On the Mechanism of the Reaction of Ozone with the Silicon–Hydrogen Bond

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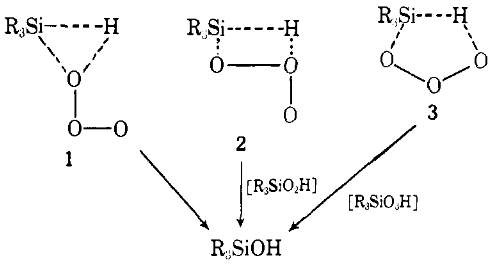
Abstract: The reaction of a silane with ozone results in the quantitative conversion of the Si–H bond to the Si–OH moiety. The mechanism of this oxidation has been elucidated by examination of: (a) relative rate data, (b) substituent effects, (c) deuterium isotope effects, (d) low-temperature nmr, and (e) uv spectroscopy. The mechanism proposed involves fast, reversible complexation of ozone (acting as a nucleophile) with the silicon atom, rate-determining electrophilic attack of ozone on the hydridic hydrogen, and decomposition into a $R_3Si\cdot\ \cdot OH$ radical pair which recombines to produce the silanol. From the relative rate data and substituent effects, a Hammett-like σ value, $\sigma_{Si}{}^*$, characteristic of substituents bound to silicon, is derived.

The reaction of ozone with organic substrates has been the subject of intensive investigation for several decades.[2,3] Its reaction with organosilicon compounds, however, was largely neglected until 1965,[4,5] when it appeared that, mechanistically, the ozonization (hereafter, "oxidation" will imply oxidation by ozone, unless otherwise noted) of organosilanes bore little resemblance to that of their carbon analogs. The oxidation of a R_3Si–Y bond (Y = H, R, OR, OH, SiR'_3) results in the formation of a silanol (R_3SiOH) and, ultimately, of a siloxane ($R_3SiOSiR_3$). The Si–H bond is of particular interest, being rapidly and quantitatively converted to the SiOH moiety. The analogous oxidation of hydrocarbons is much slower and produces a variety of products.[2,6] Oxidation of ethers[7] and aldehydes,[8,9] both involving initial cleavage of a C–H bond, also yields complex product mixtures. In contrast, an Si–H bond, regardless of the other substituents on silicon, is converted to the silanol in excellent yield.[10] These results suggest that a fundamental difference in mechanism exists between the oxidation of the Si–H and the C–H bond. The following investigation was conducted to elucidate the mechanism of the Si–H oxidation.

Results and Discussion

Although the facile conversion of the Si–H moiety to a silanol (Si–OH) by ozone has been reported,[4,5,10] the mechanism of this conversion has remained obscure. Proposed intermediates have included **1** (direct insertion of oxygen into the silicon–hydrogen σ bond); **2**, a four-centered transition state leading to a silyl hydroperoxide; and **3**, a five-centered transition state leading to a silyl hydrotrioxide. Further decomposition of the intermediates from **2** and **3** could involve ion or radical pairs.[10]



The relative rates of reaction of an extensive series of mono-, di-, and trihydrosilanes with ozone have been measured and appear in Table I. The rates are those of disappearance of the silane, which has been shown to be first order.[10] The reaction produces, initially,

Table I. Relative Rates of Oxidation of Substituted Silanes by Ozone

Silane	$k_{rel}{}^a$
Tri(perhydro-1-naphthyl)silane[b]	378
Tricyclohexylsilane	236
tert-Butyldicyclohexylsilane	226
Tri(*n*-hexyl)silane	115
Tri(*n*-butyl)silane	100
Triethylsilane	84
3,3,3-Trifluoropropyldimethylsilane	51.7
(Dichloromethyl)dimethylsilane	41.7
Tris(3,3,3-trifluoropropyl)silane	35.6
Phenyldimethylsilane	30.7
Di(isopropyl)silane	28.5
(Chloromethyl)dimethylsilane	23.6
Diphenylmethylsilane	23.0
Triphenylsilane	23.0
Di(*n*-butyl)silane	21.7
Triethoxysilane	19.0
Phenylmethylsilane	12.0
2,2′-Biphenylenylsilane	9.6
Diphenylsilane	7.9
Cyclohexylsilane	3.65
Dibenzylsilane	3.31
n-Hexylsilane	3.04
Phenylsilane	2.10

[a] All rates measured at 0°, $k_{rel}(n\text{-}C_4H_9)SiH$ = 100 by definition. [b] Mixture of *cis*- and *trans*-1-decalinyl isomers.

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[1] OSURF Research Associate.
[2] P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).
[3] L. Long, Jr., *ibid.*, **27**, 437 (1940).
[4] L. Spialter and J. D. Austin, *J. Amer. Chem. Soc.*, **87**, 4406 (1965).
[5] L. Spialter and J. D. Austin, *Inorg. Chem.*, **5**, 1975 (1966).
[6] J. E. Batterbee and P. S. Bailey, *J. Org. Chem.*, **32**, 3899 (1967).
[7] R. E. Erickson, R. T. Hanson, and J. Harkins, *J. Amer. Chem. Soc.*, **90**, 6777 (1968).
[8] R. E. Erickson, D. Bakalik, C. Richards, M. Scanlon, and G. Huddleston, *J. Org. Chem.*, **31**, 461 (1966).
[9] H. M. White and P. S. Bailey, *ibid.*, **30**, 3037 (1965).
[10] J. D. Austin and L. Spialter, *Advan. Chem. Ser.* No. 77, 26 (1968).

only the corresponding silanol. Although the silanol, upon standing in the presence of ozone, undergoes slow dehydration to the siloxane, vpc monitoring of the oxidation of triethylsilane demonstrated that the summed concentrations of triethylsilane and triethylsilanol remained constant throughout the reaction times studied.

In an attempt to gain insight into the reaction mechanism, the electron donor-acceptor properties of the substituents on silicon were varied, and the subsequent effect on the relative rates was observed. To justify any such correlation, consideration must be given to the nature of the interaction between silicon and its substituents. The "normal" inductive effects, transmitted by the σ-bond framework, should be similar for substituents on either carbon or silicon; silicon has, however, the added possibility of a π-bond interaction through its vacant, low-lying 3d orbitals if the substituent has electrons available in a p orbital of suitable symmetry.[11] This mesomeric contribution to the electronic environment of silicon cannot be ignored if the substituents on silicon have available electron pairs (*i.e.*, phenyl, ethoxy).

The simplest correlation one can envision is to relate the relative rates to some type of Hammett σ value.[12] To a first approximation, the purely inductive σ^* was a good candidate, particularly in view of the fact that most of the substituents studied were alkyl groups and not expected to exhibit any mesomeric effects. To accommodate the fact that the number of reactive sites (presumably the Si–H bond) varied in the mono-, di-, and trihydrosilanes, a summation of the σ^* values for all four substituents was taken as indicative of the silicon's total electronic environment. Plotting $\Sigma\sigma^*$ *vs.* the relative rate (k_{rel}, see the Experimental Section for the method of determination and base) produced the expected linear relationship for the alkyl substituents, but serious deviations occurred when one (or more) of the substituents was phenyl, ethoxy, $ClCH_2$, Cl_2CH-, or $CF_3CH_2CH_2-$.

For the phenyl case, where mesomeric interaction between silicon and the π system is possible, use of the standard Hammett σ, rather than σ^*, is logical ($\sigma(C_6H_5-) = 0.00$, $\sigma^*(C_6H_5-) = 0.60$); when this value substitution is made, all of the phenylsilanes studied (five total) fall on the $\Sigma\sigma^*$ *vs.* k_{rel} line.

Further justification of this approach is obtained from the relative rate data for the oxidation of substituted phenyldimethylsilanes,[13] $X-C_6H_4-Si(Me)_2H$. These data and ours have a common point in phenyldimethylsilane, and appropriate mathematical manipulation easily adjusts the two k_{rel} to a common scale. Employing the σ values in the summation, these compounds also show an excellent correlation.

A linear least-squares analysis of the alkyl-substituted silane rate data employing σ^* produces the following relationship

$$\log k_{\text{rel}} = -1.2513\Sigma\sigma^* + 2.2166$$

The values calculated for σ^* and for σ (for the $X-C_6H_4-$ species) from this equation are compared with the reported values in Table II. The plot of $\Sigma\sigma^*$ (or σ, as appropriate for aryl substituents) *vs.* k_{rel} appears in Figure 1.

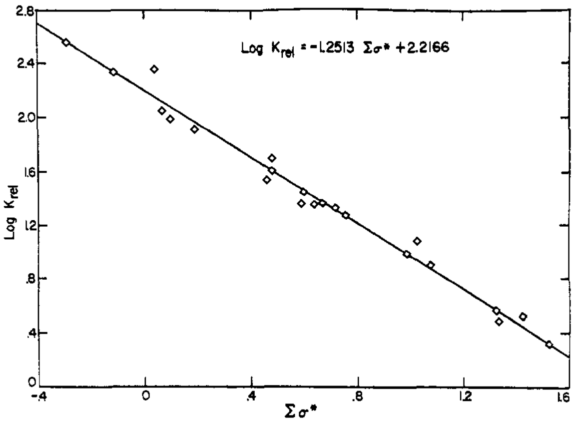

Figure 1. Least-squares plot of relative rate data.

For most substituents on silicon, the latter's electronic environment can be described by judicious choice of the appropriate σ value. However, there are several groups ($ClCH_2-$, Cl_2CH-, $CF_3CH_2CH_2-$, and CH_3CH_2O-) which are still not accommodated by this relationship. Although σ^* values have been reported for these substituents, it is clear that such are not appropriate for substitution on silicon. Common to all of these groups is the presence of an unshared electron pair in close proximity to the silicon, a factor which suggests that simple inductive considerations may not be sufficient. (The anomalous behavior of the 3,3,3-trifluoropropyl group has been noted in carbon compounds as well, and is probably not indicative of a special interaction with silicon.[14])

Table II. Reported and Calculated Values of $\Sigma\sigma^*$

Silane	Rept[a]	Calcd[b]
Tri(perhydro-1-naphthyl)silane[c]	−0.29[d]	−0.29
Tricyclohexylsilane	0.04	−0.12
tert-Butyldicyclohexylsilane	−0.11	−0.11
Tri-*n*-hexylsilane	0.07	0.12
Tri-*n*-butylsilane	0.10	0.17
Triethylsilane	0.19	0.23
(3,3,3-Trifluoropropyl)dimethylsilane	0.48[d]	0.40
(Dichloromethyl)dimethylsilane	0.48[d]	0.48
Tris(3,3,3-trifluoropropyl)silane	0.46[d]	0.53
Phenyldimethylsilane	0.49	0.58
Di(isopropyl)silane	0.60	0.61
Chloromethyldimethylsilane	0.67[d]	0.67
Diphenylmethylsilane	0.49[d]	0.68
Triphenylsilane	0.49[d]	0.68
Di(*n*-butyl)silane	0.72	0.70
Triethoxysilane	0.76[d]	0.75
Phenylmethylsilane	0.98[d]	0.91
2,2′-Biphenylenylsilane	0.99[d]	0.99
Diphenylsilane	0.98[d]	1.05
Cyclohexylsilane	1.32	1.32
Dibenzylsilane	1.42	1.36
n-Hexylsilane	1.33	1.38
Phenylsilane	1.47[d]	1.51

[a] Where applicable, Taft σ^* values for substituents are taken from J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962, p 97. [b] Calculated from the equation $\Sigma\sigma^* = (2.2166 - \log k_{\text{rel}})/1.2513$. [c] Mixture of *cis*- and *trans*-1-decalinyl isomers. [d] Calculated using the σ_{Si}^* values of Table III or, for phenyl, the Hammett σ.

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(11) M. E. Freeburger and L. Spialter, *J. Amer. Chem. Soc.*, **93**, 1894, (1971), and references cited therein.

(12) H. H. Jaffé, *Chem. Rev.*, **53**, 91 (1953).

(13) R. J. Ouellette and D. J. Marks, *J. Organometal. Chem.*, **11**, 407 (1968).

In a special set of σ values, designated as σ^*(Si), characteristic of substituents on silicon and derived from the Si–H infrared stretching frequencies, anomalies were also noted for groups possessing unshared electrons.[15] From the $\Sigma\sigma$ *vs.* k_{rel} relationship, a σ_{Si}^* [16] can be calculated for the groups not adequately treated by σ^* or σ. The calculated values of σ_{Si}^* for these anomalous groups appear in Table III. In all cases they are more negative than the corresponding σ^* values, suggestive of a partial cancellation of the inductive electron withdrawal by some form of back donation. Interaction of the unshared electrons with the silicon 3d orbitals is an attractive explanation,[11] but these observations alone do not allow discrimination between that and other explanations.[17]

Table III. Calculated Values of σ_{Si}^* for Selected Substituents

Substituent	σ_{Si}^*	σ^* [a]
1-$C_{10}H_{17}$[b]	−0.26	
$CF_3CH_2CH_2$	−0.01	0.32
Cl_2CH	−0.01	1.94
2,2′-Biphenylenyl	0.01	
C_2H_5O	0.09	1.35
$ClCH_2$	0.18	1.05

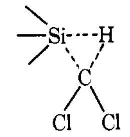
[a] Standard σ^* values; see Table II for reference. [b] Mixture of *cis*- and *trans*-1-decalinyl isomers.

The above-cited results suggest a consistent set of σ-type values for substituents on silicon, σ_{Si}^*. If the substituent group does not possess unshared electron pairs in reasonably close proximity to the silicon (*e.g.*, alkyl groups), σ_{Si}^* is equal to the standard Taft σ^*; if the group is a substituted phenyl, σ_{Si}^* is equal to the standard Hammett σ value; if, however, the group possesses unshared electrons, which can then interact within silicon *via* a mode not available to carbon, none of the carbon-based σ values is applicable. In this latter case the σ_{Si}^* must be determined by independent measurements. The values of σ_{Si}^* for such groups investigated in this study appear in Table III.

Returning now to the plot of k_{rel} *vs.* $\Sigma\sigma_{Si}^*$, the slope ρ, representing a reaction parameter, is −1.25. Its negative value denotes electrophilic attack by ozone and/or the development of a partial positive charge on silicon in the transition state. Since silicon is relatively electropositive, an electrophilic attack by ozone on silicon seems unlikely; the hydrogen bound to silicon, however, is hydridic and is the likely site on attack by an electrophile. If attack by ozone on hydrogen occurs in the rate step, then a primary deuterium isotope effect is predicted.[18]

The deuterium isotope effect, k_H/k_D, was determined for the reaction of tri(*n*-butyl)silane with ozone, from comparison of the k_{rel} for the oxidation of $(n\text{-}C_4H_9)_3SiH$ and $(n\text{-}C_4H_9)_3SiD$ *vs.* $(n\text{-}C_6H_{13})_3SiH$. The oxidation exhibits a surprisingly large primary isotope effect, $k_H/k_D = 6.9$. The calculated k_H/k_D, based on the zero-point energy effect using the infrared stretching frequencies of the Si–H and Si–D bonds in tri(*n*-butyl)silane, is 4.5 at 0°.[19] This large observed primary isotope effect is definitely indicative of the involvement of Si–H bond breaking in the rate step and, therefore, corroborates electrophilic attack by ozone on the hydridic hydrogen. The possibility that this large isotope effect is due to autoxidation by oxygen has been ruled out (*vide infra*).

The question still exists as to whether the ozone attack is an abstraction of hydrogen or an insertion into the Si–H σ bond (**2** or **3** *vs.* **1**). The reaction of dichlorocarbene with the Si–H bond, a reaction which affords only the insertion product,[20] was taken as a model for the σ-bond insertion. This insertion is postulated to proceed *via* the three-centered transition state **4**, which is structurally similar to **1**. The isotope effect, k_H/k_D, for insertion of dichlorocarbene into $(n\text{-}C_4H_9)_3SiH$ and $(n\text{-}C_4H_9)_3SiD$, determined in the same manner as for their oxidations, was found to be 1.23.[21] The large difference in the k_H/k_D values suggests that the ozone reaction does not closely resemble the carbene insertion. Furthermore, a Hammett-type $\rho\sigma$ treatment of the carbene insertion produced a ρ of −0.63,[20] compared with −1.26 for the ozone reaction. This indicates a greater separation of charge (less concertedness) in the latter, although both do involve electrophilic attack.



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The primary isotope effect and the relative rate data, however, do conflict at one point. If, indeed, attack on hydrogen is rate determining, there should be a statistical factor for attack on the di- and trihydrosilanes. These compounds are, however, correctly accommodated on the same linear plot, Figure 1, as are the monohydrosilanes.

One possible explanation for this behavior is that charge separation occurs in the transition state (producing either $\equiv Si^+$ or $\equiv Si\cdot$), and the species order of stability tertiary > secondary > primary exactly cancels the statistical factor. Although this explanation cannot be rejected out of hand, the fortuitousness required makes it unattractive.

A second possibility is that the ozone forms some kind of complex with the silane prior to attack on the hydrogen. From this complex, all hydrogens are equally accessible. In hope of observing such a complexation, the uv spectra of ozone–silane mixtures in carbon tetrachloride were examined. Although no spectral bands attributable to a silicon-ozone complex were noted, it was observed that *any* silicon-containing species catalyzed the decomposition of ozone. That is, not only triethylsilane but triethylsilanol and tetramethylsilane, as well, destroy ozone in carbon tetrachloride. This result indicates an association of the

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(14) R. H. Baney, "The $CF_3CH_2CH_2$-Group Effect and (d → p)π Bonding," 1970 Organosilicon Award Symposium, Albany, N. Y., May 23, 1970, Abstracts, p 4.

(15) C. J. Attridge, *J. Organometal. Chem.*, 13, 259 (1968).

(16) Although we do not encourage the proliferation of redundant symbols, we prefer the subscripted notation, which permits placing the group being discussed in parentheses; *i.e.*, $\sigma_{Si}^*(C_2H_5O–)$.

(17) For example, C. G. Pitt, *J. Organometal. Chem.*, 24, C35 (1970).

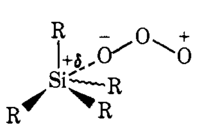
(18) F. H. Westheimer, *Chem. Rev.*, 61, 265 (1961).

(19) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, N. Y., 1960, p 20.

(20) D. Seyferth, R. Damrauer, J. Yick-Pui Mui, and T. F. Jula, *J. Amer. Chem. Soc.*, 90, 2944 (1968).

(21) L. Spialter, W. A. Swansiger, L. Pazdernik, and M. E. Freeburger, *J. Organometal. Chem.*, 27, C25 (1971).

ozone with the silicon atom, regardless of the functionality of the silicon species and completely independent of the silane substrate's ability to enter into a subsequent transformation reaction. In view of electropositive nature of silicon, the nucleophilic association of ozone with the silicon is the most likely candidate for a suitable intermediate. Possible models for this type of interaction range from one of weak electrostatic attraction, **5**, to a fully pentacoordinate silicon species, **6**.



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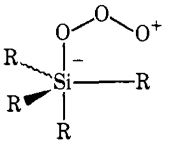

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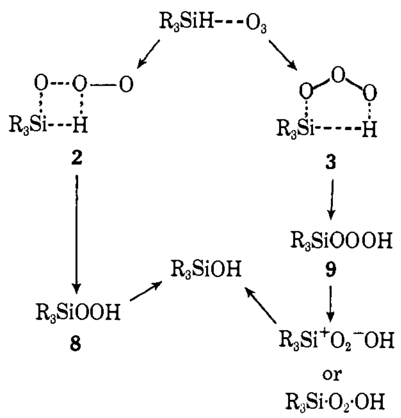
In an attempt to observe the complex, a low-temperature nmr investigation of mixtures of either triethylsilanol or tetramethylsilane with ozone was conducted. At −57° in methylene chloride, there was no discernible change in the proton nmr of either triethylsilanol or tetramethylsilane as the ozone concentration was increased to the point of saturation (a blue solution). Two possible explanations of this result are: (a) the complex exists in equilibrium with the silane and ozone and the actual concentration of complex is too small to be detected by nmr (less than 5% in this experiment), or (b) the chemical shifts of the silane protons are not altered by complexation. Of the two explanations, the first seems most reasonable, particularly if the complex has more of the character of **6** than of **5**. The exact nature of the complex is impossible to determine at this time, but one significant observation is that optically active perhydro-1-naphthylphenylmethylsilanol (**7**)[22] underwent slow racemization upon standing at room temperature in a pentane–ozone solution. This is consistent with reversible complexation to a species having some pentacoordinate character from which racemization may occur *via* pseudorotation.[23] The stereochemistry of the Si–H oxidation will be discussed later.

These data indicate that the initial step in the silane–ozone reaction is reversible formation of a silicon–ozone complex. This cannot be the rate step, or the ρ would be positive (nucleophilic attack) and no primary isotope effect would be predicted. To eliminate the statistical factor for the di- and trihydrosilanes, attack by ozone on the hydridic proton from within the complex must be much more favorable than the encounter and subsequent reaction of uncomplexed ozone and Si–H.

The problem of how the ozonation proceeds from the complex must now be addressed. If direct σ-bond insertion to give **1** is eliminated on the basis of the isotope effect, then **2** and **3** are the viable alternatives. The transition state **2** could collapse to form the silicon hydroperoxide **8**, while transition state **3** could collapse to form the silicon hydrotrioxide **9**; alternatively, **3** could collapse directly to ion or radical pairs, which could recombine to afford the silanol (Scheme I).

Scheme I



If the reaction is four centered (**2** → **8**), a silicon hydroperoxide should be formed. The reaction of triethylsilane with ozone was monitored by nmr at −57°. The only species observed under these conditions were the silane and the silanol; no evidence for a hydroperoxide (which would certainly have been stable at that temperature[24]) was detected, and chemical tests for peroxides proved negative.[5,10] As the concentration of ozone was increased from zero to saturation, the spectrum of the silane completely disappeared with the concurrent appearance of the silanol spectrum.

If the reaction is five centered (**3** → **9**), a silicon hydrotrioxide may be formed. Since there has been no report of a silyl hydrotrioxide, the stability of a species such as **9** under these conditions can only be estimated. The reported dialkyl trioxides have only marginal stability at low temperature[25,26] and alkyl hydrotrioxides, proposed as intermediates in the ozonation of alcohols and ethers,[27] decompose at *ca.* −10°, so whether or not **9** could be observed if formed is moot.

Assuming the intermediacy of a five-centered transition state, the question then arises of how **3** (or **9**) decomposes to the silanol. The breakdown could proceed *via* radical or ion pairs, as indicated in Scheme I. The large isotope effect is suggestive of a radical pathway[8] or could indicate autoxidation by the oxygen present.[8] This latter possibility can be excluded here, however, since the isotope effects for the reaction of $(n\text{-}C_4H_9)_3SiH(D)$ with ozone–argon and ozone–oxygen are identical ($k_H/k_D = 6.9$).[21]

Further information was gained from the oxidation of optically active perhydro-1-naphthylphenylsilane (**10**), which affords **7** with retention of configuration. Prolonged exposure of **7** to ozone eventually causes racemization, but the product initially has retained its configuration. Presumably, the silane **10** is also racemized by ozone (*via* complexation), but the rate of oxidation is rapid in comparison. Details of the stereochemistry of the ozonation of silanes (and other closely related oxidation processes[28]) will be the subject of a future publication.

The retention of configuration by silyl radicals has been demonstrated,[29] whereas the optical properties of siliconium ions (indeed, even their existence) have not been elucidated. For this reason, decomposition of **3** (or **9**) through a radical pair with subsequent rapid re-

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[22] G. R. Buell, L. Spialter, and J. D. Austin, *J. Organometal. Chem.*, **14**, 309 (1968).

[23] E. L. Muetterties, *Accounts Chem. Res.*, **3**, 266 (1970).

[24] R. L. Dannley and G. Jalics, *J. Org. Chem.*, **30**, 2417 (1965).

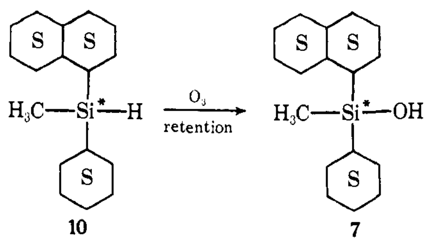
[25] P. D. Bartlett and G. Guaraldi, *J. Amer. Chem. Soc.*, **89**, 4799 (1967).

[26] T. Mill and R. S. Stringham, *ibid.*, **90**, 1064 (1968).

[27] R. W. Murray, W. C. Lumma, Jr., and J. W. -P. Lin, *ibid.*, **92**, 3205 (1970).

[28] L. Spialter and J. D. Austin, *ibid.*, **88**, 1828 (1966).

[29] A. G. Brook and J. M. Duff, *ibid.*, **91**, 2118 (1969).



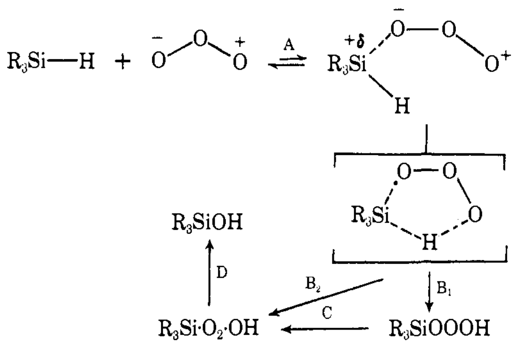
10 → **7**

combination to the silanol is the mechanism which appears most compatible with the experimental observations.

Conclusions

When all the mechanistic evidence is taken into consideration, the following reaction sequence (Scheme II)

Scheme II



appears to best satisfy the data. The silane undergoes reversible complexation (A) with the ozone, the complex being present in only small concentrations. The rate step then involves electrophilic attack by the ozone on the hydridic hydrogen, passing through a five-centered transition state.[30] This may decompose to either a silyl hydrotrioxide (B_1) or directly to the radical pair (B_2). The silyl hydrotrioxide, if present, must decompose rapidly to the radical pair (C). This radical pair then recombines with retention of configuration to afford the ultimate product, the silanol (D).[31]

Experimental Section

Materials. The silanes (with the following exception) were known compounds and were either purchased (Pierce Chemical Corp., Peninsular Chemresearch Inc., or Matheson Coleman and Bell) or synthesized by reduction of the corresponding chloro- or fluorosilanes. All compounds synthesized afforded correct elemental and spectral analyses.

2,2′-Biphenylenylsilane was prepared by the lithium aluminum hydride reduction of 2,2′-biphenylenyldifluorosilane (Stauffer Chemical Co.), melted at 36.6° and boiled at 86° (0.31 mm). *Anal.* Calcd for $C_{12}H_{10}Si$: C, 79.06; H, 5.53; Si, 15.41. Found: C, 78.92; H, 5.61; Si, 15.12.

Relative Rata Data. The general nature of the silane–ozone reaction has been described elsewhere.[10] The relative rata data were obtained by passing an ozone-oxygen mixture through 4 ml of *ca.* 4×10^{-2} *M* solutions of the mixed silanes in carbon tetrachloride. Each solution also contained an inert, saturated hydrocarbon which functioned as an internal standard for the gas chromatographic analysis. The reaction vessel was immersed in an ice–water bath during the reaction. The ozone–oxygen stream from a Welsbach Model T-23 laboratory ozonator was passed through the reaction mixture for a period of 2–4 hr, during which time samples were periodically withdrawn, sealed, and stored in a refrigerator prior to analysis. (No change in relative concentrations occurred during storage). The analyses were accomplished on a Perkin-Elmer Model 226 gas chromatograph equipped with a 150 ft × 0.01 in. i.d. capillary column of Dow Corning DC-550. The peak areas were determined with a Perkin-Elmer Model 194 printing integrator and converted to concentration units by comparison to the internal standard. The relative rate, k_{rel}, is defined

$$k_{\text{rel}} = k_A/k_B = \log (B_t/B_i)/\log (A_t/A_i)$$

where A and B are the concentrations of the two silanes initially (i) and at elapsed time t. In Table I the rates are relative to tri(*n*-butyl)silane, assigned $k_{\text{rel}} = 100$.

Low-Temperature Nmr Studies. The low-temperature nmr work was done on a Varian Associates A-60 nmr spectrometer. Samples were kept at −75° prior to insertion into the probe, which was at −57°. The solvent employed throughout was methylene chloride, which also served as an internal standard. Blank runs demonstrated that no reaction between solvent and either ozone or the silanes occurred.

Ultraviolet Spectra of Silane–Ozone Mixtures. The uv region at 260–280 mμ was monitored[32] for mixtures of ozone with triethylsilane, triethylsilanol, and tetramethylsilane in carbon tetrachloride. In all cases, even a trace of the silicon species resulted in the rapid disappearance of the characteristic ozone absorption.

Determination of k_H/k_D. The isotope effect of the ozonation of the Si–H bond was determined in the following manner: the k_{rel} for tri(*n*-butyl)silane relative to tri(*n*-hexyl)silane and for tri(*n*-butyl)deuteriosilane relative to tri(*n*-hexyl)silane were determined by the vpc technique previously described. The ratio of these two k_{rel} values was taken as k_H/k_D. The values of multiple determinations did not vary by more than 0.05. The value of 6.9 was unchanged by using ozone–argon gas mixtures in place of the ozone–oxygen gas mixture.[33]

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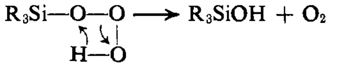
[30] In a private communication, Dr. Kenneth Wiberg, Yale University, has kindly pointed out to us that the magnitude of the isotope effect supports the five-centered activated complex which we have postulated. In the smaller ring complexes, the vibrational mode converted to the reaction coordinate is a bending mode, which would not produce a large isotope effect. In the five-centered complex, both bending and stretching modes are converted, and the large isotope effect is not unexpected.

[31] A referee has suggested that **9** could decay to product *via* a concerted pathway (i). Although such a pathway cannot be ruled out, we feel that the large isotope effect suggests the radical pair, probably from B_2. Both i and the radical mechanism would proceed with retention of configuration.



$$R_3Si{-}O{-}O \longrightarrow R_3SiOH + O_2 \qquad \text{(i)}$$

[32] T. W. Nakagawa, L. J. Andrews, and R. M. Keefer, *J. Amer. Chem. Soc.*, **82**, 269 (1960).

[33] The validity of this technique is further demonstrated by comparing the k_H/k_D observed for the dichlorocarbene insertion (1.23), *vide supra*, with the value obtained from infrared analysis of direct competition reactions of various Si–H compounds with :CCl_2, namely, 1.1 (private communication, Dr. D. Seyferth). Thus, our indirect competition experiments are in agreement with direct competition techniques. For further discussion of k_H/k_D values determined for Si–H reactions by this method, see ref 21.