[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Cyclic Organosilicon Compounds. II. Ring Size and Reactivity in the Alkali-catalyzed Hydrolysis of Silanes

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The relative reactivity of cyclic organosilanes toward alkali-catalyzed hydrolysis has been observed as a function of ring size. The order of reactivity is 5>7>straight-chain>6, where the number given is the number of atoms in the ring. This is the same order of reactivity found among alicyclic compounds in different reactions. The results are discussed in terms of the possible stereochemistry of silicon.

Several publications correlating the reaction rates of carbocyclic compounds with ring size have appeared recently. Work in this field has been stimulated by the announcement of the "I-strain" theory by H. C. Brown and his co-workers.[2] Studies by independent workers have tended to confirm Brown's generalizations concerning the reactivity of cyclic compounds.[3,4]

This paper reports observations of the reactivity of some heterocyclic compounds containing silicon as the heteroatom.[5] The reaction for which these observations were made was the alkali-catalyzed hydrolysis in which hydrogen bonded to silicon is replaced by hydroxyl. This hydrolysis of silanes is a particularly favorable reaction for rate measurements. Unlike many reactions occurring at a silicon atom, it proceeds at a rate slow enough to be measured easily at room temperature; and also, the reaction can be followed conveniently by measuring the gaseous hydrogen which is evolved.

In discussing the results of these experiments, it will be necessary to take into consideration the probable conformations of silicon-containing rings, as compared with ordinary alicyclic rings. Considering first the alicyclic rings, it is known that both cyclopentane and cycloheptane are strained because of unfavorable constellation effects,[6] while cyclohexane exists in a strain-free staggered conformation.[7] In his papers explaining the "I-strain" concept, Brown has pointed out that this internal strain is probably responsible for the abnormally rapid reactions undergone by cyclopentyl and cycloheptyl compounds, since it is presumably partially relieved in the transition state[2] (in either S_N1, S_N2, or free-radical reactions). On the other hand, the unreactivity of cyclohexyl compounds relative to straight-chain analogs is considered to be due to strain introduced in going to a three- or five-coördinate transition state.[2]

It seems reasonable that similar considerations should hold for compounds in which one carbon atom of the ring has been replaced by silicon. The tetrahedral bond angles at silicon should be more deformable than those at carbon, and this may lead to some relief of internal strain when a carbon atom is replaced by silicon in the five- and seven-membered rings. However, at least in the five-membered (cyclotetramethylenesilane) ring, this will be partly compensated by the fact that the larger silicon atom can be shown to introduce considerable angular strain into even a planar model of the molecule. (In an idealized planar model of cyclopentane, angular strain would be very small.)

Because the covalent radius of silicon is more than 50% larger than that of carbon, it is not immediately apparent that the six-membered (cyclopentamethylenesilane) ring will be able to assume a strainless staggered conformation like that of cyclohexane. That cyclopentamethylenesilane does have strainless conformations available to it can be shown by geometrical calculation.[8] One such form is shown in Fig. 1. The calculations were made assuming that all bond angles are tetrahedal; the C–C distance was taken as 1.54 Å. and the C–Si distance as 1.93 Å.[9]

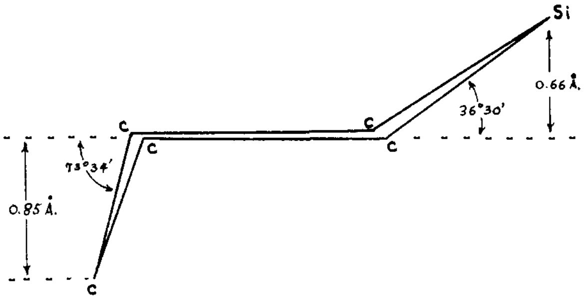

Fig. 1.

The Alkali-catalyzed Hydrolysis of Alkylsilanes.—Silicon compounds containing a hydrogen atom bonded to the silicon react with bases in the presence of water to give silanols and gaseous hydrogen. A study of the kinetics of the reaction, using trialkylsilanes of low molecular weight, has been carried out by Price.[10] The stoichiometry of the reaction is

$$R_3SiH + R'OH + OH^- = R_3SiOH + H_2 + (OR')^-$$

where R′ can be either hydrogen or an alkyl group. If R′ is hydrogen (that is, if the reaction is carried out in an aqueous medium) the reaction is strictly hydroxyl-catalyzed, and the concentration of OH^- ions does not change during the course of the reaction. Since alkylsilanes are nearly insoluble in water but are readily soluble in a mixture of

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[1] Department of Chemistry, Lehigh University, Bethlehem, Pa.

[2] H. C. Brown and M. Gerstein, THIS JOURNAL, **72**, 2926 (1950); H. C. Brown, R. S. Fletcher and R. B. Johannesen, *ibid.*, **73**, 212 (1951); H. C. Brown and M. Borkowski, *ibid.*, **74**, 1894 (1952).

[3] C. G. Overberger, H. Biletch, A. B. Finestone, J. Lilker and J. Herbert, *ibid.*, **75**, 2078 (1953).

[4] A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951).

[5] R. West, THIS JOURNAL, **76**, 6012 (1954).

[6] R. Spitzer and H. M. Huffman, *ibid.*, **69**, 211 (1947).

[7] V. Prelog, *J. Chem. Soc.*, 420 (1950).

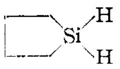
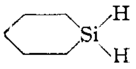
[8] Details are given in R. West, Thesis, Harvard University, 1954.

[9] L. O. Brockway and H. O. Jenkins, THIS JOURNAL, **58**, 2036 (1936).

[10] F. P. Price, *ibid.*, **69**, 2600 (1947).

TABLE I

RATES OF HYDROLYSIS OF SILANES[a]

Silane		$[OH^-]$ mole/l.	Rate constant, k_1 (min.$^{-1}$)				
			5.00°	15.00°	25.00°	35.00°	45.00°
$(C_2H_5)_2CH_3SiH$	(I)	1.85		0.0261	0.0657	0.152	
				.0258	.0642	.149	
	(I)	0.256			.0263	.0627	0.120
					.0263	.0615	.126
							.122
	(II)	0.256	.0455	.133	.341		
			.0461	.130	.349		
			.0443	.127	.345		
	(III)	1.85			.0118	.0326	
					.0117	.0324	
					.0117	.0334	
	(III)	0.256				.00916	.0222[b]
						.00910	.0232[b]

[a] Silane 0.12 M, H_2O 8.3 M. [b] 44.80°.

ethanol and water, this medium was used both in Price's study and in the experiments reported here.

Price established that the reaction is first order in silane, first order in hydroxyl ion, and probably also first order in hydroxylated solvent. The hydrolysis is thus clearly bimolecular, and must proceed either by typical S$_N$2 bimolecular displacement or through a (somewhat) stable pentacovalent intermediate as suggested by Sidgwick.[11] The two possible mechanisms can be considered equivalent for the purposes of this discussion, since both require a five-coördinate transition state.

Experimental

The silanes used in these experiments were twice fractionally distilled, and had boiling ranges of less than 0.5°. The preparations of the cyclic silanes are described in the first paper in this series,[5] while diethylmethylsilane was prepared as described by Price.[10]

An Aminco bimetallic thermoregulator, operating through a mercury switch relay, was used with the thermostat bath. It proved capable of maintaining temperatures to ±0.05°. The reaction vessel was a 50-ml. erlenmeyer flask fitted with a hypodermic syringe and a gas outlet tube, and containing a glass-encased magnetic stirrer to agitate the mixture during hydrolysis. To carry out a rate experiment, the sample of silane, usually 0.200 ml., was placed in the flask with 10 ml. of absolute ethanol. The syringe was filled with an aqueous sodium hydroxide solution, prepared from Merck 97% min. NaOH, containing 1.82 g. of water. The entire system was then placed in the thermostat for at least 45 minutes. Then, while the silane solution was stirred vigorously, the water and alkali were added rapidly from the syringe and an electric timer was started. The evolved hydrogen was collected over hydrogen-saturated water in a gas buret; the volume of hydrogen and the time were recorded at intervals through the course of the reaction.

The volume of hydrogen was taken as a measure of the amount of silane which had reacted. Reaction rates were evaluated from conventional first-order plots of the log of silane concentration *vs.* time (Table I). Excellent straight lines were obtained with I and II, up to about 75% reaction. The plots of the data from hydrolysis of III exhibited very slight curvature, which may be attributed either to a competing reaction of higher order or to a small amount of residual silane impurity.

The volume of evolved hydrogen was read to ±0.03 ml., and the error in timing was about ±1 second. The reaction rates for I and II are believed to be accurate to ±3%, which should lead to an error in the heat of activation of about ±0.5 kcal., and in the entropy of activation of about ±1 e.u. Because of the curvature mentioned above in the hydrolysis plots for III, the limits of error for this compound are estimated to be about twice as great.

Measured rates of reaction are tabulated in Table I. Diethylmethylsilane (I) was taken as a standard compound with which to compare the cyclic silanes. At 0.256 N NaOH and 8.3 M H_2O, the specific reaction rate constant for the hydrolysis of I was found to be 0.242. This is in excellent agreement with the value of 0.243 reported by Price[10] for the same compound at 0.2 N KOH and 8.61 M H_2O. At the much higher hydroxyl ion concentration of 1.85 N, the specific reaction rate constants are very greatly reduced, probably because of a salt effect.

Discussion

The data in Table I show that I reacts more slowly than cyclotetramethylenemethylsilane (II) by a factor of about 13; while cyclopentamethylenemethylsilane (III) reacts more slowly than I by a factor of about 6. The seven-membered ring of the same series, $(CH_2)_6Si(CH_3)H$, was not obtained pure, but qualitative experiments with the impure material established that it reacted faster than I but slower than II. All of these observations are in accord with the I-strain theory,[2] assuming that silanes do react with hydroxyl ion by a mechanism involving a five-coördinate transition state.

Thermodynamic functions of activation for the two cyclic silanes relative to I are given in Table II.[12] It is apparent from Table II that the heats of activation of both the five- and six-membered rings are greater than that for I.[13] The heat of

TABLE II

THERMODYNAMIC FUNCTIONS OF ACTIVATION FOR HYDROLYSIS OF SILANES

Silane	Temp., °C.	$[OH^-]$	ΔH^{+}, kcal.	Av. ΔH^{+}, kcal.	$\Delta G^{+}a - \Delta G^{+}_0$	$\Delta S^{+}a - \Delta S^{+}_0$, e.u.
I	15–25	1.85	15.7			
	25–35	1.85	15.3			
	25–35	0.256	15.7	15.5	0.0	0
	35–45	0.256	15.5			
II	5–15	0.256	16.9			
	15–25	0.256	16.7	16.8	−1.6	+10
III	25–35	1.85	18.8	18.5	+1.2	+ 6
	35–45	0.256	18.3			

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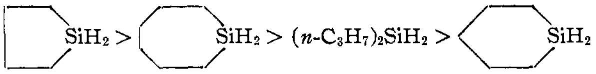
(11) N. V. Sidgwick, "The Electronic Theory of Valency," Oxford University Press, London, 1927, p. 157. See also C. G. Swain, R. M. Esteve and R. H. Jones, THIS JOURNAL, **71**, 965 (1949).

(12) The notation used follows that in L. P. Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., New York, N. Y., 1940, p. 119.

(13) The observed heat of activation for the hydrolysis of I, 15.5 kcal., is 2.2 kcal. higher than the value reported by Price[10] for the same compound. This may be explained by slight differences in the experimental conditions in the two studies, as well as by the fact that Price used KOH while NaOH was used in these experiments.

activation would be expected to be greater for III, both because the free energy of activation is greater and because of the postulated additional strain in the transition state. However, this result was not expected for the five-membered ring II. A consideration of the relative entropies of activation for the three compounds shows that it is the very large relative entropy of activation for II which overwhelms the effect of the increased heat of activation and causes II to react faster than the straight-chain compound I. The entropy of activation for III is also greater than that for the standard compound I, but in this case the heat of activation predominates so that III reacts more slowly than I. The high entropies of activation probably indicate that in this reaction compounds II and III have greater freedom of motion and a larger number of degrees of freedom in their transitions states than in the ground states. It would be of interest to compare these results with those for a reaction of ordinary carbocyclic rings, proceeding by a bimolecular displacement mechanism, but apparently no such study has been published.

Some experiments were also carried out to determine rates of hydrolysis of linear and cyclic difunctional silanes (R_2SiH_2). Theoretically it should be possible to determine the rates of hydrolysis of each of the two hydrogen atoms by a process entirely analogous to that used in radiochemistry to analyze curves representing two simultaneous first-order decay reactions. In practice, however, it was found that the first hydrogen is removed so rapidly that no estimate of the rate could be made. Approximate rates were obtained for the removal of the second hydrogen atom. The reactivity of the compounds tested decreased in the order



The order is thus the same as that observed with the monofunctional cyclic silanes. It is interesting that the order of reactivity of cyclic silanes as a function of ring size follows the same order observed for carbocyclic compounds in several different reactions.[3-5] If the assumptions made above about the conformations of silicon-containing rings are valid, then these experiments provide additional confirmation of the I-strain theory[1-3] and indicate that it may be extended to reactions occurring at elements other than carbon. In any case, it seems that the factors which operate to cause activation and deactivation of carbocyclic rings of certain sizes also operate to cause quite similar effects among cyclic organosilicon compounds.

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NOTES

Thermodynamic Functions of the Chlorofluoromethanes

BY L. F. ALBRIGHT, W. C. GALEGAR AND K. K. INNES

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Two recent studies of chlorofluoromethanes have made it possible to refine the thermodynamic calculations by Gelles and Pitzer[1] for these compounds. Claassen[2] combined his measurements of the Raman spectra of the gases with the infrared data of Plyler and Benedict[3] to estimate what he considers to be the best values of the fundamental frequencies. Thirteen of the frequencies, whose values are less than 800 cm.$^{-1}$, differ by more than 5 cm.$^{-1}$ and four by greater than 20 cm.$^{-1}$ from the values reported by Plyler and Benedict and used by Gelles and Pitzer. Masi[4] measured the heat capacity of gaseous CCl_2F_2 and reported derived values for the ideal gas, which he claims are accurate to within 0.15% at temperatures from −30 to 90°. His results are about 0.7% higher than values calculated using the rigid-rotator, harmonic-oscillator approximation. The difference was attributed to a shift of one frequency (later verified by Claassen[2]) and to the effect of anharmonicity. Masi included approximate values for the anharmonicity contribution. These values became appreciable at higher temperatures.

McCullough and co-workers[5] have presented empirical equations for correlating anharmonicity contributions for various thermodynamic functions. These equations are used in the present study.

The thermodynamic functions of chlorofluoromethanes were calculated assuming a rigid-rotator and harmonic-oscillator in the usual manner at temperatures from 100 to 1000°K. Calculations were made using the products of the moments of inertia presented by Gelles and Pitzer,[1] fundamental frequencies given by Claassen,[2] and tables of the vibrational contributions to various thermodynamic functions as presented by Taylor and Glasstone.[6] The experimental heat capacity values for CCl_2F_2 were subtracted from the calculated ones. The differences were assumed to be caused by anhar-

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(1) E. Gelles and K. S. Pitzer, THIS JOURNAL, **75**, 5259 (1953).

(2) H. H. Claassen, *J. Chem. Phys.*, **22**, 50 (1954).

(3) E. K. Plyler and W. S. Benedict, *J. Research Natl. Bur. Standards*, **47**, 202 (1951).

(4) J. F. Masi, THIS JOURNAL, **74**, 4738 (1952).

(5) J. P. McCullough, H. L. Finke, W. N. Hubbard, W. D. Good, R. E. Pennington, J. F. Messerly and G. Waddington, *ibid.*, **76**, 2661 (1954).

(6) H. S. Taylor and S. Glasstone, "A Treatise on Physical Chemistry," Vol. I, D. Van Nostrand Co., New York, N. Y., 1942, p. 655.