 1.25 (*p*-Cl) and 1.16 (*p*-CH<sub>3</sub>O).

Some years ago, we showed that the methanolysis of aryloxytriphenylsilanes is subject to general-base catalysis<sup>5</sup> and argued that the reaction occurs by a concerted-displacement mechanism (eq 1).<sup>6</sup> This



hypothesis has been lately supported by the observation that the reaction can be simultaneously catalyzed by acids and bases.<sup>7</sup>

On the basis of analogy with carbonyl-group reactions, which have much in common with displacements at silicon, one would have expected a transition state such as **1** to generate a solvent isotope effect of at least about  $2(k_{\text{ROH}}/k_{\text{ROD}})$ .<sup>8</sup> An effect in the range  $2.2 \pm 0.5$  is anticipated for nonreaction-coordinate proton bridges ("one-proton solvation bridges"),<sup>9,10</sup> while much larger effects should be found if the proton transfer shown in **1** is a component of the reaction coordinate.<sup>10</sup> Nevertheless, Latham<sup>6</sup> found  $k_{\text{CH}_3\text{OH}}/k_{\text{CH}_3\text{OD}}$  to be only  $1.25 \pm 0.06$  and  $1.35 \pm 0.06$  for methoxide-catalyzed and acetate-catalyzed methanolyses of *p*-chlorophenoxytriphenylsilane, respectively.

It has, however, become increasingly clear<sup>11</sup> that the

(1) Catalysis in Organosilicon Chemistry. V. For part IV, see C. R. Howie, J. K. Lee, and R. L. Schowen, *J. Amer. Chem. Soc.*, **95**, 5286 (1973).

(2) This research was supported by the National Science Foundation. Data reduction was carried out in the Computation Center of the University of Kansas.

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(4) Holder of a Research Career Development Award of the National Institute of General Medical Sciences, 1968-1973.

(5) R. L. Schowen and K. S. Latham, *J. Amer. Chem. Soc.*, **88**, 3795 (1966).

(6) R. L. Schowen and K. S. Latham, *J. Amer. Chem. Soc.*, **89**, 4677 (1967).

(7) C. G. Swain, K.-R. Pörschke, W. Ahmed, and R. L. Schowen, *J. Amer. Chem. Soc.*, **96**, 4700 (1974).

(8) S. L. Johnson, *Advan. Phys. Org. Chem.*, **5**, 237 (1967).

(9) S. S. Minor and R. L. Schowen, *J. Amer. Chem. Soc.*, **95**, 2279 (1973).

(10) R. L. Schowen, *Progr. Phys. Org. Chem.*, **9**, 275 (1972).

(11) F. M. Menger, *J. Amer. Chem. Soc.*, **88**, 5356 (1966); R. A. More O'Ferrall, *Chem. Commun.*, 114 (1969); V. Gold and S. Grist, *J. Chem. Soc. B*, 1665, 2272, 2282, 2285 (1971); C. G. Mitton, M. Gresser, and R. L. Schowen, *J. Amer. Chem. Soc.*, **91**, 2045 (1969).

initial-state solvation characteristics of the methoxide ion make it considerably more reactive (up to about 2.5-fold) in CH<sub>3</sub>OD than in CH<sub>3</sub>OH. For this species at least, then, a normal isotope effect from the bridging proton might be hidden by this competing inverse effect. This can be tested by using rates in mixtures of light and heavy solvent<sup>12</sup> to conduct a "proton inventory" of the transition state, in which are specified the individual contributions to the net isotope effect of each exchangeable hydrogenic site in the transition state.<sup>1,9,13</sup>

## Results

Tables I and II present first-order rate constants determined spectrophotometrically in sodium methoxide

**Table I.** First-Order Rate Constants for the Sodium Methoxide Catalyzed Methanolysis of *p*-Chlorophenoxytriphenylsilane in Binary Mixtures of CH<sub>3</sub>OH and CH<sub>3</sub>OD (Mole Fraction *n*) at 25.00 ± 0.02°,  $\mu = 0.1500^a$

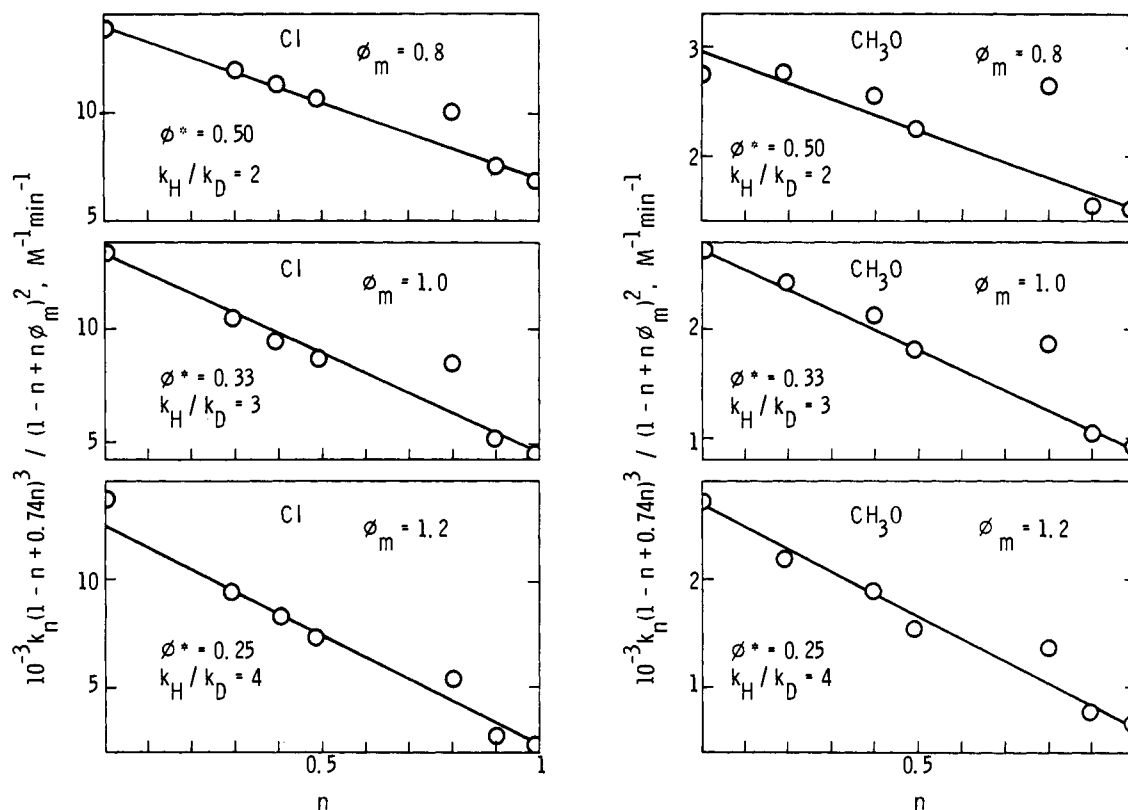
<i>n</i>	$10^2 k, \text{ min}^{-1} (10^4 [\text{NaOCH}_3], M)$
0.000	42 (0.38); 66, 84, 92 (0.65); 161, 157 (1.20); 223, 235 (1.75); 339, 341, 347 (2.58)
0.298	118 (0.79); 161 (1.14); 207 (1.49); 260 (1.84); 270 (2.19); 406 (2.89)
0.397	35 (0.28); 150 (1.22); 268 (2.15); 413 (3.09); 514 (4.03)
0.484	26 (0.13); 129 (1.07); 227 (2.00); 379 (2.94); 511 (3.88)
0.795	68 (0.24); 130 (0.80); 242 (1.55); 300 (2.12); 377 (2.68); 519 (3.43)
0.894	57 (0.28); 124 (0.65); 149 (1.05); 202 (1.40); 262 (1.97); 302 (2.53)
0.994	20, 31 (0.33); 107, 119 (1.27); 230, 237 (2.21); 323 (3.15)

<sup>a</sup> Ionic strength maintained with lithium perchlorate.

solutions for methanolysis of *p*-chlorophenoxytriphenylsilane and *p*-methoxyphenoxytriphenylsilane, respectively. These were fitted to the sodium methoxide concentrations to give the second-order constants of Table III for mixtures of CH<sub>3</sub>OH and CH<sub>3</sub>OD.

(12) A. J. Kresge, *Pure Appl. Chem.*, **8**, 243 (1964); V. Gold, *Advan. Phys. Org. Chem.*, **7**, 259 (1969).

(13) C. R. Hopper, R. L. Schowen, K. S. Venkatasubban, and H. Jayaraman, *J. Amer. Chem. Soc.*, **95**, 3280 (1973).



**Figure 1.** Plots of the left-hand side of eq 5 for the *p*-chloro (left set) and *p*-methoxy (right set) substrates, with indicated trial values of  $\phi_m$ . The slopes and intercepts yield values of  $k_0$  and  $\phi^*$  for the bridging proton of **2**, the latter being shown on each figure.

**Table II.** First-Order Rate Constants for the Sodium Methoxide Catalyzed Methanolysis of *p*-Methoxyphenoxytriphenylsilane in Binary Mixtures of  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$  (Mole Fraction  $n$ ) at  $25.00 \pm 0.02^\circ$ ,  $\mu = 0.1500^a$

$n$	$10^2 k, \text{min}^{-1} (10^4 [\text{NaOCH}_3], M)$
0.000	11 (0.38); 16, 14 (0.65); 28, 34, 32 (1.20); 45, 42 (1.75); 57, 64, 70 (2.58); 124 (4.51); 194 (7.26)
0.298	40 (1.14); 37 (1.49); 59 (1.84); 61 (2.19); 79 (2.54); 90 (2.89)
0.397	12 (0.28); 42 (1.22); 108 (3.09); 150 (4.97)
0.484	9.4 (0.13); 26 (1.07); 62 (2.00); 108 (3.88)
0.795	21 (0.24); 34 (0.80); 63 (1.55); 81 (2.12); 108 (2.68); 137 (3.43)
0.894	38 (0.65); 63 (1.40); 71 (1.97); 85 (2.53); 100 (3.28)
0.994	4.4 (0.33); 32 (1.27); 55 (2.21); 70 (3.15)

<sup>a</sup> Ionic strength maintained by lithium perchlorate.

## Discussion

Rate constants in mixtures of  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$  are related to  $n$ , the mole fraction of  $\text{CH}_3\text{OD}$ , by eq 2,<sup>12,13</sup> where  $\phi_k \equiv ([\text{D}]_k/[\text{H}]_k)/(n/[1-n])$  is an isotopic

$$k_n = k_0 \prod_i^{\nu} (1 - n + n\phi_i^{\text{T}}) / \prod_j^{\nu} (1 - n + n\phi_j^{\text{R}}) \quad (2)$$

fractionation factor<sup>12</sup> which measures the deuterium preference of the  $k$ th exchangeable hydrogenic site relative to a solvent hydrogenic site. The  $\phi_i^{\text{T}}$  in the numerator refers to transition-state sites and the  $\phi_j^{\text{R}}$  in the denominator to reactant-state sites.

**Table III.** Second-Order Rate Constants for Sodium Methoxide Catalyzed Methanolysis of *p*- $\text{XC}_6\text{H}_4\text{OSi}(\text{C}_6\text{H}_5)_3$  in Binary Mixtures of  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$  (Mole Fraction  $n$ ) at  $25.00 \pm 0.02^\circ$ ,  $\mu = 0.1500^{a,b}$

X	$n$	$k_n, M^{-1} \text{min}^{-1}$
Cl	0.000	13600
	0.298	13230
	0.397	13010
	0.484	12990
	0.795	13850
CH <sub>3</sub> O	0.894	10780
	0.994	10830
	0.000	2710
	0.298	3100
	0.397	2980
	0.484	2720
	0.795	3710
	0.894	2300
	0.994	2340

<sup>a</sup> Ionic strength maintained by lithium perchlorate. <sup>b</sup> These rate constants are reliable to about  $\pm 3-4\%$ .

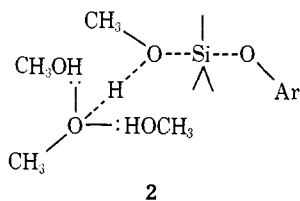
In the reactions under study, we assume that the silane reactants are about equally stable in  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$ , while we know that the isotopic fractionation factor for a solvent molecule in the solvation shell of methoxide ion has a value<sup>11</sup> of 0.74. The methoxide ion will be triply solvated<sup>1,11,13</sup> (one solvent molecule at each lone pair) so that the denominator of eq 2 is  $(1 - n + 0.74n)^3$ .

We can now rearrange eq 2 to generate eq 3, in which

$$k_n(1 - n + 0.74n)^3 = k_0 \prod_i^{\nu} (1 - n + n\phi_i^{\text{T}}) \quad (3)$$

the left-hand side is known, and the right-hand side contains the contributions to the solvent isotope effect

of the transition-state protons (fractionation factors  $\phi_i^T$ ). The observation of general-base catalysis for the reaction under study<sup>5</sup> suggests a transition state of structure 2. Transition-state contributions to the



solvent isotope effect would then come from the bridging proton (fractionation factor  $\phi^*$ ) and the two solvent protons in the solvation shell of the catalytic methoxide ion (fractionation factors  $\phi_m$ ) so that eq 4 results.

$$k_n(1 - n + 0.74n)^3 = k_0(1 - n + n\phi^*)(1 - n + n\phi_m)^2 \quad (4)$$

The latter is easily rearranged to eq 5, of which a plot

$$k_n(1 - n + 0.74n)^3 / (1 - n + n\phi_m)^2 = k_0(1 - n + n\phi^*) \quad (5)$$

of the left-hand side *vs.*  $n$  should be linear for the correct choice of  $\phi_m$ . Plots are shown in Figure 1 for  $\phi_m = 0.8, 1.0,$  and  $1.2$ . The data are not capable of discriminating strongly among these choices for either substrate. The permitted range of fractionation factors for the bridging proton (determined by the slopes in Figure 1) is  $\phi^* = 0.25$ – $0.50$ , corresponding to  $k_H/k_D = 2$ – $4$ . The lower part of this range corresponds to

solvation-bridge effects ( $2.2 \pm 0.7$ ),<sup>9</sup> and the data are therefore consistent with the view that catalysis in these reactions occurs by the one-proton solvation-bridge mechanism. That is, the formation of the silicon–oxygen bond may be assisted by strong hydrogen bonding from the nucleophilic methanol to a catalyzing base. By analogy with other reactions,<sup>9,10</sup> this is probably the most reasonable hypothesis, but the data do not exclude somewhat larger isotope effects for the bridging proton. This could still be consistent with a solvation bridge (which might have a different character and thus a larger isotope effect near a second-row center like silicon), although it might also indicate some participation of the bridging proton in the reaction coordinate.

### Experimental Section

**Materials.** Solutions in  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$  were prepared and manipulated as before.<sup>1,13</sup> *p*-Chlorophenoxytriphenylsilane was synthesized following a procedure similar to that which Gerrard and Kilburn<sup>14</sup> used to prepare *m*-trifluoromethylphenoxytriphenylsilane. Recrystallization from diethyl ether gave the silane in 87% yield, mp 96–98°. *Anal.* Calcd for  $\text{C}_{21}\text{H}_{19}\text{SiOCl}$ : C, 74.50; H, 4.95. Found: C, 74.09; H, 5.09. *p*-Methoxyphenoxytriphenylsilane was obtained from Schowen.<sup>6</sup>

**Kinetic Procedure.** Concentrated stock solutions of silanes in dioxane were prepared. Ten microliters of the silane solutions was transferred into the thermostatted cuvet of a Beckman DBG spectrophotometer, and then 2.6 ml of base solutions containing added  $\text{LiClO}_4$  (0.1500 *M*) was injected rapidly. Wavelengths used for following the kinetic progress of reaction were 284 nm for *p*-chlorophenoxytriphenylsilane and 290 nm for *p*-methoxyphenoxytriphenylsilane.

(14) W. Gerrard and K. D. Kilburn, *J. Chem. Soc.*, 1536 (1956).

## Photoelectron Spectra of Hydrazines. IV. Empirical Estimation of Lone Pair–Lone Pair Dihedral Angles and Prediction of Lone Pair Ionization Potentials for Some Cyclic and Bicyclic Hydrazines

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**Abstract:** The curve calculated for the difference in lone pair ionization potentials ( $\Delta$ ) as a function of the lone pair–lone pair dihedral angle ( $\theta$ ) using INDO calculations on idealized tetramethylhydrazine is presented, and scaling to give more realistic  $\theta$  angles from experimental spectra is discussed. The changes in  $\Delta(\theta)$  expected for flattening of the nitrogens from tetrahedral geometry have been calculated. The spectra of five cyclic dialkylhydrazines are given, from which empirical parameters are derived which are used to calculate the average ionization potentials for 12 cyclic tetraalkylhydrazines. These calculations were fairly successful for cyclic hydrazines, showing  $\Delta$  values less than 1 eV, but not satisfactory for tetraalkylhydrazines having large  $\Delta$  values.

Rademacher<sup>1</sup> and we<sup>2</sup> have noted that, since the amount of interaction between the lone pair electrons of a hydrazine should be dependent upon the dihedral angle  $\theta$  between the lone pair orbital axes,

(1) (a) P. Rademacher, *Angew. Chem.*, **85**, 410 (1973); (b) P. Rademacher, *Tetrahedron Lett.*, 83 (1974).

(2) (a) S. F. Nelsen and J. M. Buschek, *J. Amer. Chem. Soc.*, **95**, 2011 (1973); (b) *ibid.*, **95**, 2013 (1973); (c) *ibid.*, **96**, 2392 (1974).

photoelectron spectroscopy (pes) should be of use in determination of hydrazine conformations. As Hoffmann<sup>3</sup> has pointed out, the lone pair orbitals will interact to form two molecular orbitals, of which the symmetric lone pair combination ( $n_+$ ) will be bonding and hence lower in energy (higher in ionization poten-

(3) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).