

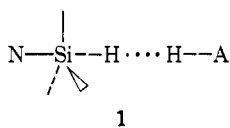
Proton Inventory of the Transition State for Hydride Expulsion from Silicon^{1,2}

Clinton R. Howie,³ J. K. Lee, and R. L. Schowen*⁴

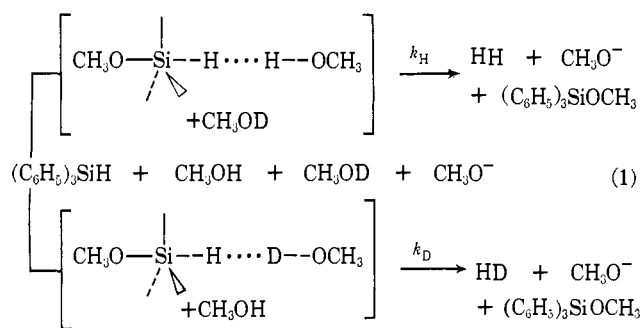
Contribution from the Department of Chemistry, University of Kansas, Lawrence, Kansas 66044. Received September 25, 1972

Abstract: The product ratio HH/HD from methoxide-catalyzed methanolysis of $(C_6H_5)_3SiH$ in binary mixtures of CH_3OH (mole fraction $1 - n$) and CH_3OD (mole fraction n) shows the primary isotope effect for proton donation from solvent methanol to be $k_H/k_D = 6 \pm 1$. Rate constants k_n in the mixed solvents are described by $k_n = k_0(1 - n + 0.17n)(1 - n + 1.1n)^2/(1 - n + 0.74n)^3$, indicating the transition state to contain, in addition to the proton-donor solvent molecule, two additional methanols with somewhat tighter OH bonds than in bulk methanol.

In our recent study¹ of catalysis in the expulsion of the very poor leaving group hydride ion (H^-) from silicon, we adjudged the transition state (1) to contain



a very strong (perhaps complete) bond from silicon to the nucleophile N (as evidenced by the large accelerations induced by electron-withdrawing substituents on silicon), a scarcely broken silicon-hydrogen bond (small k_{SiH}/k_{SiD} in combination with the substituent effect), and a still quite strong H-A bond in the electrophile which participates in formation of the product hydrogen (lack of observable general catalysis). One of the interesting features of those results was that, although proton donation from A to the hydridic hydrogen was so little advanced that general catalysis was not detected, a fairly large normal isotope effect (we thought about 4.5) seemed to be required for this proton by the rates in mixed isotopic solvents. Such a large effect for a quite "asymmetric" transition state is of concern in current interpretations of primary isotope effects.⁵



(1) Catalysis in Organosilicon Chemistry. IV. For part III, see K. O'Donnell, R. Bacon, K. L. Chellappa, R. L. Schowen, and J. K. Lee, *J. Amer. Chem. Soc.*, **94**, 2500 (1972).

(2) This research was supported by the National Science Foundation. Data reduction was carried out in the Computation Center of the University of Kansas. Further information is available in C. R. Howie, M.S. Thesis in Chemistry, University of Kansas, 1971.

(3) Education Professions Development Act Fellow.

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

(5) E. K. Thornton and E. R. Thornton in "Isotope Effects in Chemical Reactions," C. J. Collins and N. S. Bowman, Ed., Van Nostrand-Reinhold, New York, N. Y., 1970, pp 238-246.

This isotope effect need not be extracted from the rate measurements, however, because it is susceptible to independent determination. In a mixture of CH_3OH (mole fraction $1 - n$) and CH_3OD (mole fraction n), the methoxide-ion catalyzed methanolysis of triphenylsilane will lead to two products, HH and HD, formed with rate constants k_H and k_D , respectively (eq 1). If the composition of the product gas is then measured, the isotope effect can be calculated (eq 2) as the ratio

$$k_H/k_D = (X_{HH}/X_{HD})/[(1 - n)/n] \quad (2)$$

of product and reactant protium-deuterium ratios. We report here the results of experiments directed toward this end.

Results

The hydrogen evolved during the basic methanolysis of triphenylsilane in mixtures of CH_3OH and CH_3OD was analyzed isotopically by vapor-phase chromatography.⁶ The molar ratios and isotope effects obtained at three different isotopic solvent compositions are given in Table I. It should be noted that the precision of the results at $n = 0.256$ and $n = 0.501$ is far better than the large error limits cited for the product molar ratios and resulting isotope effects. The error limits are so high because at these solvent compositions, the product isotope ratio is large and the vapor-phase chromatogram consists of one big peak and one small peak. Planimetry of the latter is quite reproducible but likely to involve a considerable absolute error, which is included in the error estimate. Furthermore, the molar ratio is itself derived from the area ratio by use of a calibration curve. Because of the difficulty of accurate area measurements with small peaks, the calibration curve is error-laden at large ratios, and this effect also appears in the cited limits. Thus, while the data may exhibit a slight dependence of the isotope effect on the solvent composition, no reliable conclusion about this can be drawn. From Table I, it is, however, clear that $k_H/k_D = 6 \pm 1$. A rough mass spectrometric determination of the product HH/HD ratio at $n = 0.33$, 0.50, and 0.67 gave $k_H/k_D = 5.3$, 7.5, and 6.3, in general agreement with the vpc findings.

Discussion

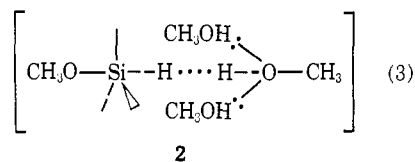
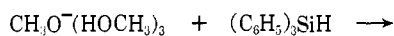
The activation process in the basic methanolysis of silanes (eq 3) involves the conversion of the triply-

(6) C. Genty and R. Schott, *Anal. Chem.*, **42**, 7 (1970).

Table I. Isotope Effects for Reaction of 0.0677 M Triphenylsilane with Binary Mixtures of CH₃OH and CH₃OD (mole fraction *n*) Containing 0.1690 M Sodium Methoxide and 0.0500 M Lithium Perchlorate at 25.00 ± 0.05°

<i>n</i> ^a	(1 - <i>n</i>)/ <i>n</i> ^a	<i>X</i> _{HH} / <i>X</i> _{HP} ^b	<i>k</i> _H / <i>k</i> _D ^b
0.256	2.91	17.18 ± 3.1	5.9 ± 1.3
0.256	2.91	17.00 ± 3.5	5.9 ± 1.4
0.256	2.91	17.00 ± 3.5	5.9 ± 1.4
0.256	2.91	16.83 ± 3.3	5.8 ± 1.5
0.256	2.91	16.74 ± 6.6	5.8 ± 2.5
0.256	2.91	16.74 ± 6.6	5.8 ± 2.5
0.256	2.91	16.74 ± 6.6	5.8 ± 2.5
0.256	2.91	16.74 ± 6.6	5.8 ± 2.5
0.256	2.91	16.70 ± 3.1	5.8 ± 1.3
0.256	2.91	16.70 ± 3.1	5.8 ± 1.3
0.256	2.91	16.42 ± 3.6	5.7 ± 1.5
0.501	0.995	6.20 ± 0.6	6.2 ± 0.9
0.501	0.995	6.09 ± 1.1	6.1 ± 1.4
0.501	0.995	6.07 ± 0.9	6.1 ± 1.2
0.501	0.995	6.07 ± 0.9	6.1 ± 1.2
0.501	0.995	6.00 ± 0.8	6.0 ± 1.2
0.501	0.995	5.91 ± 1.0	5.9 ± 1.3
0.501	0.995	5.84 ± 0.8	5.9 ± 1.0
0.501	0.905	5.78 ± 1.1	5.8 ± 1.3
0.501	0.995	5.70 ± 0.8	5.7 ± 1.0
0.501	0.995	5.69 ± 0.8	5.7 ± 1.0
0.763	0.311	2.12 ± 0.09	6.8 ± 0.6
0.763	0.311	2.08 ± 0.19	6.8 ± 0.9
0.763	0.311	2.08 ± 0.05	6.8 ± 0.4
0.763	0.311	2.03 ± 0.08	6.5 ± 0.5
0.763	0.311	2.03 ± 0.08	6.5 ± 0.5
0.763	0.311	2.03 ± 0.07	6.5 ± 0.5
0.763	0.311	2.03 ± 0.07	6.5 ± 0.5
0.763	0.311	1.99 ± 0.08	6.4 ± 0.5
0.763	0.311	1.99 ± 0.08	6.4 ± 0.5
0.763	0.311	1.99 ± 0.08	6.4 ± 0.5

^a Error limits for *n* and [(1 - *n*)/*n*] are respectively: 0.256 ± 0.005, 2.91 ± 0.12; 0.501 ± 0.010, 0.995 ± 0.040; 0.763 ± 0.015, 0.311 ± 0.012. ^b See text for explanation of error limits.



solvated⁷ methoxide ion (for the solvation shell of which the isotopic fractionation factor^{7a,c,d} $\phi_i \equiv ([\text{D}]_i/[\text{H}]_i/(n/[1 - n]))$ is 0.74) and triphenylsilane (for the solvation shell of which we take $\phi = 1$) into the transition state 2. The central methanol of the hydrogen-bonded trimer in 2 is donating its proton ("proton-transfer bridge") to the forming hydride ion. The other two methanols are solvating the lone pairs of the forming methoxide ion. Now the rate constant *k*_n in mixed isotopic methanols (mole fraction *n* of CH₃OD) for such a reaction will be given by eq 4, where ϕ^* is the

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

isotopic fractionation factor for the bridge proton in 2 and ϕ_m is for each of the lone-pair solvators (assumed to be equivalent). The denominator of the right-hand

(7) Reaction rates and equilibria in mixed isotopic solvents were reviewed by (a) A. J. Kresge, *Pure Appl. Chem.*, **8**, 243 (1964); and (b) V. Gold, *Advan. Phys. Org. Chem.*, **7**, 259 (1969). Mixtures of CH₃OH and CH₃OD: (c) R. A. More O'Ferrall, *Chem. Commun.*, 114 (1969); (d) V. Gold and S. Grist, *J. Chem. Soc. B*, 1665, 2272, 2282, 2285 (1971); (e) C. R. Hopper, R. L. Schowen, K. S. Venkatasubban, and H. Jayaraman, *J. Amer. Chem. Soc.*, **95**, 3280 (1973).

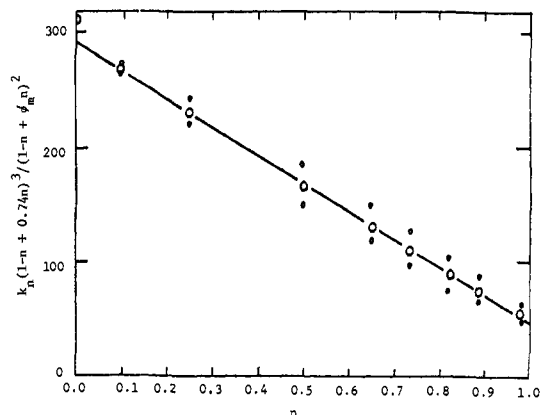


Figure 1. Plot of the left-hand side of eq 5, with $\phi_m = 1.0$ (uppermost set of points), $\phi_m = 1.1$ (middle set of points with solid line) and $\phi_m = 1.2$ (lowermost set of points) vs. mole fraction *n* of CH₃OD in binary mixtures of CH₃OH and CH₃OD. Only the curve with $\phi_m = 1.1$ is linear. From its slope and intercept, $\phi^* = 0.17$, whence the bridge primary isotope effect of 5.9.

side of eq 4 describes the effect of the solvated methoxide ion.⁷ Equation 4 can be rearranged to eq 5

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

where, if a trial value of ϕ_m is taken, the left-hand side is completely known. Further, if this ϕ_m is correct, a plot of the left-hand side vs. *n* will be linear and ϕ^* can be calculated from the slope and intercept. If the chosen value of ϕ_m is not correct, the plot will be nonlinear. Figure 1 shows that the choice of $\phi_m = 1.1$ yields a linear function, while values of $\phi_m = 1.0$ and 1.2 produce curved plots. Most conclusively of all, ϕ^* is then found to be 0.17 which gives, for the bridging proton in 2, $k_H/k_D (\equiv \phi^{*-1}) = 5.9$. This isotope effect, in exact agreement with the value of 6 ± 1 determined from competition experiments, confirms the description of 2 with $\phi^* = 0.17$ for the bridge and $\phi_m = 1.1$.

The most impressive characteristics of this transition-state proton inventory are: (1) the large primary isotope effect of 6 for transfer of a proton in an activated complex so reactant-like that no general catalysis is detectable,¹ and (2) the fractionation factors larger than unity required for the solvating methanols, indicating their OH bonds to be tighter than in bulk methanol. The primary effect may be indicative of tunneling⁵ or of a large vibrational coupling in the activated complex⁵ but nothing beyond speculation is suggested by available data. As for the solvating methanols, it may be that donation of the proton by the donor solvent molecule in the activated complex occasions its sudden motion away from its two partners, leaving them stranded in a nonequilibrium, "gas-like," un-hydrogen-bonded state, which could produce effects of about this magnitude.⁸ Otherwise, a value for ϕ_m between 1.0 (unperturbed solvent methanol) and 0.74 (solvation shell of methoxide ion) would be expected. We have already observed other cases in which these unusually large fractionation factors arise in the solvation shell of an electrophilically active methanol molecule. Until more

(8) See the discussion of nonequilibrium solvation of activated complexes and its implications by J. L. Kurz and L. C. Kurz, *J. Amer. Chem. Soc.*, **94**, 4451 (1972).

thorough investigation of reactant-state solvation is undertaken, however, no dogmatic position on this point can be taken.

Experimental Section

Materials. Lithium perchlorate (anhydrous reagent, G. Frederick Smith) was used as obtained. All organosilicon compounds were supplied by Peninsular Chem Research. Triphenylsilane was recrystallized twice from 95% ethanol (mp 44.5–45.5°, lit.⁹ 44–45°). Methanol (anhydrous, A.C.S. Analyzed Reagent from Matheson Coleman and Bell) was purified by the method of Lund and Bjerrum.¹⁰ Methanol-*d* (Diaprep, Inc.) was purified by distilling it slowly through a 48-cm Vigreux column packed with glass beads, using a Drierite tube to guard against moisture. Triphenylsilane-*d* was prepared by the procedure of Gilman and Dunn.¹¹

Gas Ratio Measurements. The molar ratio of gases HH and HD evolved in the reaction of R_3SiH with methanol of varying isotopic composition was determined by gas chromatography⁶ followed by combustion of the hydrogen sample to water and thermal-conductivity measurement of the ratio of HHO to HDO. A calibration curve was constructed by analysis of known mixtures of HH and HD, produced by complete methanolysis of known mixtures of $(C_6H_5)_3SiH$ and $(C_6H_5)_3SiD$. These mixtures were prepared volumetrically from stock solutions or gravimetrically. Measurements were made on a F&M Laboratory Chromatograph Model 700.

(9) H. Gilman and H. W. Melvin, Jr., *J. Amer. Chem. Soc.*, **71**, 4050 (1949).

(10) H. Lund and I. Bjerrum, *Ber.*, **64**, 210 (1931).

(11) H. Gilman and G. E. Dunn, *J. Amer. Chem. Soc.*, **73**, 3404 (1951).

The system consisted of a stripper column, separation column, combustion furnace, and detector. The stripper column functioned to remove air and methanol vapor from the sample so that only H_2 and HD enter the separation column. For this purpose, 10 ft of 0.25 in. o.d. copper tubing was packed with Johns Manville Chromosorb P (60–80 mesh) and maintained at -40° in an acetone–Dry Ice bath. For use in the separation column, ferric oxide-coated alumina packing was prepared according to the procedure of Shipman.¹² Ferric chloride solution (1.8 *M*) was added in increments with stirring to 200 ml of alumina (Varian, 60–80 mesh) until the alumina was dampened. Distilled water (250 ml) was added and the mixture was treated with 6 *M* ammonium hydroxide to pH 7. After settling, the excess solution was decanted, and the precipitate was filtered and washed with water until the pH of the washings was 6. The product was dried in an oven at 120° for 36 hr. Copper tubing (6 ft of 0.25 in. o.d.) was coiled in 4-in. diameter coils so that it would fit comfortably in a 4-l. dewar flask. It was packed with the ferric oxide-coated alumina and deactivated with a slow stream of carbon dioxide (about 2 cc/min) until barium hydroxide showed the passage of carbon dioxide. The column was then conditioned under flowing helium for 6 hr, and operated at -196° . The combustion furnace consisted of an 8-in. length of 0.25 in. o.d. quartz tubing packed with copper oxide, wrapped in asbestos, and placed in an 8-in. Hevi Duty combustion furnace at 700° . Connections were made by means of small stainless steel tubes and high-temperature rubber plugs. The tubing outlet to the detector was heated by means of heating tapes to prevent condensation of water.

(12) G. F. Shipman, *Anal. Chem.*, **34**, 877 (1962).

σ -Sulfurane Chemistry. Effect of Substituents on the Coupling Reactions

Barry M. Trost*¹ and Henry C. Arndt

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. Received January 22, 1973

Abstract: The reaction of *S*-aryldibenzothiophenium fluoroborates with aryllithiums reveals the ratio of formation of biaryl and dibenzothiophene (path A) compared with 2-arylthio-*o*-terphenyl (path B) which depends upon substituents. Electron-withdrawing substituents favor the former, whereas electron-donating substituents favor the latter. Similarly, styrene and dibenzothiophene formation predominates over 2-vinyl-2'-arylthiobiphenyl and/or 2-arylthio-*o*-terphenyl formation in the reaction of the above salts with vinylithium when electron-withdrawing groups are present in the *S*-aryl group. Treatment of *S*-phenyldibenzothiophenium fluoroborate with aryllithiums and of *S*-aryldibenzothiophenium fluoroborates with phenyllithium produces the same product mixture and one in which aryl–aryl coupling has occurred preferentially between the two rings which bear the most electron-withdrawing group. Interpretation of these results in terms of the tetraarylsulfuranes as intermediates is presented.

The valence shell expansion of sulfur continues to be invoked as an explanation of the many reactions occurring at sulfur. Most of these reactions involve oxidation at sulfur, and in some cases, the σ sulfurane achieves enough stability to be isolated.^{2–4} The im-

portance of these intermediates grows as their applications in problems of organic synthesis expand. Whereas it is perhaps not too surprising that such intermediates possessing strongly electronegative groups on

(1) Camille and Henry Dreyfus Teacher–Scholar Grant Recipient.
 (2) For example, see C. R. Johnson and J. J. Rigaw, *J. Amer. Chem. Soc.*, **91**, 5398 (1969); V. Calo, G. Scorrano, and G. Modena, *J. Org. Chem.*, **34**, 2020 (1969); D. C. Owsley, G. K. Helmkamp, and M. F. Rettig, *J. Amer. Chem. Soc.*, **91**, 5239 (1969); G. E. Wilson, Jr., and M. M. Yang Chang, *Tetrahedron Lett.*, 875 (1971).
 (3) (a) J. C. Martin and R. J. Arhart, *J. Amer. Chem. Soc.*, **94**, 2339, 2341, 4327 (1971); (b) R. J. Arhart and J. C. Martin, *ibid.*, **94**, 4997, 5003 (1972); (c) E. F. Perozzi and J. C. Martin, *ibid.*, **94**, 5519 (1972); (d) I. Kapovits and A. Kalman, *Chem. Commun.*, 649 (1971).
 (4) For other related work, see (a) C. R. Johnson, C. C. Bacon, and W. D. Kingsbury, *Tetrahedron Lett.*, 501 (1972); (b) N. C. Baenziger,

R. E. Buckles, R. J. Maner, and T. D. Simpson, *J. Amer. Chem. Soc.*, **91**, 5749 (1969); (c) J. W. Knapczyk and W. E. McEwen, *ibid.*, **91**, 145 (1969); (d) G. H. Wiegand and W. E. McEwen, *J. Org. Chem.*, **33**, 2671 (1968); (e) W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **92**, 2731 (1970); (f) D. J. Cram, J. Day, D. R. Rayner, D. M. von Schultz, D. J. Duchamp, and D. C. Garwood, *ibid.*, **92**, 7369 (1970); (g) M. G. Burdeen and J. G. Moffatt, *ibid.*, **89**, 4725 (1967); (h) E. J. Corey and T. Drust, *ibid.*, **90**, 5553 (1968); (i) E. Ciuffarin and G. Guaraldi, *ibid.*, **91**, 1745 (1969); (j) T. J. Barton and R. G. Zika, *J. Org. Chem.*, **35**, 1729 (1970); (k) K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *J. Amer. Chem. Soc.*, **86**, 1452 (1964); (l) D. Landini, F. Montanari, H. Hogeveen, and G. Maccagnani, *Tetrahedron Lett.*, 2691 (1964); (m) R. M. Rosenberg and E. L. Muetterties, *Inorg. Chem.*, **1**, 756 (1962).