cron particle size. The pellets cannot be used as electrodes because interparticle contact is insufficient for good electrical conduction. It would be very useful if vibrational spectroscopies could be routinely applied to normal electrode surfaces. In certain instances, vibrational spectra can be obtained on metal surfaces, but these are restricted to particular metals (surface-enhanced Raman effect^{36,37})

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Gas-Phase Photolysis of 2,2-Dimethylbutane, 2,2,3-Trimethylbutane, 2,2,3-Trimethyl-2-silabutane, and 2,2,3,3-Tetramethyl-2-silabutane at 147 nm

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The 147-nm photolyses of 2,2-dimethylbutane, 2,2,3-trimethylbutane, 2,2,3-trimethyl-2-silabutane (isopropyltrimethylsilane), and 2,2,3,3-tetramethyl-2-silabutane (*tert*-butyltrimethylsilane) are reported. In addition, the mercury-sensitized photolyses of $i-C_4H_{10}$, trimethylsilane, and mixtures of $i-C_4H_{10}$ and trimethylsilane are reported which give disproportionation to combination (D/C) ratios of 2.1 ± 0.2 and 0.28 ± 0.05 for (CH₃)₃C + (CH₃)₃C and (CH₃)₃Si + (CH₃)₃Si, respectively, and D/C ratios of 1.86 ± 0.15 and 0.55 ± 0.08 for (CH₃)₃C + (CH₃)₃Si to form 2-methyl-2-silapropene and $i-C_4H_8$, respectively. With the completion of this work, several trends and generalizations can be drawn concerning the importance of various processes in linear vs. branched alkanes and alkylsilanes. These conclusions are summarized in this report.

Introduction

The gas-phase photolyses of 2,2-dimethylbutane, 2,2,3trimethylbutane, 2,2,3-trimethyl-2-silabutane (isopropyltrimethylsilane), and 2,2,3,3-tetramethyl-2-silabutane (*tert*-butyltrimethylsilane) complete two sequences of compounds, one alkane and one alkylsilane, in which three primary hydrogens of neopentane and tetramethylsilane are sequentially replaced with methyl groups (neopentane,¹ 2,2-dimethylbutane, 2,2,3-trimethylbutane, and 2,2,3,3tetramethylbutane² for the alkane series and tetramethylsilane,³ 2,2-dimethyl-2-silabutane (ethyltrimethylsilane),⁴ 2,2,3-trimethyl-2-silabutane, and 2,2,3,3-tetramethyl-2-silabutane^{2a,5} for the alkylsilane series).

2,2-Dimethylbutane (22DMB) is the hydrocarbon analogue of recently studied 2,2-dimethyl-2-silabutane.⁴ While highly branched, 22DMB still contains two geminal secondary hydrogens as does the extensively studied propane molecule⁶ and thus provides an opportunity to compare and contrast the influences governing the photodissociation processes in linear vs. branched hydrocarbons in the same molecule.

With the exception of the photolysis of isobutane^{1,7} there are few examples of photolysis of compounds which have tertiary hydrogens. Isopropyltrimethylsilane and 2,2,3trimethylbutane are examples of alkylsilane and alkane which contain tertiary hydrogen. The results from the photolyses of these two compounds, with emphasis placed on the role of tertiary hydrogens, along with the results from *tert*-butyltrimethylsilane are compared to previously reported alkanes and alkylsilanes.

Experimental Section

Isopropyltrimethylsilane (IPTMS),⁸ tert-butyltrimethylsilane (t-BTMS),⁹ prepared by standard methods, and 2,2,3-trimethylbutane (223TMB), purchased from

(9) (a) *tert*-Butyltrimethylsilane was prepared by the reaction of methylmagnesium bromide on *tert*-butyldimethylchlorosilane (for use in ref 5). (b) *tert*-Butyltrimethylsilane was prepared by reacting *tert*-butyldimethylchlosilane with methyllithium (for use in ref 12).

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(8) Isopropyltrimethylsilane was synthesized by converting isopropyl bromide to the corresponding Grignard compound which was then added to trimethylchclorosilane.

Photolysis of Alkanes and Alkylsilane Analogues

TABLE I: Quantum Yield Results for the 147-nmPhotolysis of $22DMB^{a,b}$

product	neat	0,2	HI¢
H,	0.22 ± 0.05	0.07 ± 0.01	0.27 ± 0.06
CH₄	0.16 ± 0.01	0.09 ± 0.01	0.69 ± 0.06
C,H,	0.09 ± 0.01	0.08 ± 0.01	0.08 ± 0.01
C,H,	0.39 ± 0.03	0.06 ± 0.01	0.25 ± 0.04
C,H,	0.15 ± 0.01	< 0.01	<0.01
C ₃ H ₆	0.08 ± 0.01	0.09 ± 0.01	0.08 ± 0.01
$n - C_4 H_{10}$	0.01 ± 0.004	< 0.01	< 0.01
i-C,H	0.45 ± 0.06	0.44 ± 0.06	0.49 ± 0.12
<i>i</i> -C ₄ H ₁₀	0.06 ± 0.01	< 0.01	0.06 ± 0.01
neo-C ₅ H ₁₂	0.06 ± 0.01	<0.01	< 0.01
unknown A	≤0.03	<0.01	< 0.01
unknown B	≤0.02	< 0.01	< 0.01
2-methyl- 1-butene	0.15 ± 0.02	0.15 ± 0.02	ND
2-methyl- 2-butene	0.13 ± 0.02	0.13 ± 0.02	ND

^a All uncertainties are at the 90% confidence level. ^b All photolyses were for 30 min. ^c All O₂ and HI pressures were 10% 22DMB pressure or less. ND indicates not determined.

Pfaltz and Bauer, Inc., were purified by preparative gas chromatography. Oxygen, HI (Linde), CD_3OD (Merck Sharp and Dohme), ethene (Matheson), and 2,2-dimethylbutane (Phillips) 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.¹⁰ Samples were prepared for irradiation by using standard vacuum techniques. Typical sample pressures were 20 torr for 22DMB, 10 torr for IPTMS and 223TMB, and 4 torr for t-BTMS.

Ethene was used as the actinometer,^{1,11} and a quantum yield of 0.9 for the formation of acetylene was assumed. The ratio of light intensities through the MgF₂ windows was measured before and after each quantum yield determination.¹² Sample analysis was performed by FID gas chromatography with a 50-ft 30% squalane column at room temperature for the actinometer determinations and for the determination of low-boiling products through propane. Twentyfive feet of this same column was used at room temperature to determine low-boiling products through isobutene. A 25-ft 3% squalene column at 50 °C was used for high-boiling products. A Durapak phenyl isocyanate/porasil C column (Waters Associates, Inc., 80/100 mesh, 2 m long) was used to separate saturated and unsaturated products.

A Nuclide isotope-ratio mass spectrometer was used to analyze for H_2 as described by Doyle and Koob.⁴

Results

2,2-Dimethylbutane (22DMB). Quantum yields of the products 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 room-temperature 147-nm photolysis of pure 22DMB are, in decreasing order of importance, isobutene, ethane, hydrogen, methane, propane, 2-methyl-1-

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Figure 1. Conversion dependence of unsaturated/saturated products in the photolysis of 22DMB.

butene, 2-methyl-2-butene, ethene, propene, isobutane, neopentane, two unidentified products with quantum yields less than or equal to 0.03 and 0.02, respectively, and *n*-butane. The photolysis of 22DMB in the presence of <10% O₂ significantly decreased the yields of hydrogen, methane, ethane, propane, *n*-butane, isobutane, neopentane, and the two unidentified products. The photolysis of 22DMB in the presence of <10% HI significantly increased the production of methane and decreased ethane, propane, *n*-butane, neopentane, and the two unidentified products. All other product yields remained constant within experimental error.

Tokach and Koob^{2b} showed a conversion dependence for the production of unsaturated compounds when 2,2,3,3tetramethylbutane was photolyzed at 147 nm. They postulated that hydrogen atom attack on unsaturated species at high conversions resulted in this conversion dependence. Figure 1 shows a similar effect for the photolysis of 22DMB. It should be noted that the sharp conversion dependence on the ratio of $i-C_4H_8$ to $i-C_4H_{10}$ is enhanced by the fact that the yield of $i-C_4H_8$ to $i-C_4H_{10}$ becomes very large. The conversion dependence of the C_3H_6/C_3H_8 and C_2H_4/C_2H_6 ratios is less marked.

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 these additives were 10% of the parent pressure or less.

2,2,3-Trimethylbutane (223TMB). Quantum yields of the products measured in the neat system, in the presence of O_2 , and in the presence of greater than 450 Torr of N_2 are listed in Table II. Listed in Table III are the quantum yields of the products measured in the presence of HI, HI and high pressure N_2 (greater than 450 torr), and HI and high pressure CH_3F (greater than 300 torr). The observed products for the 147-nm photolysis of pure 223TMB are, in decreasing order of importance, isobutene, hydrogen, propene, propane, ethane, isobutane, 2,3-dimethyl-1-butene, methane, 2-methyl-2-butene, ethene, neopentane, and an unidentified product whose quantum yield is less than or equal to 0.02. The photolysis of 223TMB in the presence of O_2 results in a decrease of all products except for ethene, hydrogen, and 2-methyl-2-butene which, within experimental error, remain constant. When N_2 (greater than 450 torr) is added to pure 223TMB and is photolyzed at 147 nm, methane, ethane, and ethene decrease in yield while all other products remain equal to that in the pure

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TABLE II: Quantum Yield Results in the Photolysis of 223TMB at 147 nm^a

product	neat	N ₂ ^b	O ₂ ^c	$N_2 + O_2^{b,c}$
CH4	0.15 ± 0.01	0.10 ± 0.01	0.05 ± 0.01	0.06 ± 0.01
C,H,	0.20 ± 0.01	0.14 ± 0.02	< 0.01	< 0.01
C,H,	0.05 ± 0.004	0.03 ± 0.01	0.04 ± 0.01	0.02 ± 0.003
C.H.	0.22 ± 0.01	0.24 ± 0.03	0.06 ± 0.01	0.14 ± 0.02
i-Č,H ₁₀	0.18 ± 0.02	0.18 ± 0.03	0.03 ± 0.01	0.04 ± 0.01
C,H,	0.28 ± 0.02	0.24 ± 0.03	0.20 ± 0.02	0.18 ± 0.02
neo-C.H.,	0.03 ± 0.004	0.03 ± 0.01	< 0.01	< 0.01
unidentified	0.02 ± 0.004	0.02 ± 0.01	< 0.01	< 0.01
i-C, H.	0.50 ± 0.06	0.45 ± 0.07	0.35 ± 0.06	0.39 ± 0.07
H, Č	0.44 ± 0.10	ND	0.31 ± 0.06	ND
2-methyl-2-butene	0.12 ± 0.03	ND	0.08 ± 0.02	ND
2,3-dimethyl-1-butene	0.17 ± 0.04	ND	0.10 ± 0.02	ND

^a All uncertainties are at the 90% confidence level. ^b All N₂ additive studies were made with greater than 450 torr of N₂. ^c In all O₂ additive studies O₂ pressures were 10% 223TMB or less. ND indicates not determined.

TABLE III:Quantum Yield Results in the Photolysis of223TMB + HI at 147 nm^{a, b}

product	HI	$HI + N_2^c$	$\operatorname{HI}_{\mathrm{CH}_{3}}^{\mathrm{HI}}\mathrm{F}^{d}$
CH4	0.63 ± 0.04	0.53	0.51 ± 0.10
C,H,	0.18 ± 0.01	0.14	0.09 ± 0.02
C,H,	ND	ND	ND
C ₄ H ₈	0.45 ± 0.03	0.52	0.42 ± 0.10
<i>i</i> -Č₄H ₁₀	0.14 ± 0.01	0.17	0.14 ± 0.03
C ₃ H ₄	0.24 ± 0.02	0.21	ND
neo-C,H ₁₂	< 0.01	< 0.01	ND
unidentified	< 0.01	< 0.01	ND
i-C ₄ H ₈	0.35 ± 0.07	ND	ND
H,	0.63 ± 0.11	ND	ND
2-methyl-2-butene	0.07 ± 0.03	ND	ND
2,3-dimethyl-1-butene	0.08 ± 0.02	ND	ND

^a All uncertainties are at the 90% confidence level. ^b All HI additive studies were with <10% HI. ^c N₂ pressure was greater than 450 torr and these results are for a single determination. ^d CH₃F pressure was greater than 300 torr. ND indicates not determined.

223TMB photolysis. When 223TMB is photolyzed in the presence of N_2 and O_2 the only significant change from the photolysis of 223TMB in the presence of O_2 is the increase in propane.

The photolysis of 223TMB in the presence of HI shows an increase in methane, propane, and H_2 and a decrease in isobutane, isobutene, and 2,3-dimethyl-1-butene. All other product yields remained constant within experimental error.

The only change noted when CH_3F was added to HI and 223TMB was a decrease in C_2H_6 as compared to the 223TMB-HI photolysis. There appears to be a decrease in methane also but because of the large error limit on the methane this conclusion can not be substantiated.

Isopropyltrimethylsilane (IPTMS). Listed in Table IV are the quantum yields of the products measured in the neat system, in the presence of O_2 , and in the presence of HI for the room-temperature 147-nm photolysis of IPTMS. The observed products for the photolysis of pure IPTMS are, in decreasing order of importance, hydrogen, ethane, methane, propene, propane, a product whose boiling point is approximately 70 °C from retention time data and which is assumed to be 2,3-dimethyl-2-silabutane (isopropyldimethylsilane), ethene, isobutane, trimethylsilane, vinyltrimethylsilane, and tetramethylsilane. The addition of O₂ reduces the yields of all products except for propene, propane, ethene, trimethylsilane, and isopropyldimethylsilane which remain constant within experimental error. The photolysis in the presence of HI results in an increase in methane, propane, trimethylsilane, and isopropyldimethylsilane and a decrease in ethane, isobutane, and tetramethylsilane. All other product yields remained constant. No measurable difference was noted when IPTMS was photolyzed in the presence of greater than 400 torr of N₂ in either the pure IPTMS system or the IPTMS-O₂ system. The yield of trimethylmethoxysilane extrapolated to infinite methanol concentration is 0.10. This is the result of methanol addition to 2-methyl-2-silapropene.

tert-Butyltrimethylsilane (t-BTMS). Boudjouk and Koob^{2a} have reported the relative yields of products based on $i-C_4H_{10}$ for the photolysis of t-BTMS. We now report the quantum yields for both the neat photolysis and the photolysis in the presence of O_2 based on our determinations of the quantum yields of $i-C_4H_{10}$. These results along with the quantum yields as determined in the presence of HI are shown in Table V.

When t-BTMS is photolyzed in the presence of HI, there is a significant increase in the yields of both methane and

TABLE IV: Quantum Yield Results in the Photolysis of IPTMS at 147 nm^{a,d}

product	neat	O ₂ ^b	HIb	
CH4	0.09 ± 0.01	0.06 ± 0.01	0.45 ± 0.09	
C,H,	0.19 ± 0.02	< 0.01	0.01 ± 0.003	
C_3H_6	0.08 ± 0.01	0.09 ± 0.01	0.09 ± 0.02	
$C_{3}H_{8}$	0.06 ± 0.01	0.06 ± 0.01	0.11 ± 0.02	
C_2H_4	0.03 ± 0.01	0.04 ± 0.01	0.03 ± 0.01	
$i - \dot{\mathbf{C}}_{\mathbf{A}} \dot{\mathbf{H}}_{10}$	0.03 ± 0.01	< 0.01	< 0.01	
trimethylsilane	0.03 ± 0.01	0.02 ± 0.01	0.10 ± 0.02	
tetramethylsilane	0.01 ± 0.002	< 0.01	< 0.01	
vinyltrimethylsilane	0.03 ± 0.003	0.04 ± 0.01	0.04 ± 0.01	
unknown ^c	0.05 ± 0.01	< 0.01	0.16 ± 0.04	
H ₂	0.23 ± 0.06	0.30 ± 0.07	0.37 ± 0.09	

^a All uncertainties are at the 90% confidence level. ^b 10% of IPTMS pressure or less. ^c Unknown with a boiling point of about 70 °C according to retention time data. This compound is assumed to be isopropyldimethylsilane. ^d Quantum yield of trimethylmethoxysilane is 0.1 when IPTMS is photolyzed in the presence of methanol and the methanol concentration is extrapolated to infinity.

TABLE V: Quantum Yield Results in the Photolysis of t-BTMS at 147 nm^e

product	neat ^a	O ₂ ^{<i>a</i>, <i>b</i>}	HI ^{b, c}
CH	0.31 ± 0.07	0.22 ± 0.05	0.47 ± 0.06
C,H,	0.23 ± 0.05	0.01 ± 0.001	< 0.01
C,H	0.05 ± 0.01	0.03 ± 0.01	ND
i-Č₄H ₁₀	0.57 ± 0.12	0.36 ± 0.08	0.52 ± 0.07
trimethyl- silane	0.34 ± 0.07	0.17 ± 0.04	0.35 ± 0.05
i-C ₄ H ₈	0.74 ± 0.16	0.37 ± 0.08	0.26 ± 0.06
neo-C ₆ H ₁ ,	0.10 ± 0.02	< 0.01	< 0.01
tetramethyl- silane	0.06 ± 0.01	<0.01	<0.01
H ₂	0.26^{d}	< 0.01	$\sim 1.1 \pm 0.2$

^a Results are those based on the relative yields reported in ref 2a obtained by using the quantum yields of $i \cdot C_4 H_{10}$ reported in ref 5. All uncertainties (90% confidence level) are based on the reported uncertainty of $i \cdot C_4 H_{10}$ only since no uncertainties were reported in ref 2a. ^b 10% of t-BTMS or less. ^c Results as reported in ref 12. ^d Results as reported in ref 5. ^e Quantum yield of trimethylmethoxysilane is 0.30^c or 0.36^d when t-BTMS is photolyzed in the presence of methanol and the methanol concentration is extrapolated to infinity. ND indicates not determined.

hydrogen and a significant decrease in the yields of ethane, isobutene, tetramethylsilane, and neopentane. All other product yields remain constant within experimental error. Tokach⁵ reported no significant change in product yields when *t*-BTMS was photolyzed in the presence of 430 torr of N₂.

The results of methanol addition to 2-methyl-2-silapropene extrapolated to infinite methanol to form trimethylmethoxysilane is reported to be 0.30 by $Doyle^{12}$ and 0.36 by Tokach.⁵

Discussion

2,2-Dimethylbutane (22DMB). A comparison of the photochemistries of linear vs. branched alkanes shows obvious differences. In neoptentane¹ and 2,2,3,3-tetramethylbutane^{2b} (hexamethylethane, HME) the loss of intramolecular H₂ is negligible while in smaller alkanes H₂ elimination is the principal process.^{6c,13} It is seen, for example, in the photolysis of propane^{6c} (with appropriate isotopic labeling) that H₂ loss is from the center carbon to form a carbene which rearranges to form propene.

With the exception of isobutane,^{1,7} the vacuum ultraviolet photochemistry among acyclic alkanes has consisted of primarily either linear^{6,13} or totally branched^{1,2,7} hydrocarbons. Examples of partially branched molecules are limited.^{13c} The photochemistry of 22DMB is such an example.

Ausloos and Lias^{13c} report that in the photolysis of *n*hexane the loss of CH_4 and its cofragment, C_5H_{10} , is much less favored than is the loss of larger fragments, i.e., C_2H_6 and C_4H_8 , C_4H_{10} and C_2H_4 , or C_3H_8 and C_3H_6 . This indicates that eliminations involving primary C–C bonds are not as favorable as those which involve secondary C–C bond breakage. The major product produced via intramolecular reactions in the photolysis of 22DMB is *i*- C_4H_8 . This product is possible through a variety of channels; however, each path can be rationalized to involve secondary C–C bond breakage.

The unsaturated product with the second largest yield in the photolysis of 22DMB is 2-methyl-1butene (2M1B) followed closely (within experimental error they are equal) by 2-methyl-2-butene (2M2B). In both of these cases a primary C–C bond must be broken. Statistically the formation of 2M1B and CH_4 or $CH_3 + H$ is favored 3/1 over 2M2B and CH_4 or $CH_3 + H$. However, it is seen that these two products are formed with equal probability, indicating that the loss of secondary hydrogen is favored over the loss of primary hydrogen.

The loss of methyl radical and an ethyl radical to produce a carbene is substantiated by the production of propene (the rearranged result of the carbene produced in reaction 1). This same type of reaction is invoked in the photochemistry of both neopentane¹ and HME.^{2b}

For small linear alkanes, three-membered transition states are favored;⁶⁻¹³ however, in highly branched alkanes^{1,2,7} four- or five-membered transition states seem to be more common. This generalization also holds for 22DMB. Intramolecular C_2H_6 , 2M1B, and 2M2B are all products of four-membered transition states. Intramolecular isobutane, however, is necessarily a result of a three-membered transition state.

Methane, ethane, propane, neopentane, isobutane, and n-butane all have some radical precursors.

As will be shown in the next section, intramolecular propane shows a pressure dependence in the photolysis of 2,2,3-trimethylbutane. An analogous reaction in the 22DMB photolysis would be a pressure dependence upon the production of intramolecular ethane. There is, however, no measurable effect on any of the products when 450 torr of N_2 is added to the photolysis system.

It is useful to contrast the photochemistry of ethyltrimethylsilane (ETMS)⁴ and its analogous hydrocarbon, 22DMB. In the photochemistry of ETMS it was shown that a variety of radicals were produced including $(CH_3)_3Si$, $\phi = 0.11$; $(CH_3)_3SiCH_2$, $\phi = 0.09$; $(CH_3)_2SiC_2H_5$, $\phi = 0.08$; $(CH_3)_3SiC_2H_4$, $\phi = 0.06$. In contrast 22DMB shows the production of 2-methyl-1-butene and 2-methyl-2-butene as indicated in reactions 2 and 3.

$$22\text{DMB} \rightarrow (\text{CH}_3)_2\text{C} = \text{C}(\text{H})(\text{CH}_3) + [\text{CH}_4 \text{ or } \text{CH}_3 + \text{H}]$$
(2)

 \rightarrow CH₂=C(CH₃)(C₂H₅) + [CH₄ or CH₃ + H] (3)

Similar unsaturated products were not found in the photolysis of ETMS. Either the reactions which produce these corresponding products do not occur in ETMS photolyses or methanol (which is used to titrate 2methyl-2-silapropene) does not effectively trap such Si-C unsaturated species.

The production of propene in the photolysis of 22DMB leads one to expect that dimethylsilylene, $(CH_3)_2Si$; would be produced in the photolysis of ETMS. This carbene analogue has not been trapped without the use of large excesses of trapping agents,¹⁴ however. Thus by analogy

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from 22DMB photolysis one would predict that $(CH_3)_2Si$: is produced but there is no direct evidence for it.

Finally, if one calculates the mass balance from the products listed in the neat photolysis from Table I, a value of $C_{5.84\pm0.18}H_{13.78\pm24}$ is obtained. This calculation assumes that the two unidentified products have a formula of C_5H_{10} . This mass balance is in reasonable agreement with the expected value of C_6H_{14} .

2,2,3-Trimethylbutane (223TMB). The production of propane in the photolysis of 223TMB shows a pressure dependence. This pressure-sensitive propane is intramolecular propane as demonstrated by the increase in propane with the addition of high-pressure N_2 in the O_2 additive photolyses. This process is explained by reaction 4. Supporting evidence for reaction 4 is the decrease in

ethyl radical product (and the apparent decrease in methyl radical production but because of the error limit not an unequivocal decrease) when the 223TMB-HI mixture is photolyzed in high-pressure CH₃F. It is difficult to suggest a mechanism where ethyl radicals are produced from 223TMB photolysis that do not proceed through a "hot propane" intermediate. It is unfortunate that the error limit on the production of propane in the 223TMB-HIhigh-pressure CH₃F photolyses precludes the establishment of an increase in propane; however, the single determination of propane in the 223TMB-HI-N₂ photolysis gives an indication that in fact propane may be increasing with pressure. It should be noted that 223TMB is the only compound of this series, with the exception of neopentane, in which any of the products show a pressure dependence.

Isobutene is the most significant product in the 147-nm photolysis of 223TMB. Its formation is illustrated by reaction 5.

$$223TMB \rightarrow CH_2 = C(CH_3)C(H)(CH_3)_2 + CH_4 \text{ (or } CH_3 + H) \text{ (5)}$$

Because of the complexity of products formed, it is not possible to identify how each of the products in the photolysis of 223TMB are produced. For example, in the secondary reactions involving the formation of $i-C_4H_{10}$, there are at least two reactions that can be postulated for its formation. Reaction 6 and 7 illustrate these paths.

$$CH_3 + i \cdot C_3 H_7 \rightarrow i \cdot C_4 H_{10} \tag{6}$$

$$t - C_4 H_9 + t - C_4 H_9 \rightarrow i - C_4 H_8 + i - C_4 H_{10}$$
 (7)

Reaction 8 shows the formation of 2-methyl-2-butene.

$$223\text{TMB} \rightarrow (\text{CH}_3)_2\text{C} = \text{C}(\text{H})(\text{CH}_3) + \text{CH}_3 + \text{CH}_3 \qquad (8)$$

2-Methyl-2-butene is formed with two methyl radicals as its cofragments and not intramolecular ethane as its cofragment because intramolecular ethane has a yield of less than 0.01.

Since isobutene has such a large yield ($\phi = 0.50$) in the 147-nm photolysis of 223TMB, an investigation of its conversion dependence was performed. Figure 2 shows the conversion dependence for three sets of unsaturated to saturated products. As Tokach and Koob^{2b} reported for 2,2,3,3-tetramethylbutane and as was shown earlier for 2,2-dimethylbutane, there is a conversion dependence on the isobutene/isobutane ratio. No significant conversion dependence is noted for the propene/propane or ethene/ethane ratios. The conversion dependence of the



Figure 2. Conversion dependence of unsaturated/saturated products in the photolysis of 223TMB.

isobutene/isobutane ratio is attributed to H atom attack on isobutene.

If one calculates the mass balance of the products shown in Table II, one obtains a value of $C_{6.74\pm18}H_{15.96\pm29}$. This is in good agreement with the expected value of C_7H_{16} . This calculation assumes that the unknown species in the photolysis of 223TMB has a formula of C_5H_{10} .

Isopropyltrimethylsilane (IPTMS). It was noted in the photolysis of 223TMB that the formation of intramolecular propane was pressure sensitive. In the photolysis of IPTMS intramolecular propane is also formed (reaction 9); however, it does not show this same pressure depen-

$$IPTMS \rightarrow (CH_3)_2 SICH_2 + C_3 H_8 \tag{9}$$

dence. The production of $(CH_3)_2SiCH_2$ (the analogue of i-C₄H₈ in reaction 4) is confirmed by the formation of trimethylmethoxysilane when IPTMS is photolyzed in the presence of methanol^{3a} ($\phi = 0.10$ at infinite methanol concentration).

Another important intramolecular process involves the formation of propene ($\phi = 0.09 \pm 0.01$). See reaction 10.

$$PTMS \rightarrow C_3H_6 + (CH_3)_3SiH$$
(10)

The empirically required cofragment, $(CH_3)_3SiH$, has an intramolecular yield of 0.02 ± 0.01 thus requiring the intramolecular trimethylsilane which is formed to have excess energy so that it undergoes further decomposition. It should be noted that reaction 10 is not unique in the formation of intramolecular C_3H_6 and that several other reaction channels for its formation could be postulated.

The photolysis of IPTMS in the presence of HI and in the presence of O_2 gives evidence for the formation of four radical species: CH₃, C₃H₇, (CH₃)₃Si, and (CH₃)₂SiC-(H)(CH₃)₂. The error limit on H₂ formation precludes a judgement on the importance of H atom formation. Radicals C₃H₇ and (CH₃)₃Si are directly associated through reaction 11 and, within experimental error, the yields of

$$IPTMS \rightarrow C_3H_7 + (CH_3)_3Si$$
(11)

these two radicals are equal. The formation of CH_3 and $(CH_3)_2SiC(H)(CH_3)_2$ are also coupled as shown by reaction 12; however, there are necessarily other channels available

$$IPTMS \rightarrow CH_3 + (CH_3)_2 SiC(H)(CH_3)_2 \qquad (12)$$

for the formation of CH_3 in addition to reaction 12 since the methyl radical yield is substantially larger than the $(CH_3)_2SiC(H)(CH_3)_2$ yield. It is interesting to note that reaction 12 is important, but reaction 13 is not since

$$IPTMS \rightarrow (CH_3)_3 SiC(H)(CH_3) + CH_3$$
(13)

Photolysis of Alkanes and Alkylsilane Analogues

ethyltrimethylsilane would be formed by the $(CH_3)_3SiC-(H)(CH_3)$ radical when it is produced in presence of HI. The yield of ethyltrimethylsilane is below detection limits ($\phi < 0.01$) when IPTMS is photolyzed in the presence of HI.

If one uses the data from Table IV, one can calculate a mass balance for the 147-nm photolysis of IPTMS. One finds that from this mass balance calculation more than half of the expected products are not observed. One can only speculate on where this shortage arises; however, it seems reasonable to compare the IPTMS photolysis to its hydrocarbon analogue, 223TMB, to see what insights may be gained.

The first obvious difference between the photolysis of 223TMB and IPTMS is that the 223TMB system results in a quantum yield of approximately 0.7 more unsaturated products than are produced in the IPTMS system. In the 223TMB system five unsaturated species are formed: ethene ($\phi = 0.05$), propene ($\phi = 0.28$), isobutene ($\phi = 0.50$), 2-methyl-2-butene ($\phi = 0.12$), and 2,3-dimethyl-1-butene ($\phi = 0.17$). There are four unsaturated products in the IPTMS system: ethene ($\phi = 0.03$), propene ($\phi = 0.08$), vinyltrimethylsilane ($\phi = 0.03$), and 2-methyl-2-silapropene ($\phi = 0.10$ at infinite methanol concentration). It is reasonable that the yield of propene in the 223TMB photolysis is larger than the propene yield in the IPTMS photolysis since there are likely more reaction channels available to produce propene in 223TMB.

Methanol has been used to trap 2-methyl-2-silapropene (dimethylsilaethylene); however, even when the methanol concentration is extrapolated to infinite concentration, it has been shown to be at a maximum 85% efficient.¹⁰ It is not known at what efficiency methanol would titrate other unsaturated products which may be formed in the photolysis of IPTMS. Even if methanol does titrate these unsaturated products, the resulting additive products would likely have boiling points similar to that of IPTMS such that their gas chromatographic retention times would not allow for their detection.

Vinyltrimethylsilane is formed by reaction 14. The

$$IPTMS \rightarrow (CH_3)_3 SiCH = CH_2 + CH_4 \text{ (or } CH_3 + H)$$
(14)

formation of vinyltrimethylsilane probably proceeds through a four-membered transition state with the loss of a primary hydrogen. A three-membered transition state and subsequent rearrangement runs counter to the accumulated evidence suggesting four- and five-membered transition states dominate the photochemistry of branched molecules.

tert-Butylmethylsilane (t-BTMS). Methane, isobutane, propene, trimethylsilane, and isobutene all remain as significant products in the 147-nm photolysis of t-BTMS in the presence of O_2 . These five products are assumed to be intramolecular in nature and are shown in reaction 15-18.

$$t\text{-BTMS} \rightarrow (CH_3)_3CH + (CH_3)_2SiCH$$
 (15)

$$\rightarrow (CH_3)_2 C = CH_2 + (CH_3)_3 SiH$$
(16)

$$\rightarrow$$
 CH₄ + products (17)

$$\rightarrow C_3H_6 + CH_3 + (CH_3)_3Si$$
(18)

Since the isobutene yield is larger than the trimethylsilane yield, it is postulated that either reaction 19 or 20, or both are also occurring. The formation of $(CH_3)_2Si$ is speculative since it is not seen as a product nor is it trapped in any of the additive studies carried out, but is included as an analogue to propene formation found in the photo-

$$r - BTMS \longrightarrow (CH_3)_2 C = CH_2 + (CH_3)_3 SiH^*$$
(19)

-
$$(CH_3)_2C = CH_2 + (CH_3)_3Si + H$$
 (20)

lysis of 2,2,3,3-tetramethylbutane.^{2b}

From the results of the HI and O_2 additive experiments four atomic and radical species are postulated to be formed. They are CH₃, (CH₃)₃C, (CH₃)₃Si, and H. (CH₃)₃C and (CH₃)₃Si are directly coupled through reaction 21.

$$t\text{-BTMS} \rightarrow (CH_3)_3Si + (CH_3)_3C$$
 (21)

Within experimental error, the yields of these two radicals are equal. The formation of CH_3 and H is a result of numerous possible reactions.

It is noted, however, that the loss of a single methyl radical is apparently not allowed since no product corresponding to this loss is seen in the HI additive experiments. Either *tert*-butyldimethylsilane or isopropyltrimethylsilane would have been formed by H abstraction from HI by *tert*-butyldimethylsilyl radicals and isopropyltrimethylsilyl radicals, respectively.

Mercury-Sensitized Photolysis of i-C₄H₁₀, (CH₃)₃SiH, and Mixtures of $i-C_4H_{10}$ and $(CH_3)_3SiH$. Because of the many complicating factors involved in the photolysis of t-BTMS, it is not possible to draw conclusions concerning the importance of disproportionation to combination ratios for $(CH_3)_3C$ with $(CH_3)_3C$, $(CH_3)_3Si$ with $(CH_3)_3Si$, and $(CH_3)_3C$ with $(CH_3)_3Si$. Therefore, a study was carried out with 254-nm light (Rayonet photochemical reactor with a single low-pressure mercury lamp and a Pyrex sample cell fitted with a quartz window and a neutral density filter (OD = 3.0)) to photolyze isobutane, trimethylsilane, and mixtures of isobutane and trimethylsilane. To gain additional insight, we examined a model cross reaction, involving the exchange of C==C and Si-C for C==Si and C-C bonds using ab initio calculations. These results are in agreement with our experimental findings.

The merucry photosensitization of mixtures of isobutane and trimethylsilane (TriMS) yields four distinguishable products: $i-C_4H_8$, HME, hexamethyldisilane (HMDS), and t-BTMS. All products were suppressed by addition of 3% O₂. An additional product, trimethylmethoxysilane (TMMS), is observed when small amounts (15% of TriMS) of methanol are added to the photolysis mixture. The yield of TMMS is dependent on methanol concentration, Figure 3.

At longer photolysis times, $t \ge 5$ min, a conversion dependence was observed for i-C₄H₈ and HME in the photolysis of i-C₄H₁₀. In order to account for this dependence, we photolyzed pure samples of i-C₄H₁₀ and monitored the product ratio of i-C₄H₈/HME as a function of photolysis time. As can be seen in Figure 4, at photolysis times ≤ 5 min, the i-C₄H₈/HME ratio levels off to a value of 2.1. This value represents the disproportionation/combination (D/C) ratio for two *tert*-butyl radicals.

Relative yields of products for various mixtures of *i*- C_4H_{10} and TriMS are reported in Table VI. The yield of TMMS represents that at a methanol concentration equal to $P_{MeOH} = 0.15P_{TriMS}$. Photolysis time in all cases was 5 min. Uncertainties quoted are all at the 90% confidence interval.

To serve as a check on our experimental technique and to select a value to be used in the mixture experiment from the range of D/C reported for *tert*-butyl, we have determined D/C for $(CH_3)_3C + (CH_3)_3C$ from the Hg*-sensitized photolysis of *i*-C₄H₁₀. Under conditions of low conversion and short photolysis times, a plot of isobutene/hexa-



Figure 3. The product ratio (circles for trimethylmethoxysliane/hexamethyldisilane and squares for trimethylmethoxysliane/*tert*-butyltrimethylsliane) plotted as a function of reciprocal methanol pressure for the Hg*-sensitized photolysis of $(CH_3)_3SIH + i-C_4H_{10} + methanol$.

TABLE VI: Relative Product Yields for Hg*-Sensitized Photolysis of $Me_3SiH + i-C_4H_{10}$ Mixtures

		second provides that is an an an and			
P _{Me-SiH} , torr	20	40	40	60	
$P_{i-C_{i}H_{in}}$, torr	100	80	80	60	
HMDS	100	100	100	100	
HME	114	100	107	35	
t-BTMS	104	66	70	59	
i-C₄H ₈	292	243	263	112	
Me ₃ SiOMe ^a	219	159	164	128	
	1.84	1.98	1.94	1.69	
	0.51	0.50	0.55	0.65	
$[D/C]_1$ average = 1.86 ± 0.15 at t	he 90%	confi	dence	level	
$[D/C]_2$ average = 0.55 ± 0.08 at the 90% confidence level					
$[D/C]_1 = [(CH_3)_2SiCH_2/t \cdot BTMS]$ corrected by eq 30					
$[D/C]_{*} = [i-C_{*}H_{*}/t-BTMS]$ corrected by eq 31					

^a With 15% methanol as an additive.

methylethane vs. photolysis time could be made to yield a constant value. Then D/C is $k_{22}/k_{23} = 2.1 \pm 0.2$.

$$2t \cdot C_4 H_9 \rightarrow (CH_3)_2 C = CH_2 + (CH_3)_3 CH \qquad (22)$$

$$\rightarrow (CH_3)_3 CC (CH_3)_3 \tag{23}$$

This value is in good agreement with the values of 2.32 ± 0.05 and 2.3 ± 0.3 reported by Terry and Futrell¹⁵ and James and Suart,¹⁶ respectively, obtained by the photolysis of $(t-C_4H_9)_2N_2$, and this value of 2.1 will be used in the remaining discussion as is necessary.

Reported D/C's for $(CH_3)_3Si$ determined by various techniques differ by nearly an order of magnitude.¹⁷ Our value of 0.31 for the gas phase is the highest of those reported.¹⁷ It depends critically upon the assumptions that dimethylsilaethylene can be trapped by alcohols and that



Figure 4. The product ratio (isobutene/hexamethyldisilane) plotted as a function of photolysis time (min) for the Hg*-sensitized photolysis of $(CH_3)_3SIH + i-C_4H_{10}$.

TIME (MIN)

trimethylmethoxysilane arises only from a reaction such as 24. A solution-phase determination using the same

$$CD_{3}OD + (CH_{3})_{2}Si = CH_{2} \rightarrow (CH_{3})_{2}(CH_{2}D)SiOCD_{3}$$
(24)

assumptions¹⁷ yields a value of a comparable order of magnitude, 0.19 ± 0.05 , while a gas-phase determination^{17c} of $(CH_3)_3SiH/(CH_3)_6Si_2$ gives 0.05 and does not depend on this titration technique. Cornett et al.^{17b} specifically examined other potential contributions to the trapped product in their system and found any contributions from such sources to be small, if occurring at all. Demonstration that trimethylmethoxysilane arises from other reactions would necessitate lowering the value of D/C by the amount contributed by the yet unidentified reaction(s). The average value obtained for [TMMS]/[HMDS] is 0.28 \pm 0.05. This is set equal to k_{25}/k_{26} for further use in the discussion below.

$$2(CH_3)_3Si \rightarrow (CH_3)_2SiCH_2 + (CH_3)_3SiH \qquad (25)$$

$$\rightarrow (CH_3)_6 Si_2 \tag{26}$$

For the cross reaction of $(CH_3)_3Si$ and $(CH_3)_3C$, H transfer from either radical is possible in addition to combination, reactions 27–29.

$$(CH_3)_3Si + (CH_3)_3C \rightarrow (CH_3)_3SiC(CH_3)_3 \qquad (27)$$

$$\rightarrow (CH_3)_2 SiCH_2 + (CH_3)_3 CH$$
(28)

$$\rightarrow (CH_3)_3 SiH + (CH_3)_2 C = CH_2$$
(29)

Reaction 27 is measured by the yield of *t*-BTMS, but products from both reactions 28 and 29 are similar to those produced in reactions 22 and 25 and must be adjusted before relative rate constants can be calculated. The ratio of $(CH_3)_2SiCH_2$ from reaction 28 to *t*-BTMS is give by eq 30 and is $k_{28}/k_{27} = 1.86 \pm 0.15$.

$$\frac{[(CH_3)_2SiCH_2](28)}{[t-BTMS]} = \frac{[TMS]}{[t-BTMS]} - \frac{k_{25}[HMDS]}{k_{26}[t-BTMS]}$$
(30)

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TABLE VII: Comparison of Unsaturated to Expected Saturated Cofragments for Selected Alkanes and Alkylsilanes Photolyzed at 147 nm

parent	unsaturated product	expected saturated product	$\phi_{\rm sat}/\phi_{\rm unsat}$	ref
C,D,	C,D,	CD4	0.07/0.18 = 0.39	6c
neo-C.H.,	i-Č,H,	CH	0.23/0.70 = 0.33	1
22DMB	C,H,	$i - C_4 H_{10}$	<0.01/0.08 < 0.10	this work
	i-Ĉ₄H ₈	C ₂ H ₆	0.06/0.44 = 0.14	
	2-methyl-1-butene	CH₄	0.09/0.15 = 0.60	
223TMB	C ₃ H ₆	$i-C_{4}H_{10}$	0.03/0.20 = 0.15	this work
	i-Č₄H ₈	C,Ĥ,	0.06/0.35 = 0.17	
	2,3-dimethyl-1-butene	CH	0.05/0.10 = 0.50	
HME	i-C ₄ H ₈	$i-C_{A}H_{10}$	0.26/0.75 = 0.35	2b
HMDS	(CH _a) _s SiCH _a	(CH,),SiH	0.26/0.69 = 0.38	18
$TetraMS^{a}$	(CH,), SiCH,	ĊH,	0.32/0.50 = 0.64	3
ETMS	C.H.	(CH ₃) ₃ SiH	0.03/0.21 = 0.14	4
	(CH,),SiCH,	Ċ,H,	0.10/0.17 = 0.59	
IPTMS	Ċ.H.	(CH,),SiH	0.02/0.09 = 0.22	this work
	(CH,),SiCH,	Ċ,H.	0.06/0.10 = 0.60	
t-BTMS	i-C ₄ H ₂	(ČH,), SiH	0.09/0.30 = 0.30	this work
	$(C\tilde{H}_3)_2^{\circ}SiCH_2$	i-C4H10	0.17/0.30 = 0.57	

^a TetraMS = tetramethylsilane.

Similarly, the ratio of $i-C_4H_8$ from reaction 29 to t-BTMS is given by eq 31 or $k_{29}/k_{27} = 0.55 \pm 0.08$.

$$\frac{[i-C_4H_8](29)}{[t-BTMS]} = \frac{[i-C_4H_8]}{[t-BTMS]} - \frac{k_{22}[HME]}{k_{23}[t-BTMS]}$$
(31)

Qualitative conclusions which may be postulated are as follows: (1) disproportionation is competitive with combination reactions between $(CH_3)_3Si$ and $(CH_3)_3C$; (2) production of $(CH_3)_2SiCH_2 + i-C_4H_{10}$ is competitive with $(CH_3)_2C=CH_2 + (CH_3)_3SiH$ and may predominate.

The latter conclusion clearly indicates that $[(CH_3)_2SiCH_2 + (CH_3)_3CH]$ is not unstable with respect to $(CH_3)_3Si$ and $(CH_3)_3C$. This is not surprising in light of numerous recent indications that the heat of formation of $(CH_3)_2Si=CH_2$ is not inordinately high. What is more surprising, perhaps, is that the route to C=Si bonding is clearly competitive with that to C=C bonding.

Disproportionation of trimethylsilyl with *tert*-butyl is the second example of cross reactions between hydrocarbon and permethylated silyl radicals. The first reported observation was in the 147-nm photolysis of hexamethyldisilane where D/C $[CH_3 + (CH_3)_3Si] = 0.22.^{18}$ Observations in that somewhat unconventional system are clouded by the possibilities of nonthermal radical reactions. The appearance of cross disproportionation in a more common system perhaps is more convincing. Further, no strong thermodynamic arguments can be made excluding disproportionation nor excluding $(CH_3)_2SiCH$ as a reasonable product in a disproportionation reaction.

Summary

In summary then, the following conclusions can be drawn:

1. In the photolysis of 22DMB two unsaturated products are formed (2-methyl-1-butene and 2-methyl-2-butene) for which corresponding unsaturated compounds were not found in the photolysis of ethyltrimethylsilane. In addition, several radical species were shown to be formed in the photolysis of ethyltrimethylsilane that were not found in the photolysis of 22DMB.

2. There exists a pressure dependence on the production of intramolecular propane in the photolysis of 223TMB which gives rise to "hot" propane.

3. The photolysis of 223TMB results in the formation of more unsaturated products than the corresponding



Figure 5. The ratio of 2-methyl-2-silapropene to trimethylmethoxysilane as function of reciprocal methanol concentration for various alkylsilanes photolyzed at 147 nm.

IPTMS photolysis. Several silicon-containing unsaturated products may be postulated to be formed in the photolysis of IPTMS but because of the lack of suitable traps there is not direct evidence for their production. The single exception to this is the formation of trimethylmethoxysilane which is formed by dimethylsilaethylene addition to methanol.

4. As shown in previous alkylsilanes^{3,4,14a,14j,18} the importance of H_2 elimination is surpressed and the formation of radical products enhanced as branching becomes more important. It is noted further that four- and five-membered transition states are favored in the branched compounds while three-membered transition states are favored in linear molecules.

5. Silyl radicals behave in a similar fashion to analogous alkyl radicals. The values of D/C for $(CH_3)_3C + (CH_3)_3C$ and $(CH_3)_3Si + (CH_3)_3Si$ are 2.1 ± 0.2 and 0.28 ± 0.05, respectively, and 1.86 ± 0.15 for $(CH_3)_3Si + (CH_3)_3C$ to form 2-methyl-2-silapropene and 0.55 ± 0.08 to form *i*- C_4H_8 . This indicates that disproportionation of trimethylsilyl with *tert*-butyl radicals is competitive with combination and that the formation of $(CH_3)_2SiCH_2$ is competitive with the formation of $(CH_3)_2C=CH_2$.

6. A trend exists in which the empirically required saturated cofragment for unsaturated products is always smaller than would be expected from the observed yields of unsaturated (see Table VII). This presumably indicates that the loss of additional fragments as a method for dissipating excess energy is favored by saturated molecules over that of unsaturated molecules. It appears that the ratio of saturated to unsaturated increases when the size of the unsaturated species increases. This indicates that the unsaturated species, as it increases in size, takes with it an increasing share of the excess energy (as the unsaturated species increases in size it gains in number of vibrational modes available to dissipate the energy), allowing the saturated cofragment to be more readily stabilized and less likely to further decompose. This relationship is especially prominent in the photolysis of 2,2-dimethylbutane, 223TMB, ethyltrimethylsilane, and IPTMS cases.

7. Figure 5 shows, for a variety of alkylsilanes, the relationship of the ratio of $\phi((CH_3)_2SiCH_2)/\phi$ -((CH₃)₃SiOCH₃) vs. reciprocal methanol concentration as derived in ref 4. It is postulated that an increase in the slope of the lines in Figure 5 is an indication that radicals present in the system are competing more effectively for the $(CH_3)_2SiCH_2$; therefore, more methanol is needed to titrate the $(CH_3)_2SiCH_2$. In this plot it is assumed that only methyl radicals compete with methanol for $(CH_3)_2$ -SiCH₂.

The regularity of behavior throughout these series of hydrocarbons and alkylsilanes suggests that reasonable models eventually may be constructed to rationalize and predict the course of reactions in saturated systems such as these.

Reaction Mechanism of O⁻ + H₂O \rightarrow OH⁻ + OH at Low Incident Ion Energies

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Ion-beam collision-chamber experiments at low baricentric energies (0.17-3.5 eV) are discussed. The occurrence of ${}^{16}O^- + H_2{}^{18}O \rightarrow {}^{18}O^- + H_2{}^{16}O$ and the branching ratios between ${}^{18}O^-$, ${}^{16}OH^-$, and ${}^{18}OH^-$ as a function of energy speak in favor of the formation of an intermediate long-lived collision complex, $[H_2O_2^-]^*$ below $\sim 1 \text{ eV}$. The lifetime of the intermediate is estimated to be $\tau_d = 3.6 \times 10^{-12}$ s at 0.17 eV, on the basis of RRKM calculations. A Brauman reaction-coordinate diagram, with a double minimum, is proposed.

Introduction

There has been considerable interest recently in ionmolecule reactions which proceed via long-lived collision complexes.¹ The prerequisites for long-lived collision complex formation are the following: (a) the occurrence of a fairly deep potential well along the reaction coordinate, (b) a considerable complexity of the intermediate, i.e., a minimum number of degrees of freedom is required, and (c) relatively low center of mass kinetic energies.

The title reaction has been the subject of a fairly large number of studies.²⁻⁷ It has aroused renewed interest recently, and a crossed-beam study has been carried out on the deuterated analogue, over the relative energy range 3.2-10.5 eV.⁸ Within this energy range, the reaction was found to be direct and well approximated by the spectator-stripping model.⁸

Positive and negative ion-molecule reactions seem to behave differently, as has been first pointed out for the H_3^+ and H_3^- systems.⁹ It is of interest to compare the behavior of the title reaction with those of its neutral and positive-ion analogues. The neutral exothermic reaction

$${}^{16}O({}^{1}D) + H_{\circ}{}^{18}O \rightarrow {}^{16}OH + {}^{18}OH$$
(1)

proceeds via a direct mechanism.¹⁰ The positive endothermic ion-molecule reactions

$$O_2^+(^2\Pi_g) + H_2 \rightarrow HO_2^+ + H \tag{2a}$$

$$\rightarrow OH^+ + OH$$
 (2b)

$$H_2 O^+ + O (2c)$$

take place via a persistent $H_2O_2^+$ collision complex at low relative energies.¹¹ The ion-beam collision-chamber studies of the title reaction⁵⁻⁷ were carried out at considerably lower ion energies than those of the crossed-beam study.⁸ We will discuss these data and some additional ones to be presented here, which indicate that a long-lived collision complex is formed in this negative ion-molecule reaction at low baricentric energies.

Experimental Section

An in-line tandem mass spectrometer, previously described,¹² was utilized for these studies. Briefly, it is a beam collision-chamber apparatus which provides mass analysis of the product ions. The collection stage is fixed at $0^{\circ}(LAB)$ scattering angle. The projectile O^{-} ion is formed in the electron impact ion source of the first-stage mass spectrometer from N₂O. A mass- and energy-resolved beam is produced. This beam is decelerated in a retarding lens and impacted upon the target gas in the field-free collision chamber. The energy spread of the projectile ion beam entering the collision cell is $\pm 0.3 \text{ eV}$ (LAB) full width at half-maximum. Product ions are mass analyzed in the

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