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

Daryl J. Doyle
S. K. Tokach
Mark S. Gordon
Robert D. Koob

Available at: https://works.bepress.com/mark_gordon/32/
Trimeethylbutane, Trimeethyl-2-silabutane, and contrast the influences governing the photodissociation dialogue of recently studied 2,2-dimethyl-2-silabutane. 4 While tertiary hydrogens. Isopropyltrimethylsilane and 2,2,3-trimethylbutane are examples of alkylsilane and alkane trimethylsilane), and 2,2,3,3-tetramethyl-2-silabutane on the role of tertiary hydrogens, along with the results from tert-butyltrimethylsilane are compared to previously reported alkanes and alkylsilanes.

The gas-phase photolyses of 2,2-dimethylbutane, 2,2,3-trimethylbutane, 2,2,3,3-tetramethyl-2-silabutane (isopropyltrimethylsilane), and 2,2,3,3-tetramethyl-2-silabutane (tert-butyltrimethylsilane) complete two sequences of alkylsilanes and alkane trimethylsilane, and mixtures of i-C₄H₁₀ and trimethylsilane are reported which give disproportionation to combination (D/C) ratios of 2.1 ± 0.2 and 0.28 ± 0.05 for (CH₃)₂C + (CH₃)₂Si + (CH₃)₃Si, respectively, and D/C ratios of 1.86 ± 0.15 and 0.55 ± 0.08 for (CH₃)₂C + (CH₃)₃Si to form 2-methyl-2-silapropene and i-C₄H₈, 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, 2,2,3-trimethylbutane, 2,2,3,3-tetramethyl-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, 2,2-dimethylbutane, 2,2,3-trimethylbutane, and 2,2,3,3-tetramethylbutane⁵ for the alkane series and tetramethylsilane, 2,2-dimethyl-2-silabutane (ethyltrimethylsilane), 2,2,3-trimethyl-2-silabutane, and 2,2,3,3-tetramethyl-2-silabutane⁵ ⁶ ⁷ ⁸ for the alkylsilane series).

2,2-Dimethylbutylene (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 molecule⁹ 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,⁷ there are few examples of photolyses of compounds which have tertiary hydrogens. Isopropyltrimethylsilane and 2,2,3-trimethylbutane 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), tert-butyltrimethylsilane (t-BTMS), prepared by standard methods, and 2,2,3-trimethylbutylene (223TMB), purchased from...
TABLE I: Quantum Yield Results for the 147-nm Photolysis of 22DMBa,b

<table>
<thead>
<tr>
<th>product</th>
<th>neat</th>
<th>O2c</th>
<th>HIc</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>0.22 ± 0.05</td>
<td>0.07 ± 0.01</td>
<td>0.27 ± 0.06</td>
</tr>
<tr>
<td>CH4</td>
<td>0.16 ± 0.01</td>
<td>0.09 ± 0.01</td>
<td>0.69 ± 0.06</td>
</tr>
<tr>
<td>C2H4</td>
<td>0.09 ± 0.01</td>
<td>0.08 ± 0.01</td>
<td>0.68 ± 0.01</td>
</tr>
<tr>
<td>C2H6</td>
<td>0.39 ± 0.03</td>
<td>0.06 ± 0.01</td>
<td>0.25 ± 0.04</td>
</tr>
<tr>
<td>C3H8</td>
<td>0.15 ± 0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>C3H10</td>
<td>0.08 ± 0.01</td>
<td>0.09 ± 0.01</td>
<td>0.08 ± 0.01</td>
</tr>
<tr>
<td>n-C5H11</td>
<td>0.01 ± 0.004</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>i-C5H11</td>
<td>0.45 ± 0.06</td>
<td>0.44 ± 0.06</td>
<td>0.49 ± 0.12</td>
</tr>
<tr>
<td>i-C6H12</td>
<td>0.06 ± 0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>neo-C7H16</td>
<td>0.06 ± 0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>unknown A</td>
<td>&lt;0.03</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>unknown B</td>
<td>&lt;0.02</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>2-methyl</td>
<td>0.15 ± 0.02</td>
<td>0.15 ± 0.02</td>
<td>ND</td>
</tr>
<tr>
<td>1-butene</td>
<td>0.13 ± 0.02</td>
<td>0.13 ± 0.02</td>
<td>ND</td>
</tr>
<tr>
<td>2-butene</td>
<td>0.13 ± 0.02</td>
<td>0.13 ± 0.02</td>
<td>ND</td>
</tr>
</tbody>
</table>

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), CD3OD (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,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% squalene column at room temperature for the actinometer determinations and for the determination of low-boiling products through propane. Twenty-five 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/poreasil 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 H2 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 O2, 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-

an increase in methane, propane, and H₂ and a decrease in other product yields remained constant within experimental error. This conclusion cannot be substantiated. The only change noted when CH₃F was added to HI and 223TMB was a decrease in C₂H₆ 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.

### Table II: Quantum Yield Results in the Photolysis of 223TMB at 147 nm

<table>
<thead>
<tr>
<th>Product</th>
<th>Neat</th>
<th>CH₃F</th>
<th>HI + N₂</th>
<th>HI + CH₃F</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>0.15 ± 0.01</td>
<td>0.10 ± 0.01</td>
<td>0.05 ± 0.01</td>
<td>0.06 ± 0.01</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.20 ± 0.01</td>
<td>0.14 ± 0.02</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>C₂H₅</td>
<td>0.05 ± 0.004</td>
<td>0.03 ± 0.01</td>
<td>0.04 ± 0.01</td>
<td>0.02 ± 0.003</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>0.22 ± 0.01</td>
<td>0.24 ± 0.03</td>
<td>0.06 ± 0.01</td>
<td>0.14 ± 0.02</td>
</tr>
<tr>
<td>i-C₄H₁₀</td>
<td>0.18 ± 0.02</td>
<td>0.18 ± 0.03</td>
<td>0.03 ± 0.01</td>
<td>0.04 ± 0.01</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>0.28 ± 0.02</td>
<td>0.24 ± 0.03</td>
<td>0.20 ± 0.02</td>
<td>0.18 ± 0.02</td>
</tr>
<tr>
<td>neo-C₃H₇</td>
<td>0.03 ± 0.004</td>
<td>0.03 ± 0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>unidentified</td>
<td>0.02 ± 0.004</td>
<td>0.02 ± 0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>i-C₃H₆</td>
<td>0.50 ± 0.06</td>
<td>0.45 ± 0.07</td>
<td>0.35 ± 0.06</td>
<td>0.39 ± 0.07</td>
</tr>
<tr>
<td>H₂</td>
<td>0.44 ± 0.10</td>
<td>ND</td>
<td>0.31 ± 0.06</td>
<td>ND</td>
</tr>
<tr>
<td>2-methyl-2-butene</td>
<td>0.12 ± 0.03</td>
<td>ND</td>
<td>0.08 ± 0.02</td>
<td>ND</td>
</tr>
<tr>
<td>2,3-dimethyl-1-butene</td>
<td>0.17 ± 0.04</td>
<td>ND</td>
<td>0.10 ± 0.02</td>
<td>ND</td>
</tr>
</tbody>
</table>

*All uncertainties are at the 90% confidence level. b All N₂ 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.

### Table III: Quantum Yield Results in the Photolysis of 223TMB + HI at 147 nm

<table>
<thead>
<tr>
<th>Product</th>
<th>HI</th>
<th>HI + N₂</th>
<th>HI + CH₃F</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>0.63 ± 0.04</td>
<td>0.53 ± 0.10</td>
<td>0.63 ± 0.04</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.18 ± 0.01</td>
<td>0.14 ± 0.09</td>
<td>0.18 ± 0.01</td>
</tr>
<tr>
<td>C₂H₅</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>0.45 ± 0.08</td>
<td>0.52 ± 0.12</td>
<td>0.45 ± 0.08</td>
</tr>
<tr>
<td>i-C₄H₁₀</td>
<td>0.14 ± 0.01</td>
<td>0.17 ± 0.03</td>
<td>0.14 ± 0.01</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>0.24 ± 0.02</td>
<td>0.24 ± 0.02</td>
<td>0.24 ± 0.02</td>
</tr>
<tr>
<td>neo-C₃H₇</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>ND</td>
</tr>
<tr>
<td>unidentified</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>ND</td>
</tr>
<tr>
<td>i-C₃H₆</td>
<td>0.35 ± 0.07</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>H₂</td>
<td>0.63 ± 0.11</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>2-methyl-2-butene</td>
<td>0.07 ± 0.03</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>2,3-dimethyl-1-butene</td>
<td>0.08 ± 0.02</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

*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 N₂ and O₂ the only significant change from the photolysis of 223TMB in the presence of O₂ is the increase in propane.

The photolysis of 223TMB in the presence of HI shows an increase in methane, propane, and H₂ 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 CH₃F was added to HI and 223TMB was a decrease in C₂H₆ 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.

### Table IV: Quantum Yield Results in the Photolysis of IPTMS at 147 nm

<table>
<thead>
<tr>
<th>Product</th>
<th>Neat</th>
<th>O₂</th>
<th>HI</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>0.09 ± 0.01</td>
<td>0.06 ± 0.01</td>
<td>0.45 ± 0.09</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.19 ± 0.02</td>
<td>&lt;0.01</td>
<td>0.01 ± 0.003</td>
</tr>
<tr>
<td>C₂H₅</td>
<td>0.08 ± 0.01</td>
<td>0.09 ± 0.01</td>
<td>0.09 ± 0.02</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>0.06 ± 0.01</td>
<td>0.06 ± 0.01</td>
<td>0.11 ± 0.02</td>
</tr>
<tr>
<td>i-C₄H₁₀</td>
<td>0.03 ± 0.01</td>
<td>0.04 ± 0.01</td>
<td>0.03 ± 0.01</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>0.03 ± 0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>trimethylsilane</td>
<td>0.03 ± 0.01</td>
<td>0.02 ± 0.01</td>
<td>0.10 ± 0.02</td>
</tr>
<tr>
<td>tetramethylsilane</td>
<td>0.01 ± 0.002</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>vinyltrimethylsilane</td>
<td>0.03 ± 0.003</td>
<td>0.04 ± 0.01</td>
<td>0.04 ± 0.01</td>
</tr>
<tr>
<td>unknownc</td>
<td>0.05 ± 0.01</td>
<td>&lt;0.01</td>
<td>0.16 ± 0.04</td>
</tr>
<tr>
<td>H₂</td>
<td>0.17 ± 0.06</td>
<td>0.30 ± 0.07</td>
<td>0.37 ± 0.09</td>
</tr>
</tbody>
</table>

*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 isopropylidimethylsilane. 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.

Isopropyltrimethylsilane (IPTMS). Listed in Table IV are the quantum yields of the products measured in the neat system, in the presence of O₂, 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, propane, and i-propyldimethylsilane. 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.

t-Butyltrimethylsilane (t-BTMS). Boudjouk and Koobb have reported the relative yields of products based on i-C₄H₁₀ for the photolysis of t-BTMS. We now report the quantum yields for both the neat photolysis and the photolysis in the presence of O₂ based on our determinations of the quantum yields of i-C₄H₁₀. 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 V: Quantum Yield Results in the Photolysis of t-BTMS at 147 nm  

<table>
<thead>
<tr>
<th>Product</th>
<th>Neat a</th>
<th>O₂ b,c</th>
<th>HI d,e</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>0.31 ± 0.07</td>
<td>0.22 ± 0.05</td>
<td>0.47 ± 0.06</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.23 ± 0.05</td>
<td>0.01 ± 0.001</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>i-C₃H₈</td>
<td>0.05 ± 0.01</td>
<td>0.03 ± 0.01</td>
<td>ND</td>
</tr>
<tr>
<td>i-C₄H₁₀</td>
<td>0.57 ± 0.12</td>
<td>0.36 ± 0.08</td>
<td>0.92 ± 0.07</td>
</tr>
<tr>
<td>Trimethylsilane</td>
<td>0.34 ± 0.07</td>
<td>0.17 ± 0.04</td>
<td>0.85 ± 0.05</td>
</tr>
<tr>
<td>i-C₅H₁₂</td>
<td>0.74 ± 0.16</td>
<td>0.37 ± 0.08</td>
<td>0.26 ± 0.06</td>
</tr>
<tr>
<td>Tetramethylsilane</td>
<td>0.10 ± 0.02</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Tetramethylsilane</td>
<td>0.06 ± 0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>H₂</td>
<td>0.26d</td>
<td>&lt;0.01</td>
<td>~1.1 ± 0.2</td>
</tr>
</tbody>
</table>

a Results are those based on the relative yields reported in ref 2a obtained by using the quantum yields of i-C₄H₁₀ reported in ref 5. All uncertainties (90% confidence level) are based on the reported uncertainty of i-C₄H₁₀ 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 1.  
e Quantum yield of trimethylmethoxysilane is 0.30c or 0.36d when t-BTMS is photolyzed in the presence of methanol and the methanol concentration is extrapolated to infinity. ND indicates not determined.

Discussion

2,2-Dimethylbutane (22DMB). A comparison of the photochemical properties of linear vs. branched alkanes shows obvious differences. In neopentane and 2,2,3,3-tetramethylbutane (hexamethylethane, HME) the loss of intramolecular H₂ is negligible while in smaller alkanes H₂ elimination is the principal process. It is seen, for example, in the photolysis of propane (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, the vacuum-ultraviolet photochemistry among acyclic alkanes has consisted of primarily either linear or totally branched hydrocarbons. Examples of partially branched molecules are limited. The photochemistry of 22DMB is such an example.

Ausloos and Lias report that in the photolysis of n-hexane the loss of CH₄ and its cofragment, C₆H₁₀, is much less favored than the loss of larger fragments, i.e., C₄H₈ and C₅H₁₀, C₆H₁₀ and C₇H₁₄, or C₈H₁₄ and C₉H₁₈. This indicates that eliminations involving primary C–C bonds are not as unfavorable as those which involve secondary C–C bond breakage. The major product produced via intramolecular reactions in the photolysis of 22DMB is i-C₄H₁₀. This product is possible through a variety of channels; however, each pathway can be rationalized into secondary C–C bond breakage.

The unsaturated product with the second largest yield in the photolysis of 22DMB is 2-methyl-1-butene (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 CH₄ or CH₃+H is favored 3/1 over 2M2B and CH₄ or CH₃+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 neopentane and HME.

For small linear alkanes, three-membered transition states are favored, however, in highly branched alkanes four or five-membered transition states seem to be more common. This generalization also holds for 22DMB. Intramolecular C₄H₁₀, 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 N₂ is added to the photolysis system.

It is useful to contrast the photochemistry of ethyltrimethylsilane (ETMS) and its analogous hydrocarbon, 22DMB. In the photochemistry of ETMS it was shown that a variety of radicals were produced including (CH₃)₂Si⁺, φ = 0.11; (CH₃)₂SiCH₂⁺, φ = 0.09; (CH₃)₂SiC₂H₄⁺, φ = 0.08; (CH₃)₂SiC₃H₆⁺, φ = 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.

22DMB → (CH₃)₂C⁺C=CH(CH₃) + [CH₄ or CH₃ + H]  

(2) → CH₃⁺(CH₃)C(CH₃)₂ + [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 2-methyl-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, (CH₃)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, however. Thus by analogy

from 22DME photolysis one would predict that (CH₃)₃Si: 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 C₅H₁₀H₁₅S₃Si₂ is obtained. This calculation assumes that the two unidentified products have a formula of C₅H₁₀. This mass balance is in reasonable agreement with the expected value of C₅H₁₄.

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 N₂ in the O₂ 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–HI 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.

\[
\text{223TMB} \rightarrow \text{CH}_2=\text{C}-(\text{CH}_3)\text{C}(\text{H})(\text{CH}_3)_2 + \text{CH}_4 \quad \text{(or CH}_3 + \text{H)}
\]

(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-C₅H₁₀, there are at least two reactions that can be postulated for its formation. Reaction 6 and 7 illustrate these paths.

\[
\text{CH}_3 + \text{i-C}_2\text{H}_7 \rightarrow \text{i-C}_2\text{H}_{10}
\]

(6)

\[
\text{t-C}_2\text{H}_6 + \text{t-C}_2\text{H}_6 \rightarrow \text{t-C}_4\text{H}_{10} + \text{i-C}_2\text{H}_{10}
\]

(7)

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

\[
\text{223TMB} \rightarrow (\text{CH}_3)_2\text{C}-(\text{H})(\text{CH}_3)_2 + \text{CH}_3 + \text{CH}_3
\]

(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 (φ = 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[21] 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 propane/propane or ethene/ethane ratios. The conversion dependence of the 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 C₆H₁₆H₁₅S₃Si. This is in good agreement with the expected value of C₆H₁₆. This calculation assumes that the unknown species in the photolysis of 223TMB has a formula of C₆H₁₆.

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 dependence.

\[
\text{IPTMS} \rightarrow (\text{CH}_3)_2\text{SiCH}_2 + \text{CH}_3
\]

(9)

Another important intramolecular process involves the formation of propene (φ = 0.09 ± 0.01). See reaction 10.

\[
\text{IPTMS} \rightarrow \text{C}_3\text{H}_6 + (\text{CH}_3)_3\text{SiH}
\]

(10)

The empirically required cofragment, (CH₃)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 C₃H₆ 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 O₂ gives evidence for the formation of four radical species: CH₃, C₅H₁₀, (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 C₃H₆ and (CH₃)₂Si are directly associated through reaction 11 and, within experimental error, the yields of IPTMS → C₃H₆ + (CH₃)₃Si

(11)

these two radicals are equal. The formation of CH₃ and (CH₃)₂SiC(H)(CH₃)₂ are also coupled as shown by reaction 12; however, there are necessarily other channels available

\[
\text{IPTMS} \rightarrow \text{CH}_3 + (\text{CH}_3)_2\text{SiC}(\text{H})\text{(CH}_3)_2
\]

(12)

for the formation of CH₃ in addition to reaction 12 since the methyl radical yield is substantially larger than the (CH₃)₂Si(π-H)(CH₃)₂ yield. It is interesting to note that reaction 12 is important, but reaction 13 is not since

\[
\text{IPTMS} \rightarrow (\text{CH}_3)_2\text{SiC}(\text{H})(\text{CH}_3) + \text{CH}_3
\]

(13)
ethyltrimethylsilane would be formed by the \((\text{CH}_3)_2\text{SiC}-(\text{H})/\text{CH}_3\) 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-alapropene \((\phi = 0.10)\) 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-alapropene (dimethyldisilaethylene); however, even when the methanol concentration is extrapolated to infinite concentration, it has been shown to be at a maximum 85% efficient. 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.

Vinytrimethylsilane is formed by reaction 14. The reaction is:

\[
\text{IPTMS} \rightarrow (\text{CH}_3)_2\text{SiCH} = \text{CH}_2 + \text{CH}_4 \quad \text{(or CH}_3 + \text{H)}
\]

The 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.

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

\[
t-\text{BTMS} \rightarrow (\text{CH}_3)_2\text{CH} + (\text{CH}_3)_2\text{SiCH}
\]

\[
\rightarrow (\text{CH}_3)_2\text{C}=\text{CH}_2 + (\text{CH}_3)_2\text{SiH}
\]

\[
\rightarrow \text{CH}_4 + \text{products}
\]

\[
\rightarrow \text{C}_3\text{H}_8 + \text{CH}_3 + (\text{CH}_3)_2\text{Si}
\]

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 \((\text{CH}_3)_2\text{Si}\) 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-

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

From the results of the HI and O additive experiments four atomic and radical species are postulated to be formed. They are \(\text{CH}_3\), \((\text{CH}_3)_2\text{C}\), \((\text{CH}_3)_2\text{Si}\), and H. \((\text{CH}_3)_2\text{C}\) and \((\text{CH}_3)_2\text{Si}\) are directly coupled through reaction 21.

\[
t-\text{BTMS} \rightarrow (\text{CH}_3)_2\text{Si} + (\text{CH}_3)_2\text{C}
\]

Within experimental error, the yields of these two radicals are equal. The formation of \(\text{CH}_3\) 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 t-tert-butyldimethylsilane or isopropyltrimethylsilane would have been formed by H abstraction from HI by tert-butylidimethylsilyl radicals and isopropyltrimethyisilyl radicals, respectively.

**Mercury-Sensitized Photolysis of i-C\(_3\)H\(_{10}\), (CH\(_3\))\(_2\)SiH, and Mixtures of i-C\(_3\)H\(_{10}\) and (CH\(_3\))\(_2\)SiH**. 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 \((\text{CH}_3)_2\text{C}\) with \((\text{CH}_3)_2\text{Si}\), \((\text{CH}_3)_2\text{SiH}\), and \((\text{CH}_3)_2\text{Si}\) with \((\text{CH}_3)_2\text{SiH}\), and \((\text{CH}_3)_2\text{Si}\) with \((\text{CH}_3)_2\text{Si}\). Therefore, a study was carried out with 254-nm light (Rayonet photoreactor 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, trimethyisilane, and mixtures of isobutane and trimethyisilane. To gain additional insight, we examined a model cross reaction, involving the exchange of C=H and Si=C for C=Si and C=C bonds using ab initio calculations. These results are in agreement with our experimental findings.

The mercury photosensitization of mixtures of isobutane and trimehtyisilane (TriMS) yields four distinguishable products: \(i-C_3\text{H}_8\), HME, hexamethydisilane (HMDS), and t-BTMS. All products were suppressed by addition of 3% O. 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, \(t \geq 5\) min, a conversion dependence was observed for \(i-C_3\text{H}_8\) and HME in the photolysis of \(i-C_3\text{H}_8\). In order to account for this dependence, we photolyzed pure samples of \(i-C_3\text{H}_8\) and monitored the product ratio of \(i-C_3\text{H}_8/HME\) as a function of photolysis time. As can be seen in Figure 4, at photolysis times \(t < 5\) min, the \(i-C_3\text{H}_8/HME\) ratio levels off to a value of 2.1. This value represents the disproportionation/composition \((D/C)\) ratio for two \(i\)-butyl radicals.

Relative yields of products for various mixtures of \(i-C_3\text{H}_8\) and TriMS are reported in Table VI. The yield of TMMS represents that at a methanol concentration equal to \(P_{\text{methanol}} = 0.15P_{\text{TriMS}}\). 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 \(i\)-butyl, we have determined \(D/C\) for \((\text{CH}_3)_2\text{C} + (\text{CH}_3)_2\text{Si}\) from the H* -sensitized photolysis of \(i-C_3\text{H}_8\). Under conditions of low conversion and short photolysis times, a plot of isobutene/hexa-

\[
r-\text{BTMS} \rightarrow (\text{CH}_3)_2\text{C} \rightarrow (\text{CH}_3)_2\text{Si} + (\text{CH}_3)_2\text{SiH}
\]

\[
\rightarrow (\text{CH}_3)_2\text{C} \rightarrow (\text{CH}_3)_2\text{Si} + \text{CH}_4 + (\text{CH}_3)_2\text{SiH}
\]

\[
\rightarrow (\text{CH}_3)_2\text{C} \rightarrow (\text{CH}_3)_2\text{Si} + \text{CH}_4 + \text{products}
\]

\[
\rightarrow (\text{CH}_3)_2\text{C} \rightarrow (\text{CH}_3)_2\text{Si} + \text{CH}_4 + \text{products}
\]
trimethylmethoxysilane arises only from a reaction such as 24. A solution-phase determination using the same assumptions yields a value of a comparable order of magnitude, 0.19 ± 0.05, while a gas-phase determination of (CH₃)₂SiH/(CH₃)₂Si₂ gives 0.05 and does not depend on this titration technique. Cornett et al. 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 ± 0.05. This is set equal to k₂₆/k₂₇ for further use in the discussion below.

2(CH₃)₃Si → (CH₃)₂SiCH₂ + (CH₃)₂SiH  
(25) 

For the cross reaction of (CH₃)₃Si and (CH₃)₂C, H transfer from either radical is possible in addition to reaction 27.  

(CH₃)₃Si + (CH₃)₂C → (CH₃)₂SiC(CH₃)₃  
(27) 

Reaction 27 is measured by the yield of t-BTMS, and reactions 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 (CH₃)₂SiCH₂ from reaction 28 to t-BTMS is given by eq 30 and is k₂₆/k₂₇ = 1.86 ± 0.15.

\[
\frac{[CH₃]₂SiCH₂}{[t-BTMS]} = \frac{[TMS]}{[t-BTMS]} \cdot \frac{k₂₆}{k₂₇} 
\]  
(30)
TABLE VII: Comparison of Unsatuated to Expected Saturated Cofragments for Selected Alkanes and Alkyldisilanes Photolyzed at 147 nm

<table>
<thead>
<tr>
<th>parent</th>
<th>unsaturated product</th>
<th>expected saturated product</th>
<th>( \Phi_{\text{sat}}/\Phi_{\text{unsat}} )</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>C,Ds</td>
<td>C,Ds</td>
<td>CDs</td>
<td>0.07/0.18 = 0.39</td>
<td>6c</td>
</tr>
<tr>
<td>neo-C,H,</td>
<td>i-C,H,</td>
<td>C,H,</td>
<td>0.23/0.70 = 0.33</td>
<td>1</td>
</tr>
<tr>
<td>22DMB</td>
<td>C,H,</td>
<td>i-C,H,0</td>
<td>&lt;0.01/0.08 &lt; 0.10</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>i-C,H,10</td>
<td>C,H,10</td>
<td>0.05/0.44 = 0.14</td>
<td>18</td>
</tr>
<tr>
<td>2-methyl-1-butene</td>
<td></td>
<td>CH,10</td>
<td>0.09/0.15 = 0.60</td>
<td></td>
</tr>
<tr>
<td>223TMB</td>
<td>C,H,</td>
<td>i-C,H,0</td>
<td>0.03/0.20 = 0.15</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>i-C,H,</td>
<td>C,H,0</td>
<td>0.08/0.35 = 0.17</td>
<td></td>
</tr>
<tr>
<td>2,3-dimethyl-1-butene</td>
<td></td>
<td>CH,0</td>
<td>0.25/0.75 = 0.35</td>
<td>2b</td>
</tr>
<tr>
<td>HME</td>
<td>i-C,H,</td>
<td>i-C,H,0</td>
<td>0.26/0.69 = 0.38</td>
<td>18</td>
</tr>
<tr>
<td>HMDS</td>
<td>(CH₃)₃SiCH₂</td>
<td>(CH₃)₃SiH</td>
<td>0.32/0.50 = 0.64</td>
<td>4</td>
</tr>
<tr>
<td>TetraMS⁺</td>
<td>C,H,</td>
<td>(CH₃)₃SiH</td>
<td>0.03/0.21 = 0.14</td>
<td></td>
</tr>
<tr>
<td>ETMS</td>
<td>(CH₃)₃SiCH₂</td>
<td>C,H,0</td>
<td>0.10/0.17 = 0.59</td>
<td></td>
</tr>
<tr>
<td>IPTMS</td>
<td>i-C,H,</td>
<td>(CH₃)₃SiH</td>
<td>0.02/0.09 = 0.22</td>
<td>this work</td>
</tr>
<tr>
<td>t-BTMS</td>
<td>i-C,H,</td>
<td>(CH₃)₃SiH</td>
<td>0.06/0.10 = 0.60</td>
<td></td>
</tr>
<tr>
<td></td>
<td>i-C,H,0</td>
<td>(CH₃)₃SiH</td>
<td>0.09/0.30 = 0.30</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>i-C,H,10</td>
<td>(CH₃)₃SiH</td>
<td>0.17/0.30 = 0.57</td>
<td></td>
</tr>
</tbody>
</table>

* TetraMS = tetramethylsilane.

Similarly, the ratio of i-C,H₆ from reaction 29 to t-BTMS is given by eq 31 or \( k_{22}/k_{23} = 0.55 \pm 0.08 \).

\[
\frac{[i-C,H₆]_{[29]}}{[t-BTMS]} = \frac{k_{22}[\text{HME}]}{k_{23}[t-BTMS]} \tag{31}
\]

Qualitative conclusions which may be postulated are as follows: (1) disproportionation is competitive with combination reactions between \((\text{CH₃})₂\text{Si} + \text{CH₃} \cdot \cdot \cdot \text{CH₃} \cdot \cdot \cdot \text{CH₃} \cdot \cdot \cdot \text{Si}\); (2) production of \((\text{CH₃})₂\text{SiCH₂} + \text{C}_3\text{H}_6 \) is competitive with \((\text{CH₃})₃\text{Si} + \text{CH₃} \cdot \cdot \cdot \text{CH₃} \cdot \cdot \cdot \text{Si} \) and may predominate.

The latter conclusion clearly indicates that \((\text{CH₃})₂\text{SiCH₂} + \text{C}_3\text{H}_6 \) is not unstable with respect to \((\text{CH₃})₂\text{Si} + \text{CH₃} \cdot \cdot \cdot \text{CH₃} \cdot \cdot \cdot \text{Si} \) and may predominate.

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 \((\text{CH₃})₂\text{SiCH₂} \) 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

---

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 $\phi((\text{CH}_3)_3\text{SiCH}_2)/\phi((\text{CH}_3)_3\text{SiOCH}_3)$ 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$_3$)$_3$SiCH$_2$. Therefore, more methanol is needed to titrate the (CH$_3$)$_3$SiCH$_2$. In this plot it is assumed that only methyl radicals compete with methanol for (CH$_3$)$_3$SiCH$_2$.

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.

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**Reaction Mechanism of O$^-$ + H$_2$O $\rightarrow$ OH$^-$ + OH at Low Incident Ion Energies**

C. Lifshitz

Department of Physical Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel (Received: February 1, 1982; In Final Form: March 31, 1982)

Ion-beam collision-chamber experiments at low baricentric energies (0.17–3.5 eV) are discussed. The occurrence of $^{16}$O$^-$ + H$_2$ $\rightarrow$ $^{18}$O$^-$ + H$_2$ and the branching ratios between $^{16}$O$^-$, $^{18}$OH$^-$, and $^{18}$OH$^-$ as a function of energy speak in favor of the formation of an intermediate long-lived collision complex, [H$_2$O$_2$]$^*$ below ~1 eV. The lifetime of the intermediate is estimated to be $\tau_d = 3.6 \times 10^{-13}$ s at 0.17 eV, on the basis of RRKM calculations. A Brauman reaction-coordinate diagram, with a double minimum, is proposed.

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**Introduction**

There has been considerable interest recently in ion–molecule reactions which proceed via long-lived collision complexes. 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. It has aroused 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. Within this energy range, the reaction was found to be direct and well approximated by the spectator-stripping model.

Positive and negative ion–molecule reactions seem to behave differently, as has been first pointed out for the H$_3^+$ and H$_3^-$ systems. 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(1D) + H$_2$ $\rightarrow$ $^{18}$OH + $^{18}$OH proceeds via a direct mechanism. The positive endothermic ion–molecule reactions

\[
O_2^+(2\Pi_g) + H_2 \rightarrow HO_2^+ + H
\]

(2a)

\[
\rightarrow OH^+ + OH
\]

(2b)

\[
\rightarrow H_2O^+ + O
\]

(2c)

take place via a persistent H$_2$O$_2^+$ collision complex at low relative energies. The ion-beam collision-chamber studies of the title reaction were carried out at considerably lower ion energies than those of the crossed-beam study. 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, 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°(LAB) scattering angle. The projectile O$^-$ ion is formed in the electron impact ion source of the first-stage mass spectrometer from N$_2$O. 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 ±0.3 eV (LAB) full width at half-maximum. Product ions are mass analyzed in the

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