Photolysis of 2,2-Dimethyl-2-silabutane (Ethyltrimethylsilane) at 147 nm

Daryl J. Doyle and R. D. Koob*

Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105 (Received: December 29, 1980; In Final Form: March 20, 1981)

Eight stable products in the neat photolysis at 147 nm of ethyltrimethylsilane (ETMS) along with three additional stable products found in the presence of additives are rationalized in terms of five primary molecular products, eight atomic or free radical intermediates, and (CH₃)₂SiCH₂. In decreasing order of importance these are CH₃ $[0.45], C_2H_4 \ [0.21], \ (CH_3)_2SiCH_2 \ [0.17], \ C_2H_5 \ [0.15], \ H_2 \ [0.12], \ (CH_3)_3Si \ [0.11], \ H \cdot \ [0.10], \ CH_4 \ [0.10], \ C_2H_6 \ [0.10], \$ $(CH_3)_3SiCH_2$ [0.09], $(CH_3)_2SiC_2H_5$ [0.08], $(CH_3)_3SiC_2H_4$ · [0.06], $(CH_3)_2SiH$ [0.05], and $(CH_3)_3SiH$ [0.03]. In contrast to the photochemistry of tetramethylsilane, many competing primary processes occur and there is little indication of a dominant reaction. This multiplicity of products creates a system too complex for unambiguous elucidation but illustrates many reactions found commonly in photochemical studies of hydrocarbons. It appears that the structure of the molecule and the availability of secondary hydrogens are more important to the overall reaction mechanism than is the presence of silicon.

Introduction

While there are few examples of vacuum-ultraviolet photochemical studies of acyclic alkylsilanes,1-6 the interest in these molecules appears to be increasing. Recently three groups have published results on tetramethylsilane within 1 yr of each other.⁴⁻⁶ All previous examples in this class involve only primary hydrogens, whereas the vacuum-ultraviolet (VUV) photolysis of alkanes has shown that the bonded position of hydrogen is an important factor in the types of reactions which the molecule may undergo. Ethyltrimethylsilane has been photolyzed, and the results are reported in this paper. Particularly, these results are compared to previously reported alkylsilane and alkane photolyses, and the role of secondary hydrogens is emphasized.

Experimental Section

Ethyltrimethylsilane was prepared by standard methods⁷ and was purified to 99.9% purity by preparative gas chromatography. Oxygen, HI (Linde), CD₃OD (Merck, Sharp, and Dohme), and cyclopentanone (Eastman) were used without further purification.

The photolyses were carried out at room temperature at 147 nm by using a double-headed Xe-filled resonance lamp as described by Tokach et al.⁸ Samples were prepared for irradiation by using standard vacuum techniques. Typical sample pressures were 8 torr.

Cyclopentanone was used as the actinometer, and a quantum yield of 1.76 for ethene was assumed.⁹ The ratio of light intensities through the MgF₂ windows was measured before and after each quantum-yield determination. Sample analysis was performed by FID gas chromatogra-

S. K. Tokach and R. D. Koob, J. Phys. Chem., 84, 1 (1980).
 S. K. Tokach and R. D. Koob, J. Phys. Chem., 83, 774 (1979).
 L. Gammie, C. Sandorfy, and O. P. Strausz, J. Phys. Chem., 83,

3075 (1979)

(6) E. Bastian, P. Potzinger, A. Ritter, H. P. Schuchman, C. von Sonntag, and G. Weddle, Ber. Bunsenges. Phys. Chem., 84, 56 (1980). (7) Ethyl bromide was converted to the corresponding Grignard compound which was then added to trimethylchlorosilane

(8) S. K. Tokach, P. Boudjouk, and R. D. Koob, J. Phys. Chem., 82, 1203 (1978).

(9) Alfred A. Scala and Daniel G. Ballan, Can. J. Chem., 50, 3938 (1972).

TABLE I: Quantum Yields in the Photolysis of ETMS at 147 nm^a

neat	0 ₂	HI
0.23 ± 0.05	0.12 ± 0.02	0.22 ± 0.04
0.12 ± 0.02	0.10 ± 0.01	0.48 ± 0.05
0.28 ± 0.02	0.10 ± 0.01	0.25 ± 0.03
0.22 ± 0.02	0.21 ± 0.01	0.21 ± 0.01
0.09 ± 0.01	< 0.01	< 0.01
0.06 ± 0.02	0.03 ± 0.01	0.14 ± 0.02
0.03 ± 0.01	<0.01	0.09 ± 0.02
< 0.01	< 0.01	0.08 ± 0.03
0.03 ± 0.01	< 0.01	< 0.01
0.06 ± 0.02	< 0.01	< 0.01
< 0.01	< 0.01	0.05 ± 0.01
	$\begin{array}{c} \mbox{neat} \\ \hline 0.23 \pm 0.05 \\ 0.12 \pm 0.02 \\ 0.28 \pm 0.02 \\ 0.22 \pm 0.02 \\ 0.09 \pm 0.01 \\ 0.06 \pm 0.02 \\ 0.03 \pm 0.01 \\ < 0.01 \\ \hline 0.03 \pm 0.01 \\ 0.06 \pm 0.02 \\ < 0.01 \\ \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

 a All uncertainties are at the 90% confidence level.

^b Boiling-point range of 80-90 °C according to retentiontime data.

phy with a 25-ft 30% squalane column at room temperature for low-boiling products and a 25-ft 3% squalane column at 50 °C for higher-boiling products.

A Nuclide isotope-ratio mass spectrometer was used to analyze for H_2 . The sample cell was attached directly to the mass spectrometer inlet system. The volatile gases at -196 °C were quantitatively transferred into the mass spectrometer by the use of a Toepler pump, and the H_2/CH_4 ratios measured. The mass-spectral response to H_2 and CH_4 was calibrated by admitting known mixtures of H_2 and CH_4 and monitoring the m/e values of 2 and 15, respectively.

Results

Quantum yields of the products measured in the neat system, in the presence of O_2 , and in the presence of HI are listed in Table I. The observed products for the 147-nm photolysis of pure ethyltrimethylsilane (ETMS) are, in decreasing order of importance, ethane, hydrogen, ethene, methane, propane, trimethylsilane (TriMS), npropyltrimethylsilane, tetramethylsilane (TetraMS), and an unidentified product with a boiling point between 80 and 90 °C according to retention-time data. The photolysis of ETMS in the presence of O_2 results in a decrease in all product quantum yields except for that of ethene and methane which, within experimental error, remain constant. It is assumed that all other products have at least some radical precursors. The photolysis in the presence of HI results in the removal of propane, the increase in all

^{(1) (}a) O. P. Strausz, K. Obi, and W. Duholke, J. Am. Chem. Soc., 90, 1359 (1968); (b) K. Obi, A. Clement, H. E. Gunning, and O. P. Strausz, ibid., 91, 1622 (1969).

⁽²⁾ A. G. Alexander and O. P. Strausz, J. Phys. Chem., 80, 2531 (1976).

Photolysis of 2,2-Dimethyl-2-silabutane at 147 nm

TABLE II: Quantum Yields of Intramolecular Hydrogenfrom Selected Molecules Photolyzed at 147 nm

reaction	ΦH_2	ref
$C_3H_8 \rightarrow H_2 + cofragments$	0.82	12
$n \cdot C_4 H_{10} \rightarrow H_2 + cofragments$	0.55	13
$(CH_3)_3SiC_2H_5 \rightarrow H_2 + cofragments$	0.12	this work
$(CH_3)_6 Si_2 \rightarrow H_2 + cofragments$	< 0.01	3
$(CH_3)_4$ Si \rightarrow H ₂ + cofragments	< 0.01	4
$(CH_3)_4 C \rightarrow H_2 + cofragments$	0.02	14
$(CH_3)_6C_2 \rightarrow H_2 + cofragments$	0.03	15

other products except for hydrogen, ethane, and ethene, and the production of two new products, ethyldimethylsilane (EDMS) and dimethylsilane (DMS). In addition, the photolysis of ETMS in the presence of methanol results in the production of trimethylmethoxysilane (TMMOS) with a quantum yield of 0.17. Trimethylmethoxysilane is a result of methanol addition to 2methyl-2-silapropene.³

It is assumed that those products produced in the presence of O_2 result from intramolecular decompositions and those present in HI are intramolecular or are a result of radical abstraction of H from HI or both. In the O_2 and HI experiments the pressures of the additives were 10% ETMS pressure or less.

Discussion

Eaborn and Simmie¹⁰ performed the thermal decomposition of ETMS at 823 K. The predominant thermolysis products were ethene and trimethylsilane, along with small quantities of tetramethylsilane, methane, and a product assumed to be vinyltrimethylsilane. The addition of nitric oxide doubled the rate of disappearance of ETMS, and the rate of formation of trimethylsilane was approximately halved. All products and behaviors were rationalized in terms of a radical chain initiated solely by reaction 1. This

$$C_2H_5Si(CH_3)_3 \rightarrow C_2H_5 + \cdot Si(CH_3)_3$$
(1)

Si-C (secondary) cleavage was the only primary reaction postulated by Eaborn and Simmie. An analogous cleavage also dominates the electron impact induced decomposition of ethyltrimethylsilyl ion,¹¹ but two other reactions of importance are also seen, reactions 2 and 3. As seen below,

$$[C_2H_5Si(CH_3)_3]^+ \rightarrow [C_2H_5Si(CH_3)_2]^+ + CH_3$$
 (2)

$$[C_{2}H_{5}Si(CH_{3})_{2}]^{+} \rightarrow [(CH_{3})_{2}SiH]^{+} + C_{2}H_{4} \qquad (3)$$

the vacuum-ultraviolet photolysis of ethyltrimethylsilane provides evidence for reactions analogous to these plus a number of others.

Intramolecular Products. H_2 , CH_4 , C_2H_4 , C_2H_6 , and $(CH_3)_3SiH$ all remain as significant products in the photolysis of ETMS in the presence of O_2 . The yields of these five products are thus assigned to intramolecular reactions and are interpreted to be primary photoproduct yields. Under comparable conditions, tetramethylsilane yielded only CH_4 .⁴ The photon-induced unimolecular decomposition of $C_2H_5Si(CH_3)_3$ clearly proceeds by more varied

TABLE III: Methane Production in the 147-nm Photolysis of Selected Compounds

reaction	$\Phi \operatorname{CH}_4$	ref
$C_3D_8 \rightarrow CD_4 + cofragments$	0.07	13
$i - C_4 D_{10} \rightarrow CD_4 + cofragments$	0.009	13
$(CH_3)_{a}C \rightarrow CH_{a} + cofragments$	0.23(0.51)	14
	at 7.6 eV)	
$(CH_3)_4 Si \rightarrow CH_4 + cofragments$	0.32	4
$(CH_3)_6Si_2 \rightarrow CH_4 + cofragments$	0.08	3
$(CH_3)_6C_2 \rightarrow CH_4 + cofragments$	0.09	15
$(CH_3)_3SiC_2H_5 \rightarrow CH_4 + cofragments$	0.10	this
		work

 TABLE IV:
 Comparison of Unsaturated to Expected

 Saturated Cofragments for Selected Molecules
 Photolyzed at 147 nm

molecule	unsaturated product	expected saturated product	Φ saturated/ Φ unsaturated
C ₃ D ₈	C ₂ D ₄	CD ₄	0.07/0.18 =
$neoC_{s}H_{12}$	i-C ₄ H ₈	CH_4	0.39 0.23/0.70 =
$(CH_{3})_{6}C_{2}$	$i-C_4H_8$	<i>i</i> -C ₄ H ₁₀	0.33 = 0.42/0.99 = 0.42
$(\mathrm{CH}_3)_4\mathbf{Si}$	$(\mathrm{CH}_3)_2\mathrm{SiCH}_2$	CH_4	0.42 0.32/0.47 =
$(CH_3)_6Si_2$	$(\mathrm{CH}_3)_2\mathrm{SiCH}_2$	(CH ₃) ₃ SiH	0.26/0.41 = 0.63
$(CH_3)_3SiC_2H_5$	C_2H_4	$(CH_3)_3SiH$	0.03/0.21 = 0.14
$(CH_3)_3SiC_2H_5$	$(\mathrm{CH_3})_2\mathrm{SiCH_2}$	$C_{2}H_{6}$	0.10/0.17 = 0.59

paths than are available to $(CH_3)_4Si$. Since the two molecules differ only by a $-CH_2$ - group, the influence of this group must be considerable.

The extent of this influence is seen easily by an examination of H_2 (intramolecular) quantum yields in a number of alkanes and alkylsilanes. Table II lists intramolecular H_2 quantum yields for selected examples. In highly branched alkanes with only primary hydrogens, e.g., neopentane and hexamethylethane, and permethylated silanes, e.g., tetramethylsilane and hexamethyldisilane, intramolecular quantum yields are very small. The availability of secondary hydrogens greatly enhances the probability of intramolecular hydrogen loss, e.g., C_3H_8 , n- C_4H_{10} , and ETMS. In cases where labeling experiments have been done, propane and *n*-butane, loss of H_2 from the secondary carbon is demonstrated directly to predominate.

Intramolecular methane, which can be produced by only one (degenerate) reaction in $(CH_3)_4Si$, may arise in several ways in $(C_2H_5)Si(CH_3)_3$. As in many saturated molecules, with the exception of $(CH_3)_4Si$ and $(CH_3)_4C$, the total methane quantum yield is relatively low, amounting to only 0.10 for ETMS (see Table III). The effect is most likely due to the availability of reactions which compete effectively in all cases but the two exceptions mentioned.

Ethene is produced exclusively by unimolecular reactions. The empirically required cofragment, trimethylsilane, is found in considerably lower yield. This situation is not uncommon for VUV-induced reactions of saturated molecules (Table IV). Presumably it is more favorable to dissipate excess energy by loss of additional fragments from saturated than unsaturated molecules.

A similar situation is noted for reaction 4, the unimo-

$$C_2H_5Si(CH_3)_3 \rightarrow C_2H_6 + (CH_3)_2Si = CH_2 \qquad (4)$$

lecular production of ethane and 2-methyl-2-silapropene (MSP). The quantum yield of unimolecular ethane is 0.10 compared to 0.17 for trapped MSP.

 ⁽¹⁰⁾ C. Eaborn and J. M. Simmie, J. Organomet. Chem., 47, 45 (1973).
 (11) N. Ya. Chernyak, R. A. Khmel'nitskii, T. V. D'yakova, and V. m.
 Vdovin, J. Gen. Chem. USSR (Engl. Transl.), 36, 93 (1966).

⁽¹²⁾ P. Ausloos, R. E. Rebbert, and S. G. Lias, J. Photochem., 2, 267 (1972).

⁽¹³⁾ P. Ausloos and S. G. Lias, "Chemical Spectroscopy and Photochemistry in the Vacuum Ultraviolet", Sandorfy, Ausloos, and Robin, Eds., Reidel, Boston, MA, 1974.

⁽¹⁴⁾ R. E. Rebbert, S. G. Lias, and P. Ausloos, J. Photochem., 4, 121 (1975).

⁽¹⁵⁾ S. K. Tokach and R. D. Koob, J. Phys. Chem., 84, 6 (1980).



Figure 1. Ratio of 2-methyl-2-silapropene to trimethylmethoxysilane as a function of reciprocal methanol concentration. The solid lines are calculated as described in footnote 16. The points are representative experimental data.

Note that unlike comparable situations for $(CH_3)_4Si$, $(CH_3)_6Si_2$, and cyclic $(CH_3)_2Si(CH_2)_3$ there is a weak dependence of TMMOS on methanol concentration over the range used. This is easily understood in terms of the relative steady-state concentrations of free radicals and MSP and the rate constants for reaction of radicals and methanol with MSP. The latter rate constant may be calculated from the data of Bastian et al.⁶ and Tokach et al.⁸ to be $\sim 2 \times 10^6$ cm³ mol⁻¹ s⁻¹.¹⁶ Trimethylsilyl radicals, on the other hand, react ~ 5 orders of magnitude faster with MSP. These relationships are plotted in Figure 1 for a variety of steady-state methyl radical concentrations relative to a given MSP steady-state concentration as a function of methanol pressure. For ETMS the radicalto-MSP ratio is low enough—our methanol concentration ranged from 0.01 to 0.1 of the parent compound-that little variation larger than experimental error is observed. The steady-state radical concentration for ETMS photolysis is ~ 7 times smaller than that found in tetramethylsilane or hexamethyldisilane.

Radical Products. From the neat photolysis and photolysis of ETMS plus HI, the intermediacy of eight atomic or radical species may be deduced: H_{\cdot} , CH_3 , C_2H_5 , (C- $H_3)_3Si$, $(CH_3)_3SiCH_2$, $(CH_3)_2SiC_2H_5$, $(CH_3)_3SiC_2H_4$, and $(CH_3)_2SiH$. With the exception of $(CH_3)_2SiH$, all may be produced by simple bond cleavage from the parent ETMS. While an important contribution to the yields of these radicals is certainly primary photodissociation, secondary or concurrent fragmentation may also contribute and must do so at least for H and CH₃ production to avoid impossibly high primary quantum yields.

York, 1976.

If the measured yield of Si-containing radicals can be used as a rough guide to the importance of photoinduced primary homolytic cleavage at 147 nm, such reactions are remarkably nonselective for ETMS, as may be seen from the following: $\Phi(CH_3)_3Si = 0.11$, $\Phi(CH_3)_3SiCH_2 = 0.09$, $\Phi(CH_3)_2SiC_2H_5 = 0.08, \Phi(CH_3)_3SiC_2H_4 = 0.06.$ Of course, such comparisons are not strictly valid if multiple fragmentations occur, but the lack of strongly dominating products suggests multiple reaction paths compete effectively with one another in the 147-nm photochemistry of ETMS.

Finding dimethylsilane among the products of a photolysis in the presence of HI suggests the production of the dimethylsilyl radical. This product is unexpected in a system where there are no hydrogens bonded directly to the silicon. Clearly, an intramolecular hydrogen transfer, such as that necessary to produce "molecular" trimethylsilane, is required either prior to or concurrent with multiple bond cleavage reactions. Although such processes are commonly postulated to account for the typical shortfall in saturated cofragments mentioned in the previous section and illustrated by Table IV, this is the first example of which we are aware that a unique product is formed. The more general situation is one where fragments from rearranged products are indistinguishable from those produced directly.

Secondary Reactions. Of the products observed in the neat photolysis, all of the C₃H₈, (CH₃)₄Si, and (CH₃)₃Si- $\rm C_3H_7$ and about one-half of the $\rm H_2, \rm C_2H_6,$ and $\rm (CH_3)_3SiH$ are accounted for by secondary reactions. CH_4 and C_2H_4 are essentially all primary products. C₃H₈, (CH₃)₄Si, $(CH_3)_3SiC_3H_7$, and C_2H_6 are almost certainly methyl combination products with C_2H_5 , $(CH_3)_3Si$, $(CH_3)_3SiC_2H_5$, and ·CH₃, respectively. Secondary H₂ and (CH₃)₃SiH are most probably produced by hydrogen abstraction from the parent by H and $(CH_8)_3Si_{,}$ respectively. Within experimental error, titrated (by HI) H· and (CH₃)₃Si· equal the quantum yields of the secondary H_2 and $(CH_3)_4Si + (C-1)_4Si + (C-1)_4Si$ H_{3} SiH, respectively, which lends credence to this assertion. Similarly the sum of the quantum yields of the proposed methyl combination products equals the titrated methyl radical yield well within experimental error,

Summary

Eight stable products in the neat photolysis at 147 nm of ETMS along with three additional stable products found in the presence of additives are rationalized in terms of five primary molecular products, eight atomic or free radical intermediates, and (CH₃)₂SiCH₂.

In decreasing order of importance these are CH_3 [0.45], C_2H_4 [0.21], (CH₃)₂SiCH₂ [0.17], C_2H_5 [0.15], H_2 [0.12], $(CH_3)_3Si [0.11], H \cdot [0.10], CH_4 [0.10], C_2H_6 [0.10], H_2 [0.12], (CH_3)_3SiCH_2 [0.09], (CH_3)_2SiC_2H_5 [0.08], (CH_3)_3SiC_2H_4 \cdot [0.06], (CH_3)_2SiH [0.05], and (CH_3)_3SiH [0.03]. In contrast$ to the photochemistry of tetramethylsilane, many competing primary processes occur, and there is little indication of a dominant reaction. This multiplicity of products creates a system too complex for unambiguous elucidation but illustrates many reactions found commonly in photochemical studies of hydrocarbons. It appears that the structure of the molecule and the availability of secondary hydrogens is more important to the overall reaction mechanism than is the presence of silicon.

⁽¹⁶⁾ This calculation uses the equation $C_2H_4/Me_3SiOMe = \Phi C_2H_4/\Phi Me_2SiCH_2 + \{\Phi C_2H_4/\Phi Me_2SiCH_2\}\{K_1[W]/(K_2[MeOH])\}$ where $\Phi C_2H_4/\Phi Me_2SiCH_2$ is the intercept and $(\Phi C_2H_4)(K_1)([W])/\{(\Phi Me_2SiCH_2)(K_2)\}$ is the slope of the line given in Figure 1 of ref 8. K_1 is the slope of the line given in Figure 1 of ref 8. K_1 is the rate constant for methyl radicals reacting with Me₂SiCH₂ (see ref 6). [W] is the concentration of methyl radicals which is obtained by using 6.3×10^{-11} einstein/s for the intensity of the lamp used, 50 cm³ for the volume of the sample cell, and 0.03 as the quantum yield of ethane produced in ref 8. In addition the rate constant for combination of two methyl radicals of $3.16 \times 10^{10} \text{ L/(mol s)}$ (see ref 18) is needed to calculate [W]. K₂ is the unknown rate constant for methanol reacting with
 Me₂SiCH₂ to give TMMOS.
 (17) S. W. Benson "Thermochemical Kinetics", 2nd ed., Wiley, New