of the nitro derivatives. In summary, the rate acceleration by large R groups is less for the nitro than for the nitroso compounds because of the extra and special interaction of the R group and the nearest oxygen atom of the NO_2 group in the transition state; in the case of substitution by *t*-alkyl groups, this factor appears to be very important indeed. It would be interesting to see whether a similar effect occurs in the decomposition of N-nitroamides of tertiary carbinamines.

Acknowledgment. We wish to thank Professor Brown Murr for helpful discussions and the Army Research Office (Durham) for its support of this work (Grant DA ARO(D) 31-124-G18).

Classical General Base Catalysis of Silicon–Oxygen Bond Cleavage[1]

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Contribution from the Department of Chemistry, University of Kansas, Lawrence, Kansas. *Received March 7, 1966*

Abstract: Phenoxytriphenylsilane (I) reacts with appropriately buffered solutions of methanol to form phenol and methoxytriphenylsilane according to the kinetic law given in eq 1, where k_1, k_2, and k_3 exhibit a Brønsted correlation with $\beta = 0.7 \pm 0.2$. The results are consistent with classical (proton transfer) general base catalysis but not with nucleophilic catalysis.

It has been shown by Åkerman[2] that aryloxysilanes undergo both acid- and base-catalyzed solvolyses in aqueous ethanol but react only very slowly, if at all, in neutral solutions. The base-catalyzed solvolysis could proceed, in buffered solution, according to any of four mechanisms formulated below. Several variations on each of these mechanisms may be generated by considerations of the rate-determining step and the possible intermediacy of higher coordination number derivatives of silicon.[3] Mechanism I can be distinguished from the other mechanisms since it is the only one which would show specific base catalysis. Mechanisms II, III, and IV are analogous to the nucleophilic catalysis (II), classical general base catalysis (III), and inverse classical general base catalysis (IV) mechanisms well known in the solvolysis of carboxylate derivatives.[4] We wish to report data which permit the closer specification of the mechanism for cleavage of the silicon–oxygen bond under these conditions.

Mechanism I

$$B + ROH \rightleftharpoons BH^+ + RO^- \quad \text{(rapid)}$$

$$RO^- + R_3SiOAr \longrightarrow R_3SiOR + ArO^-$$

$$BH^+ + ArO^- \longrightarrow B + ArOH \quad \text{(rapid)}$$

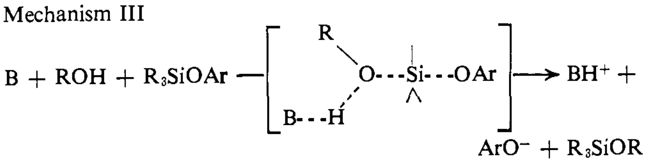
Mechanism II

$$B + R_3SiOAr \longrightarrow R_3SiB^+ + ArO^-$$

$$R_3SiB^+ + HOR \longrightarrow BH^+ + R_3SiOR$$

$$BH^+ + ArO^- \longrightarrow B + ArOH \text{ (rapid)}$$

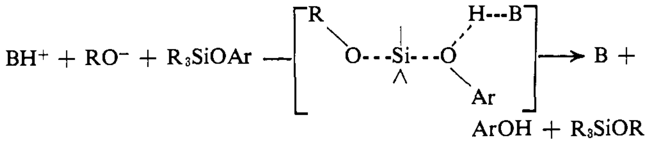
Mechanism III



$$ArO^- + BH^+ \longrightarrow B + ArOH \quad \text{(rapid)}$$

Mechanism IV

$$B + ROH \rightleftharpoons BH^+ + RO^- \quad \text{(rapid)}$$



Results

Table I shows observed and calculated rate constants for the methanolysis of phenoxytriphenylsilane (I) in

Table I.[a] Base-Catalyzed Methanolysis of Phenoxytriphenylsilane at 27.4 ± 0.1°

Buffer system	[B], *M*	[BH], *M*	$[CH_3O^-]$, *M*	10^6k_{obsd}, sec^{-1}	10^6k_{calcd}, sec^{-1}
Acetate-acetic acid	0.0500	0.0100	2.50×10^{-7}	1.81	1.87
	0.1000	0.0200	2.50×10^{-7}	2.06	2.15
	0.1500	0.0300	2.50×10^{-7}	2.39	2.43
	0.0500	0.0050	5.01×10^{-7}	3.37	3.23
	0.1000	0.0100	5.01×10^{-7}	3.60	3.51
	0.1500	0.0150	5.01×10^{-7}	3.92	3.89
	0.0500	0.0033	7.51×10^{-7}	4.83	4.85
	0.1000	0.0067	7.51×10^{-7}	5.30	5.13
	0.1500	0.0100	7.51×10^{-7}	5.78	5.41
Phenoxide-phenol	0.0005	0.0100	1.15×10^{-4}	1020	1010
	0.0010	0.0200	1.15×10^{-4}	1200	1195
	0.0020	0.0400	1.15×10^{-4}	1580	1570

[a] Ionic strength brought to 0.1500 *M* with $LiClO_4$ in all runs. Uncertainties in observed rate constants are about ±5%.

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[2] E. Åkerman, *Acta Chem. Scand.*, **10**, 298 (1956); **11**, 373 (1957).

[3] L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

[4] M. L. Bender, *Chem. Rev.*, **60**, 53 (1960).

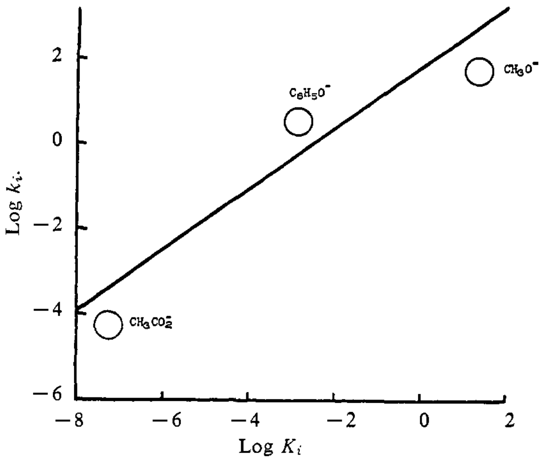


Figure 1. Brønsted catalysis law plot for the methanolysis of phenoxytriphenylsilane. The apparently enhanced catalytic efficiency of phenoxide ion may indicate a π-complexing interaction of this species (becoming less electron rich in the transition state) with the leaving group, which may be increasing in electron density.

methanol buffers at 27.4 ± 0.1° to yield methoxytriphenylsilane and phenol. The calulated rate constants were obtained from eq 1 with the values of the

$$-d[I]/dt = k_{obsd}[I] = [I]\{k_0 + k_1[CH_3CO_2^-] + k_2[C_6H_5O^-] + k_3[CH_3O^-]\} \quad (1)$$

parameters shown in Table II. The results indicate general base catalysis by both acetate and phenoxide ions.

Table II. Rate Constants for Various Catalyzing Bases in the Methanolysis of Phenoxytriphenylsilane

Base	Rate constant, k_i	K_i,[a] M
(−)[b]	2×10^{-6} sec^{-1} (k_0)	(−)
$CH_3CO_2^-$	$5.6 \pm 0.6 \times 10^{-5}$ M^{-1} sec^{-1} (k_1)	$10^{-7.30}$[c]
$C_6H_5O^-$	3.7 ± 0.4 M^{-1} sec^{-1} (k_2)	$10^{-2.66}$[d]
CH_3O^-	60 ± 7 M^{-1} sec^{-1} (k_3)	$10^{+1.39}$[e]

[a] Equilibrium constants for the reaction $B + CH_3OH = BH^+ + CH_3O^-$, corrected to units of M. [b] This small term presumably originates in catalysis by solvent or by impurities. [c] T. Shedlovsky and R. C. Kay, *J. Phys. Chem.*, **60**, 155 (1956). [d] The pK_a of phenol under our conditions (ionic strength 0.15 M) was determined spectrophotometrically as 14.26. This compares with 15.3 ± 0.5 found by England and House and 14.0 found by Kolthoff and Guss, both at zero ionic strength (footnote *e* of this table). [e] B. D. England and D. A. House, *J. Chem Soc.*, 4421 (1962); *cf.* E. Grunwald and E. Price, *J. Am. Chem. Soc.*, **86**, 4517 (1964); I. M. Kolthoff and L. S. Guss, *ibid.*, **61**, 330 (1939).

Discussion

The observation of general base catalysis eliminates mechanism I from consideration since it predicts specific catalysis. The particular observation that phenoxide ion as a general base catalyzes the displacement of phenoxide ion as a leaving group also eliminates nucleophilic catalysis (II) since such a reaction would merely regenerate the starting materials. The reaction mechanism must therefore be classical general base catalysis (III or IV). Our results prove that a molecule of methanol is present in the activated complex but do not distinguish rigorously the activated complexes of III and IV, which are geometric isomers.

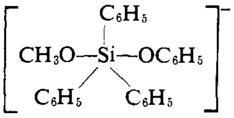
Brønsted Catalysis Law. Figure 1 demonstrates that the rate constants of eq 1 are roughly correlated by the Brønsted catalysis law[5] (eq 2) with $\beta = 0.7 \pm 0.2$.

$$\log k_i = \beta \log K_i + c \quad (2)$$

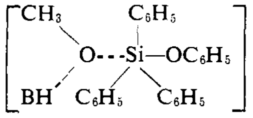
Since phenoxide ion exhibits the rate constant predicted by this equation, we conclude that the *entire* reaction proceeds by proton-transfer catalysis, the possibility of a mixture of nucleophilic and proton-transfer catalysis (in which case phenoxide would possess an inferior catalytic efficiency) being thus excluded.

The value of β may be interpreted[6] as indicating that the catalyzing base is approximately 70% protonated in the activated complex. This is a case in which the "solvation rule"[6b] presumably is applicable and indicates that the site to which the BH moiety of the activated complex is hydrogen bonding is considerably less basic than the average catalyzing base, the proton thus assuming a position nearer the catalyst. We are engaged in the measurement of kinetic isotope effects designed to test this hypothesis.

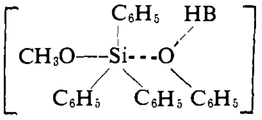
Transition-State Structure. As was indicated above, several variations on the mechanisms shown are generated by consideration of expanded-octet intermediates[3,7] for this reaction. While our results do not bear directly on this question, certain related conclusions are possible. If addition of methanol or methoxide ion to the silicon atoms occurs, the major form (after acid–base equilibration) of the quinquevalent silicon intermediate will be the ion II, which can be visualized as returning to reactants with BH catalysis *via* activated complex III, or proceeding on to products with BH catalysis *via* activated complex IV. Either of these structures corresponds to development of some negative charge on an oxygen atom: that of the methoxyl group in III, that of the phenoxy group in IV.



II



III



IV

The value of β indicates that little of this electron density is discharged onto BH. Since the charge is almost surely more stable in the phenoxy group, IV is almost surely a lower energy structure than III. This produces the conclusion that *if an addition intermediate is formed along the reaction path, its formation* (activated complex III) *is rate determining*.

If, on the other hand, the reaction is concerted, the choice between mechanisms III and IV will be decided by the relative basicities of the two oxygens in the activated complexes: the BH moiety will "solvate" the methoxyl oxygen (III) if the entering-group bond is

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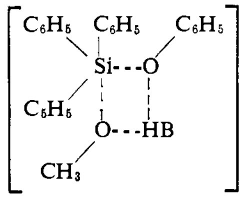
(5) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 218 ff.

(6) (a) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 238–241; (b) C. G. Swain, D. A. Kuhn, and R. L. Schowen, *J. Am. Chem. Soc.*, 87, 1553 (1965).

(7) C. G. Swain, R. M. Esteve, and R. H. Jones, *ibid.*, 71, 965 (1949).

less formed than the leaving-group bond is broken, whereas the phenoxy oxygen will be "solvated" (IV) if the reverse is true. Application of the Swain–Thornton reacting-bond rule[8] predicts the leaving-group bond to be stronger than the entering-group bond, thus favoring mechanism III. On balance, this mechanism would seem likelier than IV, with the strength of the silicon leaving-group bond (full or partial bond) being undecided by data available now. Such conclusions are in accord with the isotope-effect data previously reported by Swain.[9]

Structures III and IV are based on the assumption of 180- or 120°-flank displacement of the leaving group by the entering group, which appears the most reasonable formulation in view of the discovery of Baker, Bott, Eaborn, and Jones[10] that every act of substitution is accompanied by an act of stereochemical inversion at silicon in the methoxyl-exchange reaction of methoxy(methyl-α-naphthylphenyl)silane with solvent methanol. As a referee has kindly pointed out, 90°-flank displacement[3] could proceed through an activated complex such as V, in which simultaneous interaction of the catalyst with entering and leaving groups is possible. The generally observed sensitivity of the stereochemical pathway of organosilicon reactions to environmental and structural details[3] would be consistent with the existence of a number of mechanisms, their energetic hierarchy being variable with conditions.



V

It is our hope that studies now in progress will result in a full elucidation of this system.

Experimental Section

Materials. Buffer Solution Components. Lithium perchlorate (G. Frederick Smith Chemical Co.) and sodium acetate (Matheson Coleman and Bell), each being anhydrous reagent grade, were dried at 100° for 48 hr and stored over silica gel. Glacial acetic acid (Fisher), phenol (Mallinckrodt analytical reagent), and absolute methanol (Fisher; Mallinckrodt) were reagent grade and used with no additional purification. Sodium methoxide solutions were prepared by dissolving freshly cut sodium in methanol and standardized against Baker and Adamson primary standard potassium hydrogen phthalate.

Phenoxytriphenylsilane was prepared by distillation of ethanol from a refluxing mixture of ethoxytriphenylsilane (Anderson Chemical Co.), phenol, and sodium, according to the method by Larsson,[11] mp 105° (lit.[12] mp 103–04°).

Kinetic Procedure. A. Acetate Buffers. Reaction rates were determined spectrophotometrically by following the increase in absorbance at 271.8 mμ, using a Cary Model 14 spectrophotometer. The reaction solutions were thermostated at 27.4° in a water bath, samples being periodically withdrawn for ultraviolet absorption analysis.

B. Phenoxide Buffers. Thermostated stock solutions (5 ml each) of phenoxide buffer and silane were mixed in a 50-ml flask and quenched after the desired reaction time in 20 ml of cyclohexane, 10 ml of aqueous NaOH solution being present to extract the phenol–phenoxide buffer. Further extractions with 10 ml of dilute HCl and with 5 ml of water were followed by drying with anhydrous sodium sulfate. The decrease in phenoxytriphenylsilane concentration was followed by measuring the absorption decrease at 266 mμ of the cyclohexane solution. Control experiments showed the separation to be quantitative and rate constants to be identical to those determined by method A above.

pK_a of Phenol. The dissociation constant of phenol in methanol was determined spectrophotometrically by the method of Stearns and Wheland;[13] their equation was fitted by an iteration procedure using an IBM 7040 electronic computer. A value of $pK_a = 14.26$ was obtained for an ionic strength of 0.15 *M*, duplicating the methanolysis reaction conditions.

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[8] C. G. Swain and E. R. Thornton, *J. Am. Chem. Soc.*, **84**, 817 (1962).

[9] C. G. Swain, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1963.

[10] R. Baker, R. W. Bott, C. Eaborn, and P. W. Jones, *J. Organometal. Chem.*, **1**, 37 (1963).

[11] E. Larsson, *Chem. Ber.*, **86**, 1382 (1953).

[12] H. Gilman and G. N. R. Smart, *J. Org. Chem.*, **19**, 441 (1954).

[13] R. S. Stearns and G. W. Wheland, *J. Am. Chem. Soc.*, **69**, 2025 (1947).