[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF HARVARD UNIVERSITY]

The Action of Strong Base on Hexamethyldisiloxane

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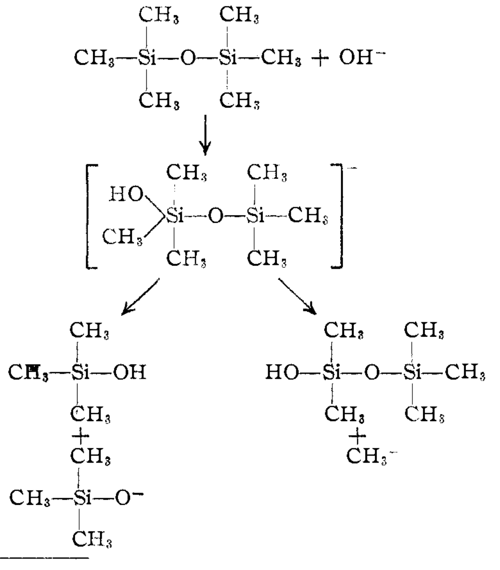
It has amply been demonstrated that cleavage of silicon-carbon bonds in various methyl siloxane systems can be brought about by the action of base of varying strength, depending on the negative substituents carried by the methyl groups. Even in unsubstituted hexamethyldisiloxane, it has been shown that under sufficiently drastic conditions methane is liberated and an inorganic silicate is deposited.[2] However, in view of the ready rearrangements of siloxane systems which have been shown to proceed in the presence of bases (and even in an alcoholic ammonia medium[2]), it would seem that under the proper conditions cleavage of the silicon-oxygen bond of siloxane systems by bases to form salts should compete very favorably with the stripping of methyl groups from the silicon nuclei. It has been the purpose of this investigation to determine these conditions, with the aim of preparing alkali-metal salts of the simple silanols by such basic action.

Hexamethyldisiloxane, $(CH_3)_3SiOSi(CH_3)_3$, was used as starting material in the present work because of its ready availability and because of the known acidity of trimethylsilanol toward strong bases.[3] It would be expected that hexamethyldisiloxane, when treated with alkali of 12 *N* strength or greater, should dissolve under the attack by hydroxyl ion. In accordance with the mechanism proposed by Swain, Esteve and Jones,[4] a pentacovalent silicon intermediate would be formed, and the reaction might then proceed either by cleavage of the silicon-carbon or the silicon-oxygen bond. As was pointed out by Krieble and Elliot,[2] the more electronegative group should be displaced, and this should be the siloxy group. This is represented by the scheme shown. The silanol and siloxy anion would then be expected to react with the basic solution to form the metallic salt, which would be withdrawn from the equilibrium because of its low solubility.



Preliminary experiments revealed, however, that at ordinary temperatures and even with very concentrated aqueous base, hexamethyldisiloxane seemed completely insoluble and unaffected. It was found that in a sealed tube a reaction proceeded at temperatures above 100° to yield methane. No silanolate was precipitated. Using a stainless steel reaction bomb fitted with a pressure gage, the course of subsequent reactions could be observed by following the pressure of methane developed during the reaction. In a homogeneous medium consisting of absolute ethanol, potassium hydroxide and hexamethyldisiloxane, it again was found that at temperatures of 170-200° the qualitative results were the evolution of methane and the deposition of a mainly inorganic silicate, in which the potassium content varied between 20-25%. When small amounts of water were added, the over-all course of the reaction remained unaltered, but the early evolution of methane was much faster (see Fig. 1).

These results indicate that in a hydroxylated solvent the displacement of methyl groups to form methane must be easier than the competing formation of the siloxy anion. If, however, a reaction could proceed in an aprotic solvent, where the only cation available would be M^+, then the most stable product would be the metallic silanolate, and the cleavage of the silicon-oxygen bond would be the expected result.

In order to test this hypothesis, experiments were carried out using dry ethyl ether as solvent. It was necessary to use solid, fused potassium hydroxide, which has only a small solubility in the ether. In spite of all attempts to keep the reactants anhydrous, some methane always was evolved and a mixture of products was obtained. An explanation readily is found, however, in the formation of water by the condensation of the resulting trimethylsilanol to yield hexamethyldisiloxane. The solid products then obtained contained some carbon, and the potassium content had reached 30-35% (theoretical for potassium trimethylsilanolate, 30.5%). No pure potassium salt was isolated, but hydrolysis of the crude product yielded a liquid which, on the basis of the infrared spectrogram and odor, was identi-

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[2] Krieble and Elliot, THIS JOURNAL, **68**, 2291 (1946).

[3] Sommer, Pietrusza and Whitmore, *ibid.*, **68**, 2282 (1946).

[4] Swain, Esteve and Jones, *ibid.*, **71**, 965 (1949).

fied as a trimethylsilanol–hexamethyldisiloxane mixture. Only very small amounts were isolated.

When dry benzene was used as solvent, a solid reaction product was obtained which contained 30–31% potassium and considerable carbon. However, additional impurities were introduced by the participation of benzene in the reaction, and the phenylated product was not identified.

The most satisfactory results were obtained when an excess of hexamethyldisiloxane itself was used as solvent. With fused and powdered sodium hydroxide, the fission of methyl groups proceeded very slowly as indicated by the pressure curve (see Fig. 1). The white solids obtained were extremely hygroscopic and averaged 35% sodium (theoretical for sodium trimethylsilanolate, 20.5%). Infrared absorption spectra of the solids suspended in mineral oil proved the presence of the desired sodium trimethylsilanolate, and also demonstrated the presence of silicates which retained Si–O–Si bonding, formed by cleavage of methyl groups to form methane. Hydrolysis of the reaction products yielded a water-insoluble liquid which was identified as hexamethyldisiloxane by its infrared absorption spectrum and by the refractive index. Separation of a pure sodium silanolate from the silicate impurity could not be accomplished, however, so that at the present time this is not a satisfactory method for the preparation of pure silanolates. Nevertheless, the formation and identification of the sodium salt proves that in aprotic solvents cleavage of the siloxane linkage can be effected by strong bases in preponderance over cleavage of methyl groups.

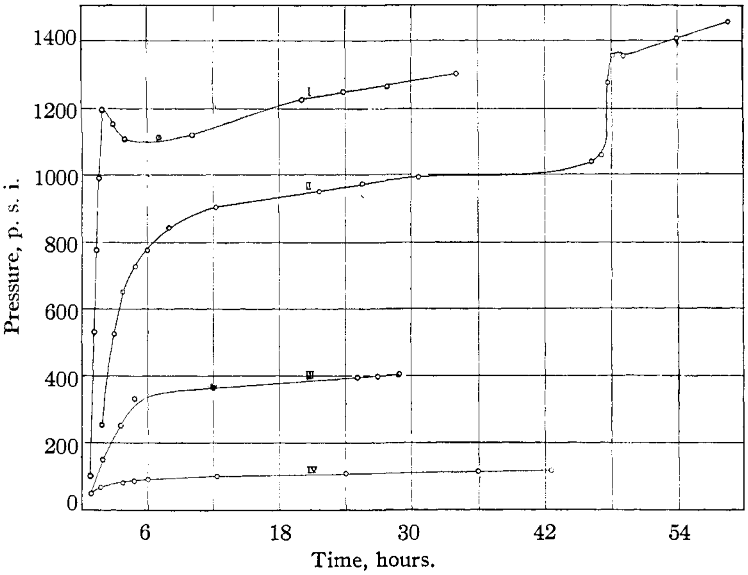

Fig. 1.—Curve I, reaction 2, Table II; Curve II, reaction 1, Table II; Curve III, reaction 5, Table II; Curve IV, reaction 8, Table II.

Experimental

The hexamethyldisiloxane was obtained from the General Electric Co. (b. p. 100°, $n^{20}D$ 1.3774). The reactions with aqueous alkali are summarized in Table I. At room temperature the reactants were stirred for long periods of time, and the aqueous layer examined for precipitation.

TABLE I

Ml. M_2[a]	Concn. NaOH, N	Solvent	Solvent, ml.	Temp., °C.	Time, days
10	8	H_2O	50	Room t.	3
10	10	H_2O	50	Room t.	3
10	12	H_2O	50	Room t.	3
10	12	H_2O	50	Reflux	1
10	12	H_2O–alc.	100	Reflux	1
10	10	H_2O	5	115	3
6	12	H_2O	6	115	3
2	20	H_2O	10	150	5 hr.[b]
5	20	H_2O–alc.	10	115	3
6	Satd.[c]	Alc.	6	140	16 hr.

[a] M_2 = hexamethyldisiloxane. [b] Tube exploded. [c] KOH.

The same procedure was used at reflux temperature. The sealed-tube reactions were carried out in Carius combustion tubing using the amounts of reactants listed in Table I. The pressure of methane was not measured but was evident upon opening the tubes.

Bomb reactions were carried out in a 110-cc. stainless steel reaction bomb. Heat was applied by means of a specially constructed electric furnace which supported the bomb at a 45° angle. The reactions are summarized in Table II. In those reactions using alcoholic potassium hydroxide, a sample was titrated to determine the basic strength. When it was necessary to use solid base, the reagent grade pellets were fused in a silver boat to remove water. Initial heating of the bomb was carried out as rapidly as possible and temperature and pressure readings were taken at five- to ten-minute intervals until the pressure rise was gradual. Thereafter, readings at intervals of one or more hours proved sufficient. After the reaction, the bomb was cooled to room temperature or lower and a reading of the residual pressure was taken. The methane was then discharged and the bomb opened. The liquid and solid portions were collected and protected from moisture. A sample of the liquid layer was distilled, and in cases where alcohol was used as solvent a sample also was titrated with acid to determine the loss of basic strength. A sample of the solid reaction product was dissolved in water and standard acid and the per cent. sodium or potassium determined by back-titration with standard base. Where possible, an infrared absorption spectrum of the solid material in suspension in mineral oil was taken using a Baird recording spectrophotometer. In a qualitative way it has been shown that the strong absorption band which appears near 8 μ in methyl siloxane systems is some function of the $Si-CH_3$ grouping.[5] The presence of this strong band in the absorption spectra of the solid reaction products indicated those cases where considerable carbon had been retained. Hydrolysis of the solid was carried out to determine whether any water-insoluble liquid was formed. (Such liquid could arise only from the hydrolysis of the silanolate to yield trimethylsilanol and subsequently hexamethyldisiloxane.)

Characterization of Solid from Reaction 9, Table II.—An infrared absorption spectrum of the solid suspended in mineral oil was taken and compared with the spectrum of pure sodium trimethylsilanolate prepared by reaction

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[5] Wright and Hunter, THIS JOURNAL, **69**, 803 (1947); Young, Servais, Currie and Hunter, *ibid.*, **70**, 3758 (1948); Richards and Thompson, *J. Chem. Soc.*, 124 (1949).

TABLE II

	Ml. M_2[a]	Solvent	Solvent, ml.	Base	G. of base	Reacn. temp., °C.	Time, hr.	Resid. P(p.s.i.)	At temp. °C.	% Na or K
1	10	Alcohol	50	KOH	2.13	194, 220, 246	93	680	5	22.2
2	10	Alc.–H_2O	50–55	KOH	2.44	200	106	655	6	24.2
3	20	Ether	30	KOH[b]	10	200	11	160	15	33.4
4	20	Ether	35	KOH	4	190	73.5	110	12	36.5
5[c]	15	Benzene	50	KOH	3	190	118	200	24	30.8
6	50	M_2	...	KOH	5	190	61.5	290	24	35.7
7	50	M_2	...	KOH[b]	5.5	185	43	440	24	..[d]
8[c]	65	M_2	...	NaOH	5	150	46.5	<100	24	31.1
9	50	M_2	...	NaOH	5	190	120	<100	24	38.3

[a] M_2 = hexamethyldisiloxane. [b] KOH not fused. [c] Platinum thimble used as liner to collect precipitate. [d] Solid hydrolyzed to yield trimethylsilanol.

of metallic sodium with trimethylsilanol. Hydrolysis of a sample of the solid from reaction 9 was carried out with cold water in a small test-tube to yield hexamethyldisiloxane. The infrared spectrogram of this liquid was identical with that obtained from a pure sample of hexamethyldisiloxane. The refractive index at 20° was 1.3772 (reported in the literature, 1.3774[6] and 1.3772[3]).

Summary

The action of sodium and potassium hydroxides on hexamethyldisiloxane in various solvents has been investigated. In hydroxyl-containing solvents at elevated temperatures the fission of methyl groups as methane appears to be the principal reaction, but in suitable aprotic solvents the formation of methane may be suppressed to favor the formation of alkali-metal salts of trimethylsilanol.

CAMBRIDGE 38, MASS. RECEIVED DECEMBER 12, 1949

(6) Burkhard, Rochow, Booth and Hartt, *Chem. Revs.*, **41**, 127 (1947).

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN, HARVARD UNIVERSITY, AND THE UNIVERSITY OF CALIFORNIA]

Thermodynamic Properties of Concentrated Polystyrene Solutions[1]

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Thermodynamic investigations in which the heat and entropy of dilution are determined as a function of composition are still insufficient to allow detailed comparison with statistical thermodynamic theories.[3–10] These properties have been determined in very dilute solutions for several cases[11–15] and in the rubber–benzene system[13,16,17] further measurements cover the range from 0.12 to 0.86 volume fraction of rubber. However no measurements exist in the range of concentrated solutions, *i. e.*, 1 to 10% polymer and at still higher concentrations data have been obtained only on one system. Yet in the comparison of theory and experiment the largest differences appear to fall in the concentrated solution region where only interpolated experimental values are available. Indeed our entire knowledge of this system below 12% concentration rests on the measurement at two temperatures of the osmotic pressures of three dilute solutions. Moreover data in the dilute solution region for some other systems are incompatible with present theories. This disagreement appeared to be particularly striking for some polystyrene solutions.[15] For this reason and in view of the absence of data on any concentrated polymer solutions the osmotic pressure of polystyrene solutions at different temperatures has been determined in the range of 0.002 to 0.10 volume fraction. Four different solvents were studied.

Experimental Details

Osmometers.—Two glass osmometers, each having a capacity of 3 cc., were used. The type employed to measure pressures up to 4 g./sq. cm. was that described by

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(1) This paper is based upon the dissertation presented by M. J. Schick in the partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Polytechnic Institute of Brooklyn in 1948. It has been presented in part at the 115th Meeting of the American Chemical Society in San Francisco, California.

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(5) E. A. Guggenheim, *Proc. Roy. Soc. (London)*, **183**, 203, 213 (1944).

(6) W. J. C. Orr, *Trans. Faraday Soc.*, **40**, 320 (1944); **43**, 12 (1947).

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(8) R. L. Scott and M. Magat, *ibid.*, **13**, 172 (1945).

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(11) K. H. Meyer, E. Wolff and C. G. Boissonnas, *Helv. Chim. Acta*, **23**, 430 (1940).

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(16) J. Ferry, G. Gee and L. R. G. Treloar, *Trans. Faraday Soc.*, **41**, 340 (1945).

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