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A KINETIC INVESTIGATION OF THE ROLE OF SOLVENT IN THE ALKALI-CATALYZED HYDROLYSIS OF ORGANOSILICON HYDRIDES *

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Summary

The role of solvent in the alkali-catalyzed hydrolysis of organosilicon hydrides, specifically, 3-[(2-methoxy)ethoxy]propyldimethylsilane, has been investigated kinetically in dioxane/water media by varying the solvent composition. Statistical analysis of the kinetic data indicates that approximately three water molecules are involved in the transition state of the rate-determining step. The mechanistic implications are discussed.

Introduction

The alkali-catalyzed hydrolysis of the silicon—hydrogen bond of organosilicon hydrides has been the subject of numerous studies since the initial kinetic investigation by Price [1—5]. A number of papers have been published in which the role of solvent in this reaction has been investigated in alcohol/water media by variation of composition [1,6], and by hydrogen isotope effects [7—10]. However, the results of these studies are inconclusive because the relative concentrations of attacking nucleophiles, OH^- and OEt^-, and solvating species, H_2O and EtOH are changed by varying solvent composition and the isotope effects are small or cannot be unequivocally assigned to the rate-determining step.

Recently, the role of solvent in the base-catalyzed alcoholysis of organosilicon hydrides, a closely related reaction, has been probed by hydrogen isotope studies [11—15]. Based on the isotopic fractionation factor for the methoxide-catalyzed methanolysis reaction, the authors conclude that three methanol molecules are involved in the transition state of the rate-determining step [13].

The work described in this paper is interpreted in terms of a similar mechanism for the alkali-catalyzed hydrolysis of organosilicon hydrides in dioxane/water

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media in which approximately three water molecules are involved in the transition state of the slow step. However, in this study the conclusions are based on an entirely independent method, the variation in rate with solvent composition.

Experimental

General

Analyses were performed by Alfred Bernhardt Microanalytical Laboratories, Germany, except % Cl, which was determined in our laboratory by a titrimetric method.

The following materials were used in the synthetic and kinetic studies: 2-methoxyethanol (reagent grade); 3-bromopropene (reagent grade); dimethyl chlorosilane (Dow Corning Corp.); tetramethylammonium hydroxide (Eastman reagent grade), 10% solution in water; *p*-dioxane (Eastman reagent grade).

Preparation of 1-allyloxy-2-methoxyethane (I)

The sodium derivative of 2-methoxyethanol, 0.87 mol, was prepared by addition of sodium metal, 20 g, 0.87 g-atom, to an ethereal solution, 300 ml, of 2-methoxyethanol, 76 g, 1.00 mol. 3-Bromopropene, 60 g, 0.49 mol, was added dropwise to the above mixture. After refluxing for 1.5 h, water, 100 ml, was added and the ethereal extract was dried over molecular sieves. Fractional distillation gave a sample of I, 52 g, 0.45 mol, (90% yield): b.p. 128°C, n_D^{25} 1.4112, d_4^{25} 0.8818, (lit. [16], b.p. 129.5—130°C, n_D^{20} 1.4129, d_4^{20} 0.8874). (Found: C, 61.84; H, 10.49. $C_6H_{12}O_2$ calcd.: C, 62.00; H, 10.42%.)

Addition of dimethylchlorosilane to I

Dimethylchlorosilane, 43 g, 0.46 mol, was added dropwise to I, 52 g, 0.45 mol, in the presence of chloroplatinic acid, 0.05 ml, (0.1 *M* solution in isopropanol). During the addition, the temperature was maintained at approximately 100°C. After refluxing for 3 h, fractional distillation under reduced pressure gave 3-[(2-methoxy)ethoxy]propyldimethylchlorosilane (II), 33 g, 0.16 mol, (35% yield): b.p. 110°C/15 mmHg, n_D^{25} 1.4362, d_4^{25} 0.9809. (Found: C, 45.79; H, 8.93; Cl, 16.37. $C_8H_{19}C_{10}Si$ calcd.: C, 45.60; H, 9.09; Cl, 16.60%.)

Preparation of 3-[(2-methoxy)ethoxy]propyldimethylsilane (III)

A solution of II, 40 g, 0.19 mol, in ether, 100 ml, was added dropwise to an ethereal solution, 100 ml, of lithium aluminum hydride, 2.5 g, 0.07 mol. After refluxing for 3 h, the reaction mixture was hydrolyzed, the ethereal layer was separated and dried over molecular sieves, and the ether was removed by distillation. Fractional distillation of the residue under reduced pressure gave III, 26 g, 0.15 mol, (78% yield): b.p. 93°C/21 mmHg, n_D^{25} 1.4244, d_4^{25} 0.8612. (Found: C, 54.29, H, 11.20. $C_8H_{20}O_2Si$ calcd.: C, 54.50; H, 11.43%.)

Apparatus and kinetic procedure

The procedure for determining rate constants has been reported previously [17,18]. The apparatus was modified as follows: 125 ml, thin-walled Erlenmeyer flask with a side arm was used as the reaction flask; an immersion-type magnetic stirrer was employed; the gas-buret was jacketed and maintained at constant temperature by circulating water from the bath. The temperature of the bath was regulated to within ± 0.10°C (thermometer calibrated against N.B.S. standard).

The dioxane/water mixtures were prepared by weight from distilled water and dioxane, freshly distilled from calcium hydride, and the molarity calculated from density measurements. The amount of base, tetramethylammonium hydroxide, present was determined by standardization against potassium hydrogen phthalate (primary standard certified). Tetramethylammonium iodide (reagent grade) was added when necessary to maintain constant ionic strength.

All calculations were carried out on a Control Data G-20 computer by optimizing coefficients, employing the least squares method.

Results and discussion

The silane, $CH_3O(CH_2)_2O(CH_2)_3Si(CH_3)_2H$, employed in this study was specifically tailored to enhance solubility in systems of high water concentrations by incorporating ether units in an organic substituent group. Similarly the basic species, $(CH_3)_4NOH$, was chosen to enhance solubility in systems of high dioxane concentrations. The range of solvent composition, 13.90—37.10 *M* in water, i.e., 24.4—65.8 wt.-% was determined by silane solubility and phase separation due to salting-out.

In order to obtain measurable rates of reaction at the higher water concentrations and temperatures, it was necessary to lower the hydroxide ion concentration. Since the reaction is sensitive to changes in ionic strength, but independent of the anion of added salt [19], the ionic strength was maintained by adding tetramethylammonium iodide (alkali plus salt, 0.044 ± 0.007 *M*).

The kinetic data for the alkali-catalyzed hydrolysis of 3-[(2-methoxy)ethoxy]-propyldimethylsilane in dioxane/water mixtures (24.7, 35.2 and 45.3°C) are reported in Table 1. The second-order rate constants, first-order in silane and hydroxide ion, are an average of at least three independent determinations. The thermodynamic activation parameters for the hydrolysis reaction for three different dioxane/water mixtures are listed in Table 2.

Role of solvent

The involvement of solvent in the hydrolysis reaction was investigated by studying the correlation between the second-order rate constant and the solvent composition. While a number of linear correlations were tested, only three are considered significant and are reported below.

Firstly, the second-order rate constant is assumed to be dependent on the water concentration as given in eq. 1, where n is the order in water. Least-squares

$$k_2 = k'_{2+n} \times [H_2O]^n \qquad (1)$$

curve fitting was carried out on the logarithmic form (eq. 2) where A, n and B

$$\log k_2 = A + n \log[H_2O] + B/\epsilon \qquad (2)$$

are adjustable coefficients. The B/ϵ term was included to account for the change in rate due to the change in the dielectric constant of the solvent system [22].

TABLE 1

KINETIC DATA FOR THE ALKALI-CATALYZED HYDROLYSIS OF 3-[(2-METHOXY)ETHOXY]-PROPYLDIMETHYLSILANE IN DIOXANE/WATER MIXTURES [a]

No.	Concentration (*M*)					T (°C)	ϵ [c]	$k_2 \times 10^2$ (l mol^{-1} sec^{-1})	$\sigma \times 10^2$ [d]
	H_2O	Dioxane	OH^- [b]	Silane [b]	I^-				
1	13.90	8.86	0.0421	0.075	—	24.7	12.2	3.09	0.05
2 [e]	17.82	8.03	0.0458	0.074	—	24.7	18.5	6.05	0.09
3	20.43	7.45	0.0409	0.073	—	24.7	22.5	7.41	0.06
4	22.83	7.01	0.0438	0.072	—	24.7	26.4	9.04	0.13
5	24.51	6.68	0.0420	0.074	—	24.7	29.3	10.5	0.3
6	28.60	5.79	0.0454	0.077	—	24.7	35.0	14.4	0.1
7	32.10	5.06	0.0206	0.063	0.0265	24.7	40.6	20.6	0.5
8	34.29	4.60	0.0220	0.073	0.0265	24.7	43.7	23.4	0.2
9	37.10	3.95	0.0241	0.059	0.0265	24.7	48.3	31.7	1.1
10	17.42	7.94	0.0375	0.067	—	35.2	17.4	12.1	0.4
11	22.97	6.79	0.0302	0.063	0.0132	35.2	25.5	20.9	0.3
12	28.69	5.63	0.0210	0.061	0.0263	35.2	34.2	29.3	0.3
13	17.19	7.88	0.0335	0.051	0.0131	45.2	16.3	25.1	0.4
14	22.77	6.73	0.0217	0.055	0.0261	45.2	24.2	39.2	1.9
15	28.27	5.62	0.0091	0.052	0.0392	45.2	31.7	58.3	1.7

[a] Data reported are the average of three determinations, for complete data, cf. ref. 20. [b] Average concentrations. [c] Dielectric constant of solvent, calcd. from the data of Akerlof and Short [21]. [d] Standard deviation. [e] Average of four determinations.

A least-squares multiple correlation based on eq. 2 yields eq. 3 with the statistical

$$\log k_2 = -5.04 + 2.80 \log [H_2O] + 5.40/\epsilon \qquad (3)$$

terms: $S_A = 0.19$, $S_n = 0.12$, $S_B = 0.85$, $S_{\log k_2} = 0.02$, $R = 0.997$. A graphical representation of the data is given in Fig. 1.

The above statistical analysis of the data on the change in the rate constant, k_2, on varying the water concentration indicates that the order of the reaction in water is 2.80 with a standard deviation of 0.12. This value is in good agreement with the value obtained by Howie et al. [13], ~3, for the number of methanol molecules involved in the transition state of the rate-determining step for the methoxide-catalyzed methanolysis of triorganosilanes based on the isotopic fractionation factor. Assuming that an average of three molecules of water are involved in the transition state and that the coefficient of the log k_{2+n} term is unity, the rate constant, k_5, is calculated to be 9.1×10^{-6} sec^{-1} l^4 mol^{-4}.

TABLE 2

THERMODYNAMIC ACTIVATION PARAMETERS FOR THE ALKALI-CATALYZED HYDROLYSIS OF 3-[(2-METHOXY)ETHOXY]PROPYLDIMETHYLSILANE IN DIOXANE/WATER MEDIA AT 24.7°C

Concentration H_2O [*M*] [a]	$\Delta G^{\neq}$ (kcal mol^{-1})	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (e.u.)
17.82	19.1	12.9	—20.8
22.83	18.8	13.3	—18.5
28.60	18.6	12.6	—20.1

[a] ± 0.18 *M*.

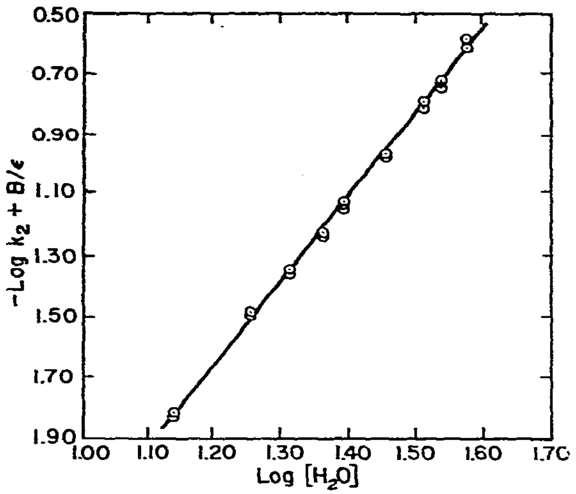


Fig. 1. Graphical representation of data correlated by eq. 2; the slope is equal to the order in water concentration.

Secondly, a mechanism is assumed in which both components of the solvent are involved in a rapid equilibrium between expanded valence shell complexes of the silane with water and dioxane, D, eq. 4.

$$R_3SiH \cdot D + H_2O \overset{K_1}{\rightleftharpoons} R_3SiH \cdot H_2O + D \tag{4}$$

Also, it is assumed that nucleophilic attack at silicon by hydroxide ions is inhibited by the presence of the complexed dioxane. Based on the above mechanism, expression 5 is obtained for k_2.

$$k_2 = \frac{k_2' K_1 \times ([H_2O]/[D])}{1 + K_1 \times ([H_2O]/[D])} \tag{5}$$

If the value of $K_1 << 1$, then eq. 5 yields the simplified expression 6.

$$k_2 = k_2' K_1([H_2O]/[D]) \tag{6}$$

Least-squares curve fitting was carried out on the logarithmic form (eq. 7)

$$\log k_2 = A' + B' \log \frac{[H_2O]}{[D]} + C'/\epsilon \tag{7}$$

where A', B', C' are adjustable coefficients, yielding eq. 8, with the statistical

$$\log k_2 = -1.64 + 1.17 \log \frac{[H_2O]}{[D]} + 0.12/\epsilon \tag{8}$$

terms: $S_{A'} = 0.17$, $S_{B'} = 0.07$, $S_{C'} = 0.09$, $S_{\log k_2} = 0.01$, $R = 0.999$.

The above statistical analysis of the data on the change in the rate constant, k_2, with the change in the solvent composition indicates that the order of the reaction is approximately one in water and minus one in dioxane. In this correlation, the solvent-dielectric constant term is of little significance.

Eq. 5 can be rearranged to the linear form (eq. 9).

$$\frac{1}{k_2} = \frac{1}{k_2'} + \frac{[\mathrm{D}]}{k_2' K_1 [\mathrm{H_2O}]} \tag{9}$$

Least-squares curve fitting was carried out on eq. 9 in the form indicated below (eq. 10), where A'' and B'' are adjustable coefficients, yielding eq. 11 with the

$$\frac{1}{k_2} = A'' + B'' \frac{[\mathrm{D}]}{[\mathrm{H_2O}]} \tag{10}$$

$$\frac{1}{k_2} = -1.66 + 41.70 \frac{[\mathrm{D}]}{[\mathrm{H_2O}]} \tag{11}$$

statistical terms: $S_{A''} = 0.17$, $S_{B''} = 0.48$, $S_{1/k_2} = 0.41$, $R = 0.998$.

While the dioxane/water system is complex [23,24], the fact that the above linear relationships are observed with respect to water concentration over approximately a three-fold change in the solvent composition indicates that the relationship can be used to determine the number of water molecules involved in the transition state of the rate-determining step. Although molecular aggregates have been shown to be present in dioxane/water mixtures, the half-lives of these species are very short compared to the hydrolysis process [23]. Therefore, any fluctuations in the solvent species are averaged out with respect to the hydrolysis process.

The above correlations for the change in the second-order rate constant for the alkali-catalyzed hydrolysis of a triorganosilane with solvent composition indicate that in dioxane/water mixtures the transition state of the slow step contains one or three molecules of water. If one water molecule is involved, then dioxane must inhibit attack at silicon by hydroxide ion, probably by forming an expanded valence shell complex.

In order to insure that the change in the second-order rate constant is due only to solvent effects and not mechanistic changes, the thermodynamic activation parameters were determined over a wide range of solvent composition, cf. Table 2. The consistency of these parameters indicates that no important mechanistic changes occur. The negative entropy of activation indicates a transition state of a greater order than reactants and is consistent with a mechanism in which the transition state is formed by the coming together of several, different, previously independent species.

While statistically we cannot choose between the two mechanistic possibilities, the model in which the transition state contains three water molecules is strongly favored because of the following reasons:

(1) The intercept, $1/k_2'$, determined for eq. 9 is negative; therefore, this model is not valid.

(2) The involvement of approximately three water molecules in the transition state is consistent with the results obtained for the methoxide-catalyzed methanolysis of triorganosilanes by an independent method based on isotopic studies [13].

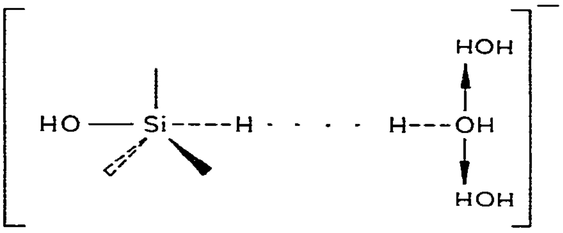
(3) A fortuitous correlation with dioxane concentration might be expected since increasing the water concentration of the solvent mandates a decrease in

the dioxane concentration (for the equation, $\log [H_2O] = A''' + B''' \log [D]$, $R = 0.966$).

(4) Compounds in which three organic groups are attached to silicon do not form strong coordinate bonds with neutral oxygen-containing bases [25].

Mechanistic implications

Based on mechanistic studies for the base-catalyzed hydrolysis and alcoholysis of triorganosilanes, [1—15,26], the proposed transition state for the alkali-catalyzed hydrolysis process is given in A *. In this complex, which need not be linear, the bond order between the base, OH^-, and silicon is nearly unity, the Si—H and O—H bonds are only partially broken so that the transition state resembles reactants rather than products, and the H—H bond is only partially formed. In A, two additional water molecules are hydrogen-bonded to the oxygen of the third water in order to solvate the hydroxide ion as it is formed. This transition state is analogous to the proposed transition state for the methoxide-catalyzed methanolysis of triorganosilanes based on the isotopic fractionation factor [13].



(A)

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