increasing ethanol concentration as eluent, resulted in the isolation of a chromatographically homogeneous N,N′-diacetylchitobiose which crystallized from aqueous methanol in long, slender needles.

Crystallized N,N′-diacetylchitobiose melts at 245–247° with decomposition. The crystals exhibit mutarotation in aqueous solution: $[\alpha]^{25}\text{D}$ extrapolated to zero time was +39.5° (*c* 1.0, H_2O). The equilibrium rotation, reached after 60 minutes was $[\alpha]^{25}\text{D}$ +18.5° (*c* 1; H_2O). Therefore the crystalline N,N′-diacetylchitobiose is presumably the α-isomer. The crystals take up water readily thereby losing their crystalline structure. They are only slightly soluble in dry methanol. One mole of NaOI was consumed per mole of disaccharide.[7] The Morgan–Elson reaction[8] was negative with and without prior treatment with Na_2CO_3. This is consistent with a recent observation by Kuhn, *et al.*,[9] for 4-substituted N-acetyl-D-glucosamines. One mg. of the crystallized disaccharide produced a color equivalent to only 30 γ of free N-acetyl-D-glucosamine. This is due to a slight formation of N-acetyl-D-glucosamine by the action of Na_2CO_3.

Crystallized N-N′-diacetylchitobiose is hydrolyzed into two moles of N-acetyl-D-glucosamine by a crude enzyme preparation from *Lactobacillus bifidus* var. *Penn*,[10] which is known to split alkyl-N-acetyl-β-D-glucosaminides with liberation of N-acetyl-D-glucosamine.[11] The same enzyme does not attack the corresponding alkyl-N-acetyl-α-D-glucosaminides.[11] The growth promoting activity for *Lactobacillus bifidus* var. *Penn* when autoclaved with the medium was 800 γ per unit. When added under sterile conditions one growth unit was contained in 2.2 mg.

Experimental

Hexa-*O*-acetyl-di-N-acetylchitobiose.—Hexa-*O*-acetyl-di-N-acetylchitobiose was obtained from decalcified lobster chitin according to Bergmann, *et al.*,[2] in long colorless needles. Upon three recrystallizations the melting point and optical rotation remained unchanged; m.p. 290–291° dec., $[\alpha]^{30}\text{D}$ +55.3° (*c* = 1, CH_3COOH).

Anal. Calcd. for $C_{28}H_{40}O_{17}N_2$ (676.3): C, 49.68; H, 5.96; N, 4.14. Found: C, 49.68; H, 6.03; N, 4.16.

N,N′-Diacetylchitobiose.—2.3 g. of hexa-*O*-acetyl-di-N-acetylchitobiose was dissolved in 50 ml. of dry methanol, cooled to 0° and 50 ml. of methanol saturated with ammonia at 0° was added immediately. The solution was kept for 24 hours at room temperature and then evaporated to dryness below 50° *in vacuo*. Dry methanol was added and the material again evaporated to dryness. The amorphous residue was reprecipitated from dry methanol.

1.3 g. of the amorphous product was dissolved in 20 ml. of water and chromatogrammed on a charcoal/Celite column, prepared from 80 g. of Norite A and 80 g. of Celite.[12] The flow rate of the column was 1.5–2 ml. per minute. After washing the column with 2 l. of water, 2.5 l. of 2.5% and 3 l. of 5% ethanol, a chromatographically homogeneous N,N′-diacetylchitobiose (R_{lac} = 1.49) was eluted in the first three 500-ml. fractions of 7.5% ethanol. The three 7.5% ethanolic fractions were combined and evaporated to dryness *in vacuo*. The residue was dissolved in 30 ml. of dry methanol, filtered and again evaporated. During this operation very tiny needles were visible. For a final recrystallization the needles were treated with 10 ml. of hot dry methanol, then water added dropwise until they dissolved. The solution was kept for crystallization at room temperature, 230 mg. of slender needles were obtained having a melting point at 245–247° with decomposition. (The crystals become brown at 237–239°); $[\alpha]^{25}\text{D}$ (extrapolated to zero time) +39.5 (*c* 1, H_2O). The equilibrium rotation reached after 60 minutes was $[\alpha]^{25}\text{D}$ +18.5° (*c* 1, H_2O).

Anal. Calcd. for $C_{16}H_{28}O_{11}N_2$ (424.2): C, 45.26; H, 6.65; N, 6.60. Found: C, 44.93; H, 6.72; N, 6.44.

Paper chromatography was carried out on Whatman filter paper No. 1. The solvent used was the upper layer of an ethyl acetate:pyridine:H_2O = 2:1:2 mixture.

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[7] M. Macleod and R. Robison, *Biochem. J.*, **23**, 517 (1929).

[8] W. T. J. Morgan and L. A. Elson, *ibid.*, **28**, 988 (1934).

[9] R. Kuhn, A. Gauhe and H. H. Baer, *Ber.*, **87**, 1138 (1954).

[10] P. György, C. S. Rose and G. F. Springer, *J. Lab. and Clin. Med.*, **43**, 543 (1954).

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[12] Johns-Manville No. 535.

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Hydrogen Isotope Effects in the Alkaline Cleavage of Triorganosilanes[1]

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The effects of isotopic substitution on the rates of hydrolysis of triphenyl- and tripropylsilane in piperidine–water and ethanol-water solvents have been studied in order to acquire information concerning the reaction mechanisms. Substitution of deuterium or tritium for protium in either the silane or the solvent in every case reduced the reaction rate. The results indicate that the rate-determining step in the reaction involves the rupture of the silicon–hydrogen bond and that in the transition state the hydrogen atom from the silane is strongly bonded to that from the solvent.

The alkaline cleavage of the silicon–hydrogen bond in trialkyl- or triarylsilanes has been the subject of several recent investigations. The reactions can be represented stoichiometrically by the equation

$$R_3SiH + OH^- + HS \longrightarrow R_3SiOH + H_2 + S^-$$

where HS represents a molecule of the solvent. Price[2] found that the evolution of hydrogen from trialkylsilanes dissolved in alcoholic potassium hydroxide was essentially quantitative, and that the reaction was first order with respect to silane, hydroxide and, probably, solvent. Gilman and Dunn[3] showed that the closely related hydrolysis of triarylsilanes in piperidine–water was a pseudo first-order reaction which had a positive value of ρ in the Hammett equation. These results, together with others,[4] indicate that the reactions of silanes with

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[1] Presented at the Los Angeles Meeting of the American Chemical Society, March 15–19, 1953.

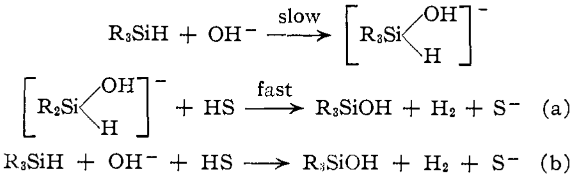
[2] F. P. Price, THIS JOURNAL, **69**, 2600 (1947).

[3] H. Gilman and G. E. Dunn, *ibid.*, **73**, 3404 (1951).

[4] (a) H. Gilman and S. P. Massie, Jr., *ibid.*, **68**, 1128 (1946); (b) R. N. Meals, *ibid.*, **68**, 1880 (1946).

base proceed not by siliconium ion formation, but by nucleophilic attack upon silicon.

Two mechanisms consistent with this view can be formulated



$$R_3SiH + OH^- \xrightarrow{\text{slow}} \left[R_3Si\begin{matrix}\diagup OH\\ \diagdown H\end{matrix}\right]^-$$

$$\left[R_2Si\begin{matrix}\diagup OH\\ \diagdown H\end{matrix}\right]^- + HS \xrightarrow{\text{fast}} R_3SiOH + H_2 + S^- \quad (a)$$

$$R_3SiH + OH^- + HS \longrightarrow R_3SiOH + H_2 + S^- \quad (b)$$

In mechanism a, the rate-determining step involves only the attack of hydroxide ion on silicon to form a pentacovalent intermediate similar to those invoked[5] for other reactions of silicon, the availability of such a reaction path being attributed to the ability of silicon to expand its valence shell beyond eight electrons. The formation of hydrogen then occurs in a fast reaction between this intermediate and the solvent. In mechanism b, the hydrolysis may be regarded as proceeding either in a single step by a termolecular reaction or in two steps by the rapid, reversible, formation of a pentacovalent complex followed by a slower reaction with the solvent. Swain[6] has pointed out that the distinction between the possibilities mentioned for mechanism b has little, if any, physical significance and has used the term "concerted" to describe such a displacement.

In principle, mechanisms a and b can be distinguished by determining the dependence of reaction rate on solvent concentration since the latter appears in the rate equation only for mechanism b. The observed[2] dependence of the rate of hydrolysis of trialkylsilanes on the concentration of water in the alcoholic solvent suggests that the reaction path is better represented by mechanism b, but this conclusion is open to some question because of the possible change in hydroxide ion concentration[7] produced by the change in water concentration.

A study of the effect on reaction rate of isotopic substitution for hydrogen in the reactants offers greater promise for distinguishing between the two mechanisms since both silicon–hydrogen and solvent–hydrogen bonds are broken in the rate-determining step of mechanism b, whereas no hydrogen bond is broken in that of mechanism a. A marked diminution in the rate of hydrolysis upon substitution of deuterium or tritium for the protium in a silane, for example, would indicate[8] that the silicon–hydrogen bond is ruptured in the rate determining process. Utilizing this approach, Gilman, Dunn and Hammond measured, in separate experiments, the rates of hydrolysis of triphenylsilane-*d* and triphenylsilane in piperidine–water and found,[9] unexpectedly, that the deuterated compound reacted six times faster than the normal compound.

The occurrence of a large abnormal isotope effect was not substantiated, however, when this reaction was further investigated, employing a competitive method to eliminate variables and using tritium to enhance the isotope effect; preliminary results[10] indicated that triphenylsilane-*t* was hydrolyzed only 0.8 as fast as the normal compound. The magnitude of the isotope effect when a hydrogen bond is ruptured in the rate-determining step of a reaction is commonly much greater than 20%; such a small effect can be reconciled with rupture of the silicon–hydrogen bond in mechanism b, however, if the hydrogen of the silane is strongly bonded to that of the solvent in the transition state. Alternatively, it can be explained by a weakening of the silicon–hydrogen bond in the pentacovalent intermediate of mechanism a.

In the hope of acquiring more information concerning the mechanism of the hydrolysis and the nature of the transition state, the study of isotope effects has been expanded to include solvent effects. The influence on reaction rate of substitution of tritium and, in some cases, deuterium for the hydrogen in the silane and the solvent has been determined, both by competitive and direct measurements, for the hydrolysis of triphenylsilane in piperidine–water and of triphenyl- and tripropylsilane in ethanol–water containing potassium hydroxide.

Experimental

Materials.—The isotopic triphenylsilanes were prepared, using essentially the procedure described by Gilman and Dunn,[3] by the reduction of triphenylchlorosilane (Dow-Corning, Purified Grade, recrystallized from hexane) with lithium aluminum hydride and deuteride (Metal Hydrides, Inc.) and with lithium aluminum tritide.[11] After purification by fractional distillation at reduced pressure, the silanes melted at 44° and, when hydrolyzed, yielded 100 ± 1% of the theoretical volume of hydrogen. The gas obtained from triphenylsilane-*d* contained 98.4% HD, 1.4% H_2 and 0.1% D_2. Triphenylsilane-*t* yielded gas containing 190 millicuries of tritium per mole; the same value was obtained for the total amount of tritium in the silane.

Tripropylsilane and tripropylsilane-*t* (85 microcuries per millimole) were prepared similarly by the reduction of tri-*n*-propylchlorosilane obtained from the reaction of *n*-propylmagnesium chloride with silicon tetrachloride. Fractions of the silanes distilling from 171–172° produced 97% of the theoretical quantity of hydrogen on hydrolysis.

Piperidine (Matheson Chemical Co., purified by fractional distillation from potassium hydroxide) was adjusted to a water concentration of 1.00 *M*. Ethanol (U. S. Industrial Chemicals Co., absolute) was diluted to give a water concentration of 3.59 *M* (8% water by weight). Stock solutions of the tritium-containing solvents were prepared using water containing known amounts of tritium. The amount of tritium per equivalent of active hydrogen was 30 millicuries in the ethanol solution and 60 millicuries in the piperidine solution. Reagent grade potassium hydroxide was added to the ethanol solutions.

Ethanol-*d* was prepared by hydrolysis of freshly prepared sodium ethylate with heavy water and was purified by fractional distillation. After addition of sufficient heavy water to give a solution 4.00 *M* in D_2O, as determined by titration with Karl Fischer reagent, the deuterium content of the hydroxyl hydrogen was about 95%. An ethanol solution was prepared similarly from sodium ethylate and ordinary

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(5) (a) N. V. Sidgwick, "The Electronic Theory of Valency," London, Oxford University Press, 1927, pp. 159–160; (b) C. G. Swain, R. M. Esteve, Jr., and R. H. Jones, THIS JOURNAL, **71**, 965 (1949); (c) H. Gilman, A. G. Brook and L. S. Miller, *ibid.*, **75**, 4531 (1953); (d) C. R. Hauser and C. R. Hance, *ibid.*, **73**, 5846 (1951).

(6) C. G. Swain, *ibid.*, **70**, 1119 (1948), and later papers by the same author.

(7) (a) J. W. Baker and A. J. Neale, *Nature*, **172**, 583 (1953); (b) E. F. Caldin and G. Long, *ibid.*, **172**, 583 (1953).

(8) (a) C. Reitz, *Z. physik. Chem.*, **A179**, 119 (1937), (b) F. H. Westheimer and N. Nicolaides, THIS JOURNAL, **71**, 25 (1949); see, however, (c) V. J. Shiner, Jr., *ibid.*, **75**, 2925 (1953); (d) E. S. Lewis and C. E. Boozer, *ibid.*, **76**, 791 (1954)

(9) H. Gilman, G. E. Dunn and G. S. Hammond, *ibid.*, **73**, 4499 (1951).

(10) L. Kaplan and K. E. Wilzbach, *ibid.*, **74**, 6152 (1952).

(11) K. E. Wilzbach and L. Kaplan *ibid.*, **72**, 5795 (1950).

water for use in the comparative rate measurements. Potassium metal was dissolved in these solutions to give the desired concentration of potassium hydroxide.

Isotopic Analysis.—For the determination of tritium, each sample of evolved gas was quantitatively transferred, with a Toepler pump, into an evacuated ionization chamber. The chamber was then filled to atmospheric pressure with tank hydrogen, and the ion current collected with an applied potential of 180 volts was measured[12] with a vibrating reed electrometer. Water and organic compounds containing tritium were analyzed by sealed tube reductions using the zinc fusion technique.[13]

Deuterium was determined in unequilibrated gas samples by means of a mass spectrometer which had been calibrated with known mixtures.

Measurement of Isotopic Rate Ratios.—Reactions were carried out in a 50-ml. round-bottom flask sealed to a male ground glass joint and containing a magnet sealed in glass. On the neck of this flask was mounted a unit having a side arm for attachment to the vacuum system and a dropping-funnel with a female ground glass joint for attachment of a tilt-flask. A 20-ml. aliquot of the solvent was pipetted into the tilt-flask which was then mounted on the dropping-funnel. The solvent was freed from dissolved gas by several cycles of evacuation at −80° and rewarming to room temperature. The stopcock of the dropping funnel was closed, the reaction flask was removed, and a sample of the liquid silane, approximately 2 millimoles, was weighed in from a pipet. The silane was degassed, and the reactants were brought to the desired reaction temperature. The solvent was then added rapidly to the silane and the solution was stirred magnetically.

In competitive experiments, the reaction mixture was cooled to −80° at suitable intervals, the evolved gas samples were quantitatively transferred with a Toepler pump through traps at −195° into storage bulbs, and the reaction mixture was rewarmed in a time short compared with that required for gas evolution. In experiments with isotopically labeled silanes, samples were collected until the hydrolyses were completed in order to obtain material and isotopic balances. In experiments with labeled solvents only three or four samples were taken since the isotopic composition of successive samples was essentially constant because of the large excess of solvent. At the completion of an experiment, the quantity of gas in each storage bulb was measured manometrically and its isotopic composition was determined.

For the determination of rate constants in non-competitive experiments, the reactions were initiated in the same way, but were followed, without interruption, by the increase in pressure in a system with a constant known volume. First-order rate constants were calculated from the expression

$$k = \frac{2.3}{t_2 - t_1} \log \frac{p_\infty - p_2}{p_\infty - p_1}$$

p_∞ was calculated from the weight and purity of the silane; p_t was obtained by subtracting the vapor pressure of the solvent from the pressure measured at time t. Second-order constants were obtained by dividing the first-order constants by the concentration of potassium hydroxide.

The Reaction Products.—Since the nature of silicon-containing products from the hydrolyses of triorganosilanes in alcohol-water has not been reported, determination of whether silanols or ethoxysilanes are produced seemed important, particularly in view of recent reports[7] that a large fraction of the base added to ethanol containing a few per cent. of water is present in the form of ethoxide ion. Rather than attempt a quantitative chemical separation of the reaction products, a radiochemical estimate of the quantity of ethoxysilane was made. Tripropyl- and triphenylsilane were quantitatively hydrolyzed at room temperature in solvent containing ethanol labeled[11] with tritium on the methylene carbon atom, and the tritium content of the organic product was measured after separation from solvent. On the plausible assumption that there is no isotope effect produced by a tritium atom so far removed from the reaction site, it was calculated that the product obtained from tripropylsilane contained 1.3 mole % of ethoxysilane; that from triphenylsilane contained 7.2 mole %.

That each molecule of hydrogen obtained by hydrolysis of the silanes contained one atom of hydrogen from the silane and one from the solvent was established by isotopic analysis of the products of reactions involving deuterated reactants. Triphenylsilane-*d*, hydrolyzed in either piperidine–water or alkaline ethanol–water, yielded gas containing 98.4% HD, 1.4% H_2 and 0.2% D_2. The hydrolysis of ordinary tripropylsilane in a solution of potassium hydroxide in deuterated ethanol–water, the hydroxyl hydrogen of which consisted of about 95% deuterium, gave a gaseous product containing 93.6% HD, 6.3% H_2 and 0.1% D_2.

The Absence of Hydrogen Exchange.—Since the validity of the measurements depends on the absence of hydrogen exchange between solvent and evolved gas and since hydrogen gas is known[14] to exchange with hydroxylic solvents under the influence of basic catalysts, the extent of exchange under our experimental conditions was investigated. A 0.5 *N* solution of potassium hydroxide in ethanol–water, hydroxyl-labeled with tritium, was stirred for one hour at 25° with hydrogen gas at a pressure of 260 mm. The gas was then found to contain only 0.002% of the tritium activity expected for statistical distribution of tritium between the gas and hydroxyl hydrogen. Further confirmation that isotopic exchange is negligible in the reactions studied is found in the high HD content of the gaseous products described above.

Results

The hydrolysis reactions studied in this investigation were: (a) triphenylsilane in a piperidine solution 1.00 *M* in water; (b) triphenylsilane in an ethanol solution 3.59 *M* in water and 0.01 *M* in potassium hydroxide; (c) tri-*n*-propylsilane in an ethanol solution 3.59 *M* in water and 0.6 *M* in potassium hydroxide.

Silicon–Hydrogen Bond Rupture.—Isotopic rate ratios for rupture of the silicon–hydrogen bond were determined for all of the above reactions in competitive experiments. The rate ratios were calculated from the volume and isotopic content of successive samples of evolved gas by means of the expression

$$\frac{k_{\mathrm{SiH}}}{k_{\mathrm{SiX}}} = \frac{\mathrm{d}[\mathrm{H_2}]}{[\mathrm{SiH}]} \Big/ \frac{\mathrm{d}[\mathrm{HX}]}{[\mathrm{SiX}]} = \log \frac{[\mathrm{H_2}]_\infty - [\mathrm{H_2}]_{t_2}}{[\mathrm{H_2}]_\infty - [\mathrm{H_2}]_{t_1}} \Big/ \log \frac{[\mathrm{HX}]_\infty - [\mathrm{HX}]_{t_2}}{[\mathrm{HX}]_\infty - [\mathrm{HX}]_{t_1}}$$

where SiH and SiX refer to the normal and isotopic silanes and where $[H_2]_t$ and $[HX]_t$ are, respectively, the amounts of hydrogen and isotopic hydrogen collected up to time t. The results of the measurements are summarized in Table I, and experimental points for representative runs are shown in Tables II and III. The mean deviation of points within a given run was less than one per cent., as was also the difference between the average ratios for duplicate runs.

TABLE I

ISOTOPIC RATE RATIOS FOR RUPTURE OF SILICON–HYDROGEN BONDS

Temp., °C.	Silane	Solvent	k_{SiH}/k_{SiX}
25	$(C_6H_5)_3SiH$-*d*	Piperidine–H_2O[a]	1.152 ± 0.004
0	$(C_6H_5)_3SiH$-*t*	Piperidine–H_2O[a]	1.288 ± .008
25	$(C_6H_5)_3SiH$-*t*	Piperidine–H_2O[a]	1.257 ± .003
25	$(C_6H_5)_3SiH$-*t*	C_2H_5OH–H_2O–KOH[b]	1.400 ± .006
25	$(n\text{-}C_3H_7)_3SiH$-*t*	C_2H_5OH–H_2O–KOH[c]	1.490 ± .011

[a] 1.00 *M* H_2O. [b] 0.01 *M* KOH, 3.59 *M* H_2O. [c] 0.6 *M* KOH, 3.59 *M* H_2O.

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(12) K. E. Wilzbach, A. R. Van Dyken and L. Kaplan, *Anal. Chem.*, **26**, 880 (1954).

(13) K. E. Wilzbach, L. Kaplan and W. G. Brown, *Science*, **118**, 522 (1953).

(14) W. K. Wilmarth, J. C. Dayton and J. M. Flournoy, THIS JOURNAL, **75**, 4549 (1953).

TABLE II

THE ISOTOPE EFFECT IN THE HYDROLYSIS[a] OF TRIPHENYLSILANE-*t* IN PIPERIDINE–H_2O

Fraction	H_2, mmole	HT, µcuries	Reaction cumulative, %	k_{SiH}/k_{SiT}
1	0.1687	15.50	8.68	1.256
2	.2117	32.89	19.57	1.263
3	.2022	32.53	29.98	1.255
4	.2601	43.33	43.37	1.255
5	.2240	38.90	54.90	1.259
6	.8765	196.4	100.00	
Total	1.9432	369.5	Mean	1.258 ± 0.003

[a] 0.513 g. of triphenylsilane-*t* in 20 ml. of piperidine, 1.00 *M* in H_2O, at 25°.

TABLE III

THE ISOTOPE EFFECT IN HYDROLYSIS[a] OF TRIPHENYLSILANE-*d* IN PIPERIDINE-H_2O

Fraction	Gas, mmole	Mole fraction HD	Mole fraction H_2	Reacn. cumulative, %	k_{SiH}/k_{SiD}
1	0.213	0.4467	0.5530	11.4	1.155
2	.189	.4505	.5492	21.5	1.157
3	.210	.4566	.5431	32.7	1.152
4	.235	.4642	.5358	45.2	1.145
Total	1.874	.4804	.5193	100.0	
				Mean	1.152 ± 0.004

[a] 0.252 g. of triphenylsilane, 0.246 g. of triphenylsilane-*d* in 20 ml. of piperidine, 1.00 *M* in H_2O, at 25°.

The value of 1.15 obtained for k_{SiH}/k_{SiD} in the hydrolysis of an equimolal mixture of triphenylsilane and triphenylsilane-*d* in piperidine–water is in marked disagreement with the value of $^1/_6$ reported[9] by Gilman, Dunn and Hammond from direct measurements on the separate isotopic molecules. Since it is conceivable[15] that this disagreement might be the result of the difference between a competitive and non-competitive method, we attempted to check the result of Gilman, *et al.* Values found for the first-order rate constants for the hydrolysis of 0.10 *M* solutions in piperidine 1.00 *M* in water at 25 ± 0.5° were 1.0×10^{-4} sec.$^{-1}$ for both triphenylsilane and triphenylsilane-*d*. Although the temperature regulation in these experiments was too poor to permit the accurate measurement of the small isotope effect observed in the competitive experiment, the results show that there is no large isotope effect in the non-competitive system.

Solvent–Hydrogen Bond Rupture.—The relative rates of removal of tritium and protium from solvents containing tracer concentrations of tritium were also determined. Since the molar ratio of solvent to silane was more than 100, and since each fraction of evolved gas was equivalent to about 0.1 mole % of the solvent it was possible to calculate the rate ratios from the equation

$$\frac{k_{SH}}{k_{ST}} = \frac{(ST)/(SH)}{(HT)/(H_2)}$$

where $(HT)/(H_2)$ and $(ST)/(SH)$ are proportional to the tritium content per mole of hydrogen in the gas and per equivalent of active hydrogen in the solvent, respectively. The change in $(ST)/(SH)$ during evolution of each gas sample was calculated and the average of the initial and final values was used in determining the rate ratios. In every experiment the isotopic rate ratios determined from analysis of three or four successive gas samples agreed within 1%. All of the ratios were calculated assuming a statistical distribution of tritium between water and piperidine or ethanol in the solvent mixture since data from which to calculate the true distribution are not available. The results obtained in this way are summarized in Table IV.

TABLE IV

ISOTOPIC RATE RATIOS FOR RUPTURE OF SOLVENT–HYDROGEN BONDS IN THE HYDROLYSIS OF SILANES

Temp., °C.	Silane	Solvent	k_{SH}/k_{ST}
0	$(C_6H_5)_3SiH$	Piperidine–H_2O[a]	3.32 ± 0.01
25	$(C_6H_5)_3SiH$	Piperidine–H_2O[a]	3.05 ± .02
25	$(C_6H_5)_3SiD$	Piperidine–H_2O[a]	3.00 ± .02
25	$(C_6H_5)_3SiH$	C_2H_5OH–H_2O-KOH[b]	6.96 ± .06
25	$(C_6H_5)_3SiD$	C_2H_5OH–H_2O–KOH[b]	7.25 ± .05
25	$(n\text{-}C_3H_7)_3SiH$	C_2H_5OH-H_2O–KOH[c]	3.98 ± .02

[a] 1.00 *M* H_2O. [b] 0.01 *M* KOH, 3.59 *M* H_2O. [c] 0.6 *M* KOH, 3.59 *M* H_2O.

In addition to these competitive experiments, the rate of hydrolysis of tripropylsilane at 25 ± 0.1° in an ethanol solution 3.47 *M* in water and 0.53 *M* in potassium hydroxide was compared with that in an otherwise identical deuterated solvent of about 95% isotopic purity. The measured second order rate constants were 1.74×10^{-4} sec.$^{-1}$ l. mole^{-1} in the normal and 1.21×10^{-4} sec.$^{-1}$ l. mole^{-1} in the "heavy" solvent, giving a ratio, k_{SH}/k_{SD}, of 1.44.

The Temperature Dependence.—The isotopic ratios in the hydrolysis of triphenylsilane in piperidine–water, measured at 25° and at 0°, are fitted by the equations

$$\frac{k_{SiH}}{k_{SiT}} = [0.96 \pm 0.08]e^{(79 \mp 28)/T}$$

and

$$\frac{k_{SH}}{k_{ST}} = [1.21 \pm 0.12]e^{(276 \mp 30)/T}$$

Although the uncertainties in the experimental values of the pre-exponential factors are rather large, the results show that the major part of the isotope effects is associated with the temperature-dependent factor.

Discussion

The Reaction Mechanism.—In the discussion of the reactions studied in this investigation it will be assumed that the mechanisms of hydrolysis of the two silanes in the two solvent mixtures employed are very similar. This assumption appears to be justified by the similarity of the reaction kinetics for triphenylsilane in piperidine–water[3] to that for tripropylsilane in alcohol–water[2] as well as of the effects of isotopic substitution on all systems studied.

The magnitudes of the isotope effects (Table I) for the rupture of the silicon–hydrogen bonds in the silanes are, as already indicated, sufficiently close to unity so that an unequivocal choice between mechanisms a and b cannot be made on this basis

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(15) That such a difference might arise under certain conditions has been pointed out by L. Kaplan, THIS JOURNAL, **76**, 4645 (1954). It would not be expected in this case, since the hydrogen is abstracted from a silane molecule which participates in the rate determining step.

alone. The rather large change in the isotopic rate ratio for triphenylsilane upon changing the solvent from piperidine–water to ethanol–water is, however, a strong argument in favor of mechanism *b*, since it implies considerable interaction in the transition state between the silane hydrogen and the solvent.

The effect of isotopic substitution in the solvent on the reaction rates, as measured in competition experiments (Table IV), is of little help in establishing the mechanism of the reactions. The markedly lower rates of removal of tritium than of protium demonstrate the existence of a transition state in which the solvent–hydrogen bond is weakened; although this transition state must occur in the slowest step involving the solvent, this step need not be rate determining for the over-all reaction. The comparison of the separately measured reaction rates for a given silane in ordinary and in deuterated solvent, on the other hand, does give information about the rate-determining step. The greater rate of hydrolysis of tripropylsilane[16] in ordinary alcohol–water than in the deuterated solvent provides additional evidence that the solvent participates in the rate-determining step, as required by mechanism b.[17]

The Transition State.—The relative rates of isotopic reactions have been interpreted in terms of the theory of absolute reaction rates.[18] If the transmission coefficients for the isotopic reactions are assumed to be equal, the isotopic rate rates may be written

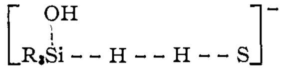
$$\frac{k_1}{k_2} = \frac{\left(\frac{M_2}{M_1}\right)^{3/2}}{\left(\frac{M_2^{\ddagger}}{M_1^{\ddagger}}\right)^{3/2}} \frac{\left(\frac{A_2B_2C_2}{A_1B_1C_1}\right)^{1/2}}{\left(\frac{A_2^{\ddagger}B_2^{\ddagger}C_2^{\ddagger}}{A_1^{\ddagger}B_1^{\ddagger}C_1^{\ddagger}}\right)^{1/2}} \frac{\prod^{3n-6} \frac{1-e^{-u_{i1}}}{1-e^{-u_{i2}}} e^{\Delta u_i/2}}{\prod^{3n-7} \frac{1-e^{-u_{i1}^{\ddagger}}}{1-e^{-u_{i2}^{\ddagger}}} e^{\Delta u_i^{\ddagger}/2}} \qquad (1)$$

where the subscripts 1 and 2 refer to the isotopes, the superscript $\ddagger$ refers to the transition state, M is the molecular weight, A, B and C are the principal moments of inertia, $u_i = h\nu_i/kT$, and $\Delta u_i = u_{i_1} - u_{i_2}$. The products are taken over the $3n - 6$ vibrations (ν_i) of the normal molecules and over the $3n - 7$ vibrations ($\nu_i^{\ddagger}$) of the transition state.

The significance of the various factors in equation 1 and their magnitude have been discussed at some length by Melander[18c] for reactions of the hydrogen isotopes. Although in some cases a considerable part of the isotope effect might be expected to result from the essentially temperature-independent pre-exponential factors, this does not seem to be the case for the reactions studied here, since, in the hydrolysis of triphenylsilane in piperidine–water, the temperature-independent factors of both $k_{\text{SiH}}/k_{\text{SiT}}$ and $k_{\text{SH}}/k_{\text{ST}}$ are close to unity. Accordingly the isotope effects will be discussed primarily in terms of the zero-point energy factor.

$$\frac{k_1}{k_2} = e^{(h/2kT)[\Sigma(\nu_{i1} - \nu_{i2}) - \Sigma(\nu_{i1}^{\ddagger} - \nu_{i2}^{\ddagger})]} \qquad (2)$$

The transition state for the alkaline hydrolysis of a triorganosilane by mechanism b might be formulated as



$$\left[\begin{matrix} \text{OH} \\ \vdots \\ \text{R}_3\text{Si} - - \text{H} - - \text{H} - - \text{S} \end{matrix}\right]^-$$

where the dotted lines represent partially formed or ruptured bonds of unspecified strength. That the extent of bonding varies from one set of reactants to another is indicated by the fact that values of $k_{\text{SiH}}/k_{\text{SiT}}$ for the hydrolysis of triphenylsilane are different for alcohol–water than for piperidine–water and that values of both $k_{\text{SiH}}/k_{\text{SiT}}$ and $k_{\text{SH}}/k_{\text{ST}}$ for hydrolysis in alcohol–water are different for triphenyl- than for tripropylsilane. For systems as complex as those studied in the present investigation an exact calculation of the theoretical value of the isotopic rate ratio is quite impracticable. It is, nevertheless, of some interest to calculate, with the aid of simplifying assumptions, approximate values for some limiting configurations of the transition state, and to compare these calculated values with the experimental results.

In these calculations it will be assumed that all frequencies except those involving the reacting hydrogen atoms are invariant to isotopic substitution and that the isotopic frequency shifts for the transverse vibrations of the hydrogens are small in comparison with those for the longitudinal vibrations.[19] For the reacting molecules, the stretching frequencies in cm.$^{-1}$ are taken[20] as SiH = 2135, SiD = 1547, SiT = 1282; OH = 3259, OT = 1988. For

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[16] The hydrolysis reactions of triphenylsilane are less amenable to study in deuterated solvents. The concentation of deuteroxide ion produced by the equilibrium

$$C_5H_{10}ND + D_2O \rightleftarrows C_5H_{10}ND_2^+ + OD^-$$

is probably considerably lower than that of hydroxide ion in the ordinary solvent. (W. E. K. Wynne-Jones, *Trans. Faraday Soc.*, **32**, 1397 (1936), reports the autoprotolysis constant of D_2O as about one-fifth that of H_2O.) This equilibrium isotope effect might well be large enough to obscure the kinetic effect under investigation. The hydrolysis of triphenylsilane in alcohol–water is kinetically complicated by the diminution of the (low) hydroxide ion concentration by the triphenylsilanol formed in the reaction.

[17] It should be noted that the ratio (1.44) of the reaction rates in the two solvents is not directly comparable with the value of 3.98 found for $k_{\text{SH}}/k_{\text{ST}}$ in the corresponding competitive experiment since, in the deuterated solvent, not only is there isotopic substitution in the solvent molecule, but there is also an isotopic change in the reacting hydroxide ion. The observation that the rate ratio for the separate reactions is smaller than the value of about 2.5 which would be expected for $k_{\text{SH}}/k_{\text{SD}}$ in a competitive experiment at tracer deuterium concentrations can be explained by the greater reactivity of deuteroxide than of hydroxide ion. S. H. Maron and V. K. LaMer, THIS JOURNAL, **60**, 2588 (1938), list five reactions for which the rates of reaction of deuteroxide ion in heavy water are 20 to 40% greater than those of hydroxide ion in light water. This effect may be attributable, at least in part, to the zero-point energy difference associated with an O–H bending frequency present in the product (or transition state) but not in the reacting hydroxide ion.

[18] (a) J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949); (b) J. Bigeleisen and M. Wolfsberg, *ibid.*, **21**, 1972 (1953); (c) L. Melander, *Ark. för Kemi*, **2**, 211 (1950); (d) H. Eyring and F. W. Cagle, Jr., *J. Phys. Chem.*, **56**, 889 (1952).

[19] For example, the frequency differences between trichlorosilane and trichlorosilane-*d* are for the stretching vibrations 611 cm.$^{-1}$ and for the bending vibrations 194 cm.$^{-1}$; F. Halverson, *Rev. Mod. Phys.*, **19**, 117 (1947).

[20] The SiH and SiD values are those measured for triphenylsilane (L. Kaplan, THIS JOURNAL, **76**, 5880 (1954)); that for SiT is calculated. Use of the SiH frequency of 2108 cm.$^{-1}$ in tripropylsilane would have little effect on the calculation of $k_{\text{SiH}}/k_{\text{SiT}}$. The OH frequency is that observed in liquid ethanol (L. G. Bassett, *et al.*, U. S. Atomic Energy Commission Document NYO-607 (1950)). Use of the vapor phase frequency of 3689 cm.$^{-1}$ (E. K. Plyler, *J. Research Natl. Bur. Standards*, **48**, 281 (1952)) would increase the calculated values of $k_{\text{SH}}/k_{\text{ST}}$ by 50%.

the transition state two limiting cases are considered: (1) the reacting hydrogen atoms are completely free, the frequencies therefore being zero, and (2) the bond between the reacting hydrogen atoms is essentially that in a gaseous hydrogen molecule, the frequencies being taken[21] as HH = 4405, HD = 3817, HT = 3598 and DT = 2846. Substitution of the appropriate frequencies in equation 2, using $T = 298°$K., gives for case (1), $k_{\mathrm{SiH}}/k_{\mathrm{SiD}} = 4.1$, $k_{\mathrm{SiH}}/k_{\mathrm{SiT}} = 7.8$. The assumptions for case (2) lead to values of $k_{\mathrm{SiH}}/k_{\mathrm{SiD}} = 1.00$ and $k_{\mathrm{SiH}}/k_{\mathrm{SiT}} = 1.12$. The experimental values of 1.15 for $k_{\mathrm{SiH}}/k_{\mathrm{SiD}}$ for the one reaction studied and 1.29, 1.40 and 1.49 for $k_{\mathrm{SiH}}/k_{\mathrm{SiT}}$ for three reactions, are in much better agreement with the values calculated for case (2) than with those for case (1).

For oxygen–hydrogen bond rupture the calculated values of $k_{\mathrm{SH}}/k_{\mathrm{ST}}$ are for case (1) 21.5, and for case (2) 3.1 or 2.1 for hydrolysis of a protium or deuterium silane, respectively. The experimental values (Table IV) are 4.0 for tripropylsilane, 7.0 for triphenylsilane and 7.2 for triphenylsilane-*d*.

Although the calculations are only approximate, for reasons already mentioned, the experimental results are sufficiently close to the values calculated for case (2) to support the hypothesis of considerable hydrogen–hydrogen bonding in the transition state.

That the calculated value of $k_{\mathrm{SH}}/k_{\mathrm{ST}}$ for the deuterosilane is considerably smaller than that for the protium compound, while the experimental values are nearly equal, is probably attributable to the crudeness of the calculations. In particular, if instead of a free hydrogen molecule in the transition state there is some residual bonding of hydrogen to silicon, the theoretical values for the two compounds would be considerably closer. Taking into account the pre-exponential factors of equation 1 might also help resolve the discrepancy.

Acknowledgment.—We are indebted to Dr. D. A. Hutchison and Mr. L. G. Pobo for mass spectrometric analyses.

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[21] H. C. Urey, *J. Chem. Soc.*, 562 (1947).

[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF HARVARD UNIVERSITY]

The Reaction of Organotin Halides with Diazomethane

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Halomethyl derivatives of tin have been prepared in good yield by the reaction of diazomethane with six organotin halides, and the fully alkylated derivatives of the type R_3SnCH_2X have been prepared. The adverse physiological effects of compounds of the type $(CH_3)_2(CH_2X)SnX$ are pointed out. The properties of 14 new organotin compounds are reported.

While side-chain chlorination and bromination of methylsilicon compounds are well known preparative methods for halomethylsilanes, such procedures cannot be applied to the preparation of halomethyltin compounds because the halogens, even under the mildest possible conditions, cause cleavage of the carbon–tin bond.[2] For example, chlorination of tetramethyltin gives methyltin chlorides and methyl chloride. Recent attempts to prepare chloroethyltin compounds by photochemical chlorination and by treatment of tetraethyltin with sulfuryl chloride in the presence of a peroxide catalyst similarly were unsuccessful, and only carbon–tin bond cleavage was observed.[3]

Recent work on the reaction of diazoalkanes with halides of tin[4,5] showed that an α-haloalkyl group may be introduced by this method

$$\gt\mathrm{Sn{-}Cl} + \mathrm{CH_2N_2} \longrightarrow \gt\mathrm{Sn{-}CH_2Cl} + \mathrm{N_2}$$

However, only tin tetrahalides and their α-haloalkyl derivatives were treated in this manner before our study.

We have extended the application of the diazomethane reaction to five alkyltin halides and one aryltin halide. Treatment of dimethyltin dichloride, dibromide, or diiodide with slightly more than one equivalent of diazomethane in ether at 5° accompanied by *extremely vigorous stirring* during the addition gave the corresponding halomethyldimethyltin halides in yields of 70–80, 73 and 78%, respectively. The liquid products are all powerful lachrymators and vesicants, decreasing somewhat in potency as the atomic weight of the halogen increases. They are extremely irritating to the eyes, nose and throat, and cause very painful irritations of sensitive areas of the skin, particularly on the eyelids. In direct contact with the skin, even in solution, they cause painful blisters similar to those caused by alkylmercuric halides. Some irritating effects were even noticed during recrystallization of solid, high-melting halomethyltin fluorides. The trialkyltin halides in general are known to be decidedly toxic as well as irritating.[6,7] It is strongly recommended that great caution be exercised in handling the halogenated trialkyltin halides described in this report.

The physiological properties of the halomethyldimethyltin halides do *not* seem to be due to the presence of the halomethyl groups; rather they seem to be a function of the trialkyltin group. This is dem-

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[2] E. Krause and A. v. Grosse, "Die Chemie der metallo-organischen Verbindungen," Gebrueder Borntraeger, Berlin, 1937, pp. 335–363.

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[4] A. Ya. Yakubovich, S. P. Makarov, V. A. Ginsburg, G. I. Gabrilov and E. N. Merkulova, *Doklady Akad. Nauk S.S.S.R.*, **72**, 69 (1950); *C. A.*, **45**, 2856 (1951).

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[7] Private communication, E. S. Hedges, Director of Research, International Tin Research and Development Council.