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The Oxidative Cleavage of Organosilanes. III. Ozone and the Silicon-Alkyl, -Aryl, -Hydrogen, and -Oxygen Bonds¹

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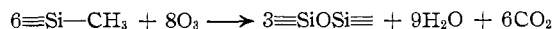
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The cleavage by ozone of Si-Y bonds, where Y is hydrogen, hydroxyl, alkoxy, alkyl, aryl, or silicon, has been examined. It is found that ozone, at room temperature, causes rupture in all cases with the formation of hydroxysilanes or siloxanes, depending upon the nature of Y and other substituents on silicon.

Introduction

Although extensive reviews have been made of the reaction of ozone with organic compounds,³ there is almost nothing reported of the reaction with the corresponding silicon compounds.

Barry and Beck⁴ noted that the oxidation of organic groups on silicon by oxygen or ozone, especially at elevated temperatures, produced siloxane bonds according to the equations



They also observed that ozone readily attacked poly-(methylphenyldisiloxanes) at room temperature, presumably by destroying the aromatic ring. Vinyl and hydrogen on silicon were susceptible to ozone attack, the former reacting quickly with ozone even at -55° . No other experimental details of reaction conditions or products were given, and all citations made were to unpublished work.

We have studied the reaction of ozone with a variety of silanes and find that ozone cleaves Si-X bonds where X is alkyl, aryl, hydrogen, or silicon. Silanols and alkoxy silanes also react readily to give disiloxanes.

Experimental Section

Ozone, as a 4% mixture in oxygen, was obtained from a Welsbach T-23 ozonizer capable of generating 2-3 g of ozone/hr. This ozone-oxygen mixture is the reagent in this report.

Vapor phase chromatography was carried out on a Barber-Colman 61-C gas chromatograph utilizing 100-ft stainless steel capillary columns of 0.01-in. i.d. coated with Apiezon L or DC 550 silicone, as appropriate. A hydrogen flame ionization detector was used. Identity of reaction products was established by comparison with authentic samples independently prepared and by elemental microanalysis, as necessary.

Compounds synthesized by procedures in the literature included octaethylcyclotetrasiloxane [bp 159-161° (10 mm) (lit.⁵ 158° (10 mm))], octaethyltrisiloxane [bp 114-116° (1 mm) (lit.⁶ 113° (1 mm))], hexaethylcyclotrisiloxane [bp 248-250° (760 mm) (lit.⁷ 246° (750 mm))], and 1,3-dimethyl-1,1,3,3-tetraethyl-di-

siloxane [bp 191-193° (760 mm) (lit.⁸ 192° (760 mm))]. The other reagents and reference organosilanes in this study were obtained from Pierce Chemical Co., Rockford, Ill., and were purified by distillation. All compounds used were better than 98% pure according to gas chromatographic analysis.

Triethylsilane.—Ozone was bubbled through 5 g of pure, distilled triethylsilane at room temperature. An exothermic reaction occurred and, with no cooling, the temperature rose to 40°. When vapor phase chromatography indicated, within 30 min, that no triethylsilane remained, the reaction product was distilled to give triethylsilanol (bp 153-154°) in 95% yield. Further details and amplified studies of this reaction, Si-H cleavage to silanol, are reported elsewhere.⁹

Triethylsilanol.—Treatment of triethylsilanol (5 g) with ozone at room temperature for 12 hr afforded about 50% conversion to hexaethyldisiloxane. The vapor phase chromatogram of the crude reaction product indicated, in addition, small amounts (<5%) of hexaethylcyclotrisiloxane, octaethylcyclotetrasiloxane, and octaethyltrisiloxane. Extended treatment of the reaction mixture increased the amounts of these siloxanes. They were not distilled from the reaction mixture but were identified and quantities estimated by vapor phase chromatography, using authentic samples prepared as described above.

Triethylethoxysilane.—This was allowed to react with ozone at room temperature to give hexaethyldisiloxane as the principal product together with small (<5%) amounts of hexaethylcyclotrisiloxane, octaethylcyclotetrasiloxane, and octaethyltrisiloxane. A small quantity of a second, acidic, liquid layer also was formed. The entire reaction mixture was shaken with a slight deficiency of aqueous sodium bicarbonate solution, and the aqueous layer was separated and washed with ether. Removal of the water under reduced pressure gave a white solid which was strongly peroxidic when tested with potassium iodide solution. This sodium salt of the acid was then refluxed with *p*-nitrobenzyl bromide to give a solid melting at 77-78°. (The *p*-nitrobenzyl ester of acetic acid has mp 78°.¹⁰)

Anal. Calcd for C₉H₉NO₄: C, 55.38; H, 4.65; N, 7.18. Found: C, 55.42; H, 4.83; N, 7.17.

Competition Reaction between Triethylsilanol and Triethylethoxysilane.—A solution containing triethylsilanol (1 mmole) and triethylethoxysilane (1 mmole) in 25 ml of hexane was treated with ozone at room temperature and samples were taken at appropriate time intervals. Vapor phase chromatography for the estimation of triethylsilanol proved to be unsatisfactory. Solutions of pure triethylsilanol in hexane gave irreproducible results, due, possibly, to decomposition in the flash heater or on the chromatographic column. However, the analysis for triethylethoxysilane was satisfactory. Infrared spectroscopy was used as a qualitative and quantitative means of analysis for triethylsilanol, by observing the O-H band at *ca.* 2.9 μ. When the vapor phase chromatogram indicated that no triethylethoxy-

(1) Preliminary communications: L. Spialter and J. D. Austin, *J. Am. Chem. Soc.*, **88**, 1828 (1966); **87**, 4406 (1965).

(2) Visiting Research Associate under contract with Ohio State University Research Foundation.

(3) P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958); L. Long, Jr., *ibid.*, **27**, 437 (1940).

(4) A. J. Barry and H. N. Beck in "Inorganic Polymers," F. G. A. Stone and W. A. G. Graham, Ed., Academic Press Inc., New York, N. Y., 1962, pp 221, 236, 256, and 296.

(5) D. G. Dobay, U. S. Patent 2,769,829 (Nov 6, 1956).

(6) W. Patnode and D. F. Wilcox, *J. Am. Chem. Soc.*, **68**, 362 (1946).

(7) D. G. Dobay, U. S. Patent 2,769,830 (Nov. 6, 1956).

(8) L. Beranek and V. Bazant, *Chem. Listy*, **50**, 1250 (1956).

(9) L. Spialter and J. D. Austin, to be published.

(10) S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1945, p 186.

silane remained, a large O-H band for unreacted triethylsilanol was still present in the infrared spectrum. Thus, the rate of cleavage of an Si-OC₂H₅ bond is much greater than that for an Si-OH bond.

Cleavage of Silicon-Alkyl Bond. (a) **Tetraethylsilane.**—This was allowed to react with ozone at room temperature to give a mixture of hexaethylidisiloxane, octaethylcyclotetrasiloxane, hexaethylcyclotrisiloxane, and octaethyltrisiloxane. Numerous other small peaks, with longer retention times, were observed and these presumably correspond to higher siloxanes. The mentioned siloxanes comprised ca. 95% of the reaction product. Of these, hexaethylidisiloxane was the principal reaction product, accounting for 60% of the reaction. The yield of other siloxanes increased as the reaction time was extended. A small amount of a second, acidic, liquid layer was formed and was treated exactly as in the case of triethylethoxysilane above. The dried sodium salt of the acid was peroxidic but the *p*-nitrobenzyl ester prepared therefrom corresponded to that of acetic acid, mp 77–78°. ¹⁰

(b) **Hexaethylidisiloxane.**—This was treated with ozone at room temperature to give a mixture of octaethylcyclotetrasiloxane, hexaethylcyclotrisiloxane, and octaethyltrisiloxane, as indicated by vapor phase chromatography. The ethyl group was accounted for in an acidic second layer as observed above.

The cleavage of a silicon-ethyl bond in both tetraethylsilane and hexaethylidisiloxane required reaction times of ca. 18–40 hr. Even after 40 hr the reaction was not complete.

The ratio of siloxanes obtained in the cleavage of tetraethylsilane and hexaethylidisiloxane, to within 10%, was 20:8:1 for octaethylcyclotetrasiloxane:hexaethylcyclotrisiloxane:octaethyltrisiloxane.

In one experiment during the cleavage of tetraethylsilane, the effluent stream of ozone-oxygen was passed into a trap of standard 0.1 *N* sodium hydroxide solution. After 50% conversion of tetraethylsilane had occurred, the amount of sodium hydroxide neutralized by the effluent gases corresponded to less than 2% of a cleavage reaction producing volatile acid such as carbon dioxide. It was concluded that no carbon dioxide was produced in the reaction and the small amount of sodium hydroxide neutralized was brought about by some carryover by the gas stream of material from the acid layer in the reaction mixture.

(c) **Triethylmethylsilane.**—This was allowed to react with ozone at room temperature. The vapor phase chromatogram of the crude reaction mixture showed the principal reaction product to be 1,3-dimethyl-1,1,3,3-tetraethylidisiloxane. A number of smaller peaks with longer retention time were also observed. No hexaethylidisiloxane could be detected.

(d) **Relative Rates of Reaction of Tetraethylsilane and Triethylmethylsilane.**—A solution of tetraethylsilane (1 mmole) and triethylmethylsilane (1 mmole) in hexane (25 ml) was treated with ozone. The relative rates of reaction of the silanes were determined by disappearance of the silanes as analyzed by vapor phase chromatography. It was found that the rate of cleavage of tetraethylsilane was more than ten times faster than that of triethylmethylsilane.

(e) **Diethyldimethylsilane.**—Even after passage of ozone through diethyldimethylsilane for 48 hr, at room temperature no reaction, as detected by vapor phase chromatography, was observed.

Cleavage of Silicon-Aryl Bond.—Trimethylphenylsilane reacted exothermally with ozone at room temperature. After ca. 1 hr the vapor phase chromatogram indicated complete disappearance of starting material. The only siloxane produced was hexamethylidisiloxane which was subsequently recovered by distillation in ca. 95% yield. A small amount of insoluble, tar-like material (0.35 g from 5 g of starting material), formed during the reaction, was not worked up.

Cleavage of Si-Si Bond.—Hexamethylidisilane gave an exothermic reaction with ozone at room temperature to produce, within 1 hr, hexamethylidisiloxane in greater than 95% conversion. The vapor phase chromatogram of the crude reaction product showed no other siloxane to be present. Nitrogen was

then bubbled through the crude reaction products for 8 hr to entrain excess dissolved ozone. When tested with potassium iodide solution, the product showed no peroxide to be present.

Reaction with Oxygen.—Under the conditions of our experiments, pure oxygen alone at room temperature did not cause any of the above reactions to occur, even after three- to fivefold longer reaction times.

Discussion

Triethylsilanol and Triethylethoxysilane.—Both triethylsilanol and triethylethoxysilane, independently treated with ozone, gave hexaethylidisiloxane as the main product. The vapor phase chromatogram of each reaction mixture after 100% conversion indicated the presence of higher siloxanes in small (<5%) quantities. Thus, the rate of condensation of both triethylsilanol and triethylethoxysilane to the disiloxane is greater than the rate of cleavage of a silicon-alkyl bond. In the case of triethylethoxysilane, peroxyacetic acid was also produced (identified as described below) so that it is possible that some cleavage of the ethoxy group may have been catalyzed by the presence of acid.¹¹ However, such catalysis is not deemed probable because peroxyacetic acid is weak, approximating hydrogen cyanide in strength,^{12a} although a *pK* of 8.2 has been reported.^{12b} Similarly in the case of triethylsilanol, the small amount of acid produced by the cleavage of an ethyl group may catalyze the dehydration reaction. This is also considered unlikely because of the weakness of the acid and since it has been reported that triethylsilanol is largely unaffected by boiling for 11 hr with an equal volume of 0.1 *N* aqueous hydrochloric acid.¹³

In a competition reaction between triethylsilanol and triethylethoxysilane for ozone it was found that the rate of cleavage of a Si-OC₂H₅ bond was greater than for Si-OH. The method of analysis for triethylsilanol was unsatisfactory (see above) so that it is impossible to give a quantitative estimate of the relative rates.

Tetraethylsilane showed far more cleavage of silicon-ethyl bonds, as identified by siloxanes in the vapor phase chromatogram, than did triethylsilanol or triethylethoxysilane under the same conditions. Thus, it is reasonable to say that in the case of triethylsilanol and triethylethoxysilane, the ozone is causing cleavage of Si-OH and Si-OC₂H₅ rather than acid-catalyzed hydrolysis. If this were not so, more siloxanes produced by cleavage of silicon-ethyl bonds should have been observed.

Cleavage of Silicon-Alkyl Bond.—Cleavage of a silicon-ethyl bond was observed when tetraethylsilane and hexaethylidisiloxane were independently treated with ozone. For tetraethylsilane, the principal reaction product was hexaethylidisiloxane, as identified by vapor phase chromatography. However, before all of the tetraethylsilane had reacted, more

(11) C. Eaborn, "Organosilicon Compounds," Butterworth and Co. Ltd., London, 1960.

(12) (a) B. Phillips, F. C. Frostick, Jr., and P. S. Starcher, *J. Am. Chem. Soc.*, **79**, 5982 (1957); (b) A. J. Everett and G. J. Minkoff, *Trans. Faraday Soc.*, **49**, 410 (1953).

(13) L. H. Sommer, E. W. Pietrusza, and F. C. Whitmore, *J. Am. Chem. Soc.*, **68**, 2282 (1946).

peaks were observed in the chromatogram. These new products were shown to be octaethylcyclotetrasiloxane, hexaethylcyclotrisiloxane, and octaethyltrisiloxane. Hexaethyltrisiloxane, independently, gave the same products when treated with ozone. These siloxanes were not isolated but were identified by comparing chromatograms of the reaction products with those of authentic samples. The three mentioned siloxanes accounted for *ca.* 90% of the reaction products. A number of smaller peaks with longer retention time were observed and, presumably, these were higher siloxanes.

The ethyl group cleaved off was oxidized to peroxyacetic acid and water. The sodium salt of the crude acid produced by the cleavage was peroxidic although its analysis corresponded to a mixture of acetic and peroxyacetic acids. It has been previously reported that the sodium salt of peroxyacetic acid hydrolyzes readily in water,¹⁴ and the free acid is unstable in the presence of water, slowly decomposing to acetic acid, particularly when heated.¹² Acetic acid was apparently produced here during workup of the acid (which involved heating) which in the initial crude product was peroxidic. It is therefore deduced that the primary reaction product was peroxyacetic acid. Under the experimental conditions, acetic acid alone was unaffected by ozone.¹⁵ Paillard and Briner reported that some peroxyacetic acid was produced when acetic acid was treated with ozone, but the yield was very low. It was concluded¹⁵ that acetic acid can be considered practically inert to the action of ozone.

The ratio of the siloxanes obtained by the ozone cleavage of tetraethylsilane and hexamethyldisiloxane was consistent to within about 10%, being 20:8:1 for octaethylcyclotetrasiloxane:hexaethylcyclotrisiloxane:octaethyltrisiloxane. It appears that cyclic polysiloxanes are preferentially produced, compared to the linear compounds, under the experimental conditions.

Cleavage of Triethylmethylsilane and Diethyldimethylsilane.—Triethylmethylsilane reacted with ozone at room temperature at a much slower rate than did tetraethylsilane. The crude product showed no hexaethyltrisiloxane. The main reaction produced was 1,3-dimethyl-1,1,3,3-tetraethylsiloxane, identified by vapor phase chromatography. Several peaks with longer retention times, presumably higher cyclic and linear siloxanes, were observed. It may be concluded from this experiment that the rates of cleavage of alkyl groups by ozone may be placed in the orders: (a) $(C_2H_5)_3Si-C_2H_5 > (C_2H_5)_2CH_2Si-C_2H_5$; (b) $(C_2H_5)_3Si-C_2H_5 > (C_2H_5)_3Si-CH_3$. It is not clear what role steric and electronic effects play in the cleavage. The inductive effect (+I) of a triethylsilyl group is greater than that of a diethylmethylsilyl group and, if ozone is regarded as an electrophile, then this leads to a conclusion consistent with relation a. However, it has been observed in other cases of ozone cleavage⁹

that the rate of Si-H bond cleavage increases as the steric requirements of the other substituents attached to the silicon increase. If this latter implication is extended to the cleavage of alkyl groups, then conclusion a may be justified by accepting some form of steric acceleration as well as an electronic effect. Similarly, conclusion b is consistent with steric acceleration.

Diethyldimethylsilane did not react with ozone at room temperature even after prolonged reaction time. Thus the reactivity of tetraalkylsilanes toward ozone falls in the orders: $(C_2H_5)_3Si-C_2H_5 > (C_2H_5)_2CH_2Si-C_2H_5 > (C_2H_5)_2(CH_3)_2Si$; $(C_2H_5)_2CH_2Si-C_2H_5 > (C_2H_5)_3Si-CH_3$. It should be noted that Barry and Beck⁴ have reported that organic groups on silicon are oxidized by oxygen and ozone at elevated temperatures, but their citation to an unpublished reference mentions only the methyl group.

Cleavage of Trimethylphenylsilane.—When ozone was passed into trimethylphenylsilane at room temperature, hexamethyldisiloxane was recovered in 95% yield. The vapor phase chromatogram of the crude reaction product showed only hexamethyldisiloxane. The reaction was complete in *ca.* 1 hr., indicating that the net rate of cleavage of a silicon-aryl bond by ozone is considerably faster than the rate of cleavage of a silicon-alkyl bond.

It was also observed that a small amount of thick, black tar (about 0.4 g from 5 g of starting material) had formed, presumably a by-product from the reaction of the phenyl ring with ozone. Ozone is known to react with benzene³ but in the case of trimethylphenylsilane it is impossible at present to say whether ozone cleaves the silicon-phenyl bond and then oxidizes the phenyl ring or whether initial attack is at the phenyl ring followed by cleavage of the silicon-carbon bond. It is noteworthy that chlorine, also a strong oxidizing agent, is not a particularly active cleavage reagent for phenyl-silicon bonds, preferring, instead, to chlorinate the ring.¹¹

Cleavage of Si-Si Bond.—Hexamethyldisilane reacted exothermally with ozone at room temperature to give hexamethyldisiloxane in 95% yield. After bubbling of nitrogen through the crude reaction product, no peroxide, by iodide test, could be detected. The vapor phase chromatogram of the reaction product showed that no siloxanes, either cyclic or linear, higher than hexamethyldisiloxane were formed during the time required to effect complete cleavage of the disilane. This would indicate that the rate of cleavage of an Si-Si bond is considerably faster than the rate of cleavage of a silicon-alkyl bond. This is consistent with the fact that, whereas the disilane was completely cleaved in *ca.* 1 hr, cleavage of a silicon-ethyl bond in tetraethylsilane was incomplete even after approximately 24 hr of reaction time.

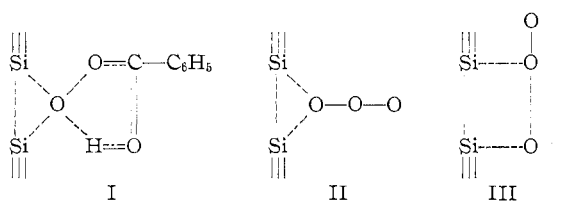
This cleavage by ozone is analogous to a recently described oxidation of disilanes with a peroxidic acid.¹⁶

(14) P. A. Giguere and A. W. Olmos, *Can. J. Chem.*, **34**, 689 (1956).

(15) H. Paillard and E. Briner, *Helv. Chim. Acta*, **25**, 1528 (1942).

(16) H. Sakurai, T. Imoto, N. Hayashi, and M. Kumada, *J. Am. Chem. Soc.*, **87**, 4001 (1965).

A variety of disilanes were treated with perbenzoic acid, and it was found that oxygen was directly inserted into the silicon-silicon bond to give the corresponding disiloxane. A mechanism was suggested which involved electrophilic attack by a cyclic hydrogen-bonded form of the peracid leading to a transition state of type I. Ozone has been regarded



as an electrophilic reagent³ and a corresponding transition state for the ozone cleavage would be of form II. Four-center transition states (III) have been proposed for many reactions of organosilicon compounds¹⁷ but in the present case such a transition state should lead to bis(trimethylsilyl)peroxide. Since no evidence of a peroxide was observed and since the product obtained by distillation was hexamethyldisiloxane, it is unlikely that any bis(trimethylsilyl) peroxide was formed. Bis(trimethylsilyl) peroxide has been reported to decompose with rearrangement¹⁸ but no evidence of rearranged products was indicated by vapor phase chromatography in the present studies.

It is, therefore, considered reasonable that the ozonization of a disilane proceeds by a mechanism involving a three-center transition state—or the analogous pentacovalent intermediate—of type II.

General Comments.—Silanes are generally more reactive toward ozone than are the corresponding carbon compounds. The oxidation of linear paraffin hydrocarbons by ozone at room temperature has been studied by Schubert and Pease, who proposed a free-radical mechanism.¹⁹ In the ozonization of ethers, Price and Tumolo²⁰ found that the major reaction involved carbon-hydrogen bond cleavage but some

carbon-oxygen and carbon-carbon cleavage was also observed. During the course of the cleavage of the silicon-alkyl bond no carbon dioxide was observed, indicating that the carbon-carbon bond was relatively unreactive toward ozone under the experimental conditions. The ethyl group was oxidized to peroxyacetic acid so that some carbon-hydrogen cleavage, but only in the α position, did occur, although whether before rupture of the bond to silicon or after is not certain.⁶ The rate of cleavage of Si-H and Si-Si was much faster than the cleavage of the silicon-alkyl bond, which is consistent with the general relative reactivity of these silanes. It may be concluded that Si-X bonds are cleaved more readily by ozone than C-X bonds, for the X substituents of this work.

Since the silicon-carbon bond strength (83–85 kcal/mole) has been estimated to be about the same as that for the carbon-carbon bond (83 kcal/mole),^{21,22} even though cleavage of a silicon-carbon bond is predominant, it appears likely that some characteristic mechanism involving silicon may be playing an important role. Similar increased reactivity has been noted¹ in the combustion of organosilanes²² relative to hydrocarbons.²³ Such studies have shown that silanes have a much faster burning rate than the corresponding carbon compounds and that the flame velocity of silanes is more sensitive to molecular structure than that of the hydrocarbon.¹⁸

The present work adds to the evidence that silanes react *via* a mechanism which is different and, probably, unavailable to carbon, such as one involving the participation of d orbitals.

(21) G. G. Hess, F. W. Lampe, and L. H. Sommer, *ibid.*, **87**, 5327 (1965). It is to be noted, however, that the thermochemistry of bonds to silicon is receiving comments from others: *e.g.*, J. A. Connor, R. N. Haszeldine, and G. J. Leigh in "Scientific Communications of the International Symposium on Organosilicon Chemistry, Sept 1965, Prague," Czechoslovakian Academy of Sciences, Prague, 1965, p 111; J. A. Connor, G. Finney, G. J. Leigh, R. N. Haszeldine, P. J. Robinson, R. D. Sedgwick, and R. F. Simmons, *Chem. Commun.*, 178 (1966).

(22) R. L. Schalla, G. R. McDonald, and M. Gerstein in "Fifth International Symposium on Combustion," Reinhold Publishing Corp., New York, N. Y., 1955, pp 705–710; M. Gerstein in "Seventh International Symposium on Combustion," Butterworth and Co. Ltd., London, 1959, pp 903–905.

(23) M. Gerstein, O. Levine, and E. L. Wong, *J. Am. Chem. Soc.*, **73**, 418 (1951).

(17) L. H. Sommer, "Stereochemistry, Mechanism, and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

(18) R. A. Pike and L. H. Shaffer, *Chem. Ind.* (London), 1294 (1957).

(19) C. S. Schubert and R. N. Pease, *J. Am. Chem. Soc.*, **78**, 2044 (1956).

(20) C. C. Price and A. L. Tumolo, *ibid.*, **86**, 4691 (1964).