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EVIDENCE FOR PROTON TRANSFER CONCOMITANT WITH HYDRIDE EXPULSION FROM SILANES

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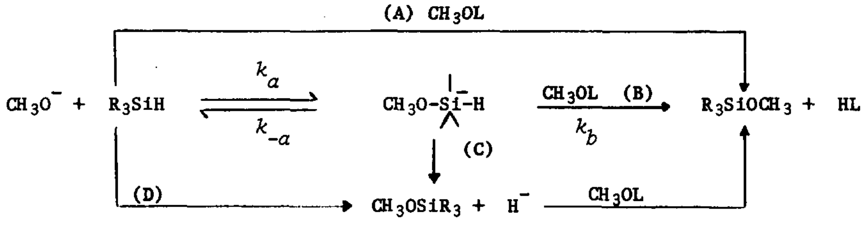
In protic solvents containing base, silanes decompose to form hydrogen concurrently with solvolytic substitution at silicon (1). Overall, a new bond to silicon is formed, a silicon-hydrogen bond is broken and a proton is abstracted from solvent. These three processes may occur with varying degrees of microscopic simultaneity, as summarized by the four mechanistic possibilities A to D of Scheme I for the basic methanolysis of triorganosilanes. Mechanism A represents a completely concerted reaction, B prior formation of the new bond to silicon followed by hydride expulsion concerted with proton abstraction, C prior formation of the same pentavalent-silicon intermediate but with stepwise hydride expulsion and proton abstraction and D the concerted displacement of hydride ion followed by proton abstraction. In both C and D, it is assumed that the expelled hydride ion would more rapidly remove a proton from solvent than seek out and react with the product methoxysilane so that its formation can be taken as irreversible. It is also assumed that hydride ion, if formed, would be a steady-state intermediate.

Scheme I



Kaplan and Wilzbach (2), using a competitive method (comparison of product and solvent isotope ratios), measured solvent tritium isotope effects (k_H/k_T = 3-7 in aqueous piperidine and ethanol), which are consistent with primary isotope effects for proton transfer (3) but do not distinguish the possibilities of Scheme I. Whenever proton transfer occurs, selection between isotopic solvent molecules will be observed in a competition experiment. A measured ratio of first-order rate constants k_H/k_D = 1.44, for R = n-C_3H_7 in ethanol with 3.47 *M* water and 0.53 *M* KOH *vs* an otherwise identical system with 95% deuterium in exchangeable positions, cannot be interpreted because of the complexity of the medium and unknown secondary effects. Both deuterium and tritium isotope effects at the hydride position (R_3SiH *vs* R_3SiD or R_3SiT) are normal but less than 1.5 (2,4) so that they may be either secondary or primary effects and again do not distinguish Mechanisms A-D.

Table I shows our measurements of the second-order rate constants for methoxide-catalyzed methanolysis of triphenylsilane in mixtures of CH_3OH and CH_3OD. These values were obtained from plots of methoxide-ion concentration *vs* observed first-order rate constants so that each tabulated constant represents 9-15 kinetic runs at sodium methoxide concentrations from 0.01 to 0.04 *M*. Figure 1 shows a plot of k^n_2 *vs* n, the atom fraction of deuterium in the exchangeable position of the solvent. Its notable characteristics are its strong nonlinearity and the reduction in rate produced by added deuterium. These data may be used to exclude Mechanisms C and D, in which the free hydride ion is produced, and to narrow the possibilities open within A and B.

Table I. Second-Order Rate Constants for the Methoxide-Ion Catalyzed Methanolysis of Triphenylsilane in Mixed CH_3OH and CH_3OD at 25.00 ± 0.05°. μ = 0.1 *M* ($LiClO_4$ added).

n, atom fraction D in CH_3OL	$10^3k^n_2$, $M^{-1}sec^{-1}$
0.000	311.4 ± 3.7
0.098	295.9 ± 1.3
0.246	294.7 ± 5.0
0.495	275.5 ± 5.9
0.653	262.8 ± 3.9
0.730	241.3 ± 4.1
0.818	211.1 ± 4.6
0.883	193.6 ± 4.8
0.982	164.3 ± 2.1

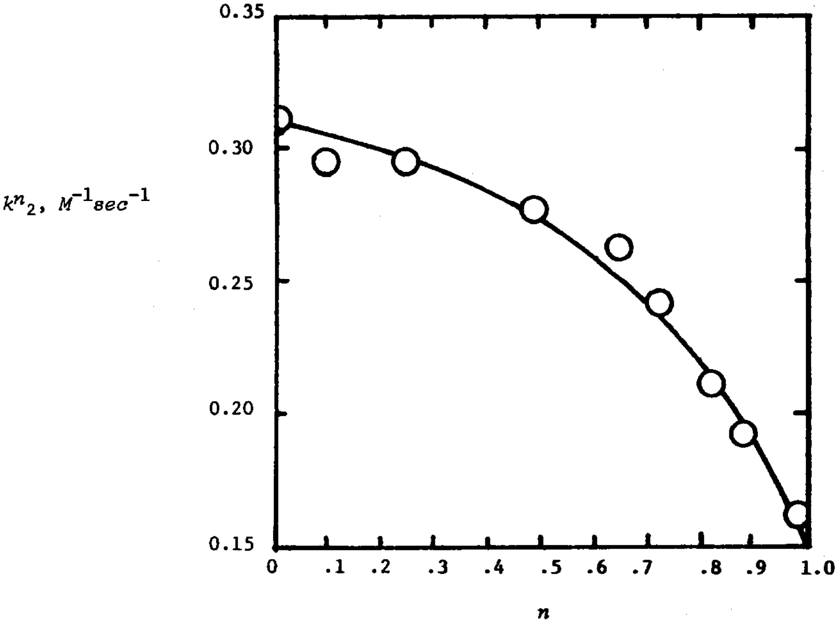


Figure 1.

An uncomplicated methoxide-consuming reaction, such as Mechanism B with k_a rate-determining or Mechanism C with either of the first two steps rate-determining, would have been expected to proceed more rapidly in the deuterated solvent. For example, rate-determining addition of methoxide ion to the carbonyl group of carbonate and acetate esters yields solvent isotope effects k_{CH_3OD}/k_{CH_3OH} of 1.5 to 2.1 (5). More O'Ferrall's (6) isotopic fractionation factor (7) ϕ of 0.76 for CH_3O^-, determined by an n.m.r. technique, predicts such inverse effects of up to 2.3 if the effects are assumed to arise from hydrogen bonding of three methanol molecules (one for each lone pair) to the reactant ion, which are liberated on activation. The fact that the reaction proceeds 1.9 times slower in the 98.2% deuterated solvent than in the completely protiated solvent shows that proton transfer from the solvent is contributing to the rate-determining process. Thus irreversible formation of hydride ion is excluded.

If the observed normal isotope effect arose simply from a single proton transfer in a single transition state throughout the range of mixed isotopic media, the rate constant would have decreased linearly from k_H in CH_3OH to k_D in CH_3OD (eq. 1). The nonlinearity in

$$k^{n}{}_{2} = k'_H[CH_3OH] + k'_D[CH_3OD] = k_H + (k_D - k_H)\ n \qquad (1)$$

Fig. 1 thus excludes this possibility as well.

The following model can adequately account for the data although it is definitely not unique. We assume that Mechanism A, or Mechanism B with k_b rate-determining, holds with the transition state experiencing no differential solvation from CH_3OH and CH_3OD and with the proton transfer giving a primary isotope effect $k_H/k_D = 4.5$ (corresponding to an isotopic fractionation factor $\phi = 0.22$). The rate constant $k^{n}{}_{2}$ is then given by eq. 2 (7, 8); that is,

$$k^{n}{}_{2} = (1 - n + 0.22\ n)\ k^{o}{}_{2}/\ (1 - n + 0.76\ n)^3 \qquad (2)$$

there is a competition between a tendency to go faster in CH_3OD because this solvent destabilizes CH_3O^- (the third power enters because three equivalent solvent molecules bind to the ion) and a (linear) tendency to go more slowly in CH_3OD because of the primary isotope effect. Eq. 2 is plotted as the solid line in Fig. 1. No acceptable model with k_a rate-determining in Mechanism B can be generated, although it is possible to fit the data by assuming that there is (for some reason) *no* secondary solvent isotope effect on either k_a or $k_a k_b/k_{-a}$ and by selecting the primary isotope effect and the ratio k_{-a}/k_b such that a change in rate-determining step occurs at about $n = 0.6$. The assumption of complete loss of the secondary solvent isotope effect in *both* transition states would seem hard to justify.

We conclude that expulsion of free hydride ion does not occur along the main reaction pathway for basic methanolysis of silanes and that proton transfer from solvent is occuring in the transition state, at least in highly deuterated solvent.

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