Oxidation of Alkyl Ions, C\textsubscript{n}H\textsubscript{2n+1}^+ + (n = 1-5), in Reactions With O\textsubscript{2} and O\textsubscript{3} in the Gas Phase

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Rate constants and product ion branching fractions are reported for the reactions of C\textsubscript{2}H\textsubscript{5}^+, C\textsubscript{3}H\textsubscript{7}^+, t-C\textsubscript{3}H\textsubscript{7}^+, s-C\textsubscript{3}H\textsubscript{7}^+, t-C\textsubscript{4}H\textsubscript{9}^+, and t-C\textsubscript{6}H\textsubscript{13}^+ with O\textsubscript{2} and O\textsubscript{3} at 300 K in a variable-temperature selected-ion flow tube (VT-SIFT). The reaction rate constant for CH\textsubscript{3}^+ with O\textsubscript{2} is large and approximately equal to the thermal energy capture rate constant given by the Su–Chesnavich equation. The C\textsubscript{2}H\textsubscript{5}^+, t-C\textsubscript{3}H\textsubscript{7}^+, and s-C\textsubscript{3}H\textsubscript{7}^+ ions are somewhat less reactive, reacting at approximately 7–46% of the thermal capture rate. The HCO\textsuperscript{+} and C\textsubscript{2}H\textsubscript{5}O\textsuperscript{+} ions are the major products in these reactions. The t-C\textsubscript{4}H\textsubscript{9}^+ and t-C\textsubscript{6}H\textsubscript{13}^+ ions are found to be unreactive, with rate constants <5 \times 10\textsuperscript{-12} cm\textsuperscript{3} s\textsuperscript{-1}, which is the present detection limit of our apparatus using this ozone source. Ozone is a singlet in its ground state, and ab initio calculations at the B3LYP/6-31G(d) level of theory indicate that reactant complexes can be formed, decreasing in stability with the size of alkyl chains attached to the cationic carbon atom. The decreasing reactivity of the alkyl ions with increasing order of the carbocation is attributed to a greatly reduced O\textsubscript{2} binding energy. The ions listed above do not undergo body reactions with O\textsubscript{2}, k < 5 \times 10\textsuperscript{-10} cm\textsuperscript{3} s\textsuperscript{-1}, despite the availability of reaction channels with exothermicities of several hundred kilojoules per mole. Ab initio calculations at the B3LYP/6-31G(d) level of theory indicate that the O\textsubscript{2} reaction systems form weak complexes with large C–O bond distances (repulsive at smaller distances) on the lowest energy triplet potential energy surface. Access to the singlet surface is required for bond formation; however, this surface is not accessible at thermal energies.

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Oxidation of Alkyl Ions, C_{n}H_{2n+1}^{+} (n = 1−5), in Reactions with O_{2} and O_{3} in the Gas Phase

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Rate constants and product ion branching fractions are reported for the reactions of CH_{3}^{+}, C_{2}H_{5}^{+}, s-C_{3}H_{7}^{+}, t-C_{3}H_{7}^{+}, and t-C_{3}H_{11}^{+} with O_{2} and O_{3} at 300 K in a variable-temperature selected-ion flow tube (VT-SIFT). The reaction rate constant for CH_{3}^{+} with O_{2} is large and approximately equal to the thermal energy capture rate constant given by the Su−Chenavarch equation. The C_{2}H_{5}^{+}, s-C_{3}H_{7}^{+}, and s-C_{6}H_{13}^{+} ions are somewhat less reactive, reacting at approximately 7−46% of the thermal capture rate. The HCO^{+} and C_{2}H_{2}O^{+} ions are the major products in these reactions. The t-C_{3}H_{7}^{+} and t-C_{3}H_{11}^{+} ions are found to be unreactive, with rate constants <5×10^{-12} cm^{3} s^{-1}, which is the present detection limit of our apparatus using this ozone source. Ozone is a singlet in its ground state, and ab initio calculations at the B3LYP/6-31G(d) level of theory indicate that reactant complexes can be formed, decreasing in stability with the size of alkyl chains attached to the cationic carbon atom. The decreasing reactivity of the alkyl ions with increasing order of the carbocation is attributed to a greatly reduced O_{2} binding energy. The ions listed above do not undergo two-body reactions with O_{2}, k < 5×10^{-13} cm^{3} s^{-1}, despite the availability of reaction channels with exothermicities of several hundred kilojoules per mole. Ab initio calculations at the B3LYP/6-31G(d) level of theory indicate that the O_{2} reaction systems form weak complexes with large C−O bond distances (repulsive at smaller distances) on the lowest energy triplet potential energy surface. Access to the singlet surface is required for bond formation; however, this surface is not accessible at thermal energies.

I. Introduction

Carbenium ions are found in a wide variety of environments, including interstellar clouds, chemical vapor deposition plasmas, and combustion environments. Studies of the oxidation of these ions have historically been focused on C_{n}H_{2n}^{+} ion reactions with O atoms. These reactions have been studied to elucidate the synthetic chemistry occurring in interstellar clouds. Fehsenfeld et al. examined the reaction of CH_{3}^{+}, Bohme, Mackay, and Schlitt examined the reaction of CH_{3}^{+}, and Viggiano et al. examined reactions of CH_{4}, CH_{3}^{+}, C_{2}H_{5}^{+}, C_{2}H_{5}^{+}, and C_{2}H_{5}^{+}, and C_{2}H_{5}^{+} and later isotopomers of CH_{3}^{+} (CD_{3}H_{2}−x). More recently, Le Page et al. reported the investigation of aromatic hydrocarbon ions C_{6}H_{5}^{+}, C_{7}H_{8}^{+}, C_{10}H_{9}^{+}, and C_{12}H_{11}^{+} with H, N, and O atoms. Of these ions, C_{6}H_{5}^{+}, C_{7}H_{8}^{+}, and C_{10}H_{9}^{+} were found to react with atomic oxygen. The C_{6}H_{5}^{+} cation showed striking reactivity toward atoms, compared to the relative reactivity of phenyl and naphthyl ions, which was attributed to the triplet nature of the C_{6}H_{5}^{+} ion in its ground state. Results of a study of 13 C_{m}H_{2m}^{+} ions (m ≤ 6) with O, O_{2}, and NO carried out by Scott et al. showed that most of the hydrocarbon ions studied exhibit relatively rapid reactions with O atoms that proceed at substantial fractions of the collision rate. One notable exception found by Scott et al. was the C_{3}H_{7}^{+} ion, one of the subject ions in the present study, which showed no reactivity with O atoms.

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The formation and destruction mechanisms of hydrocarbon ions in combustion environments is an area of recent interest. In particular, plasma sources are being explored as ignition and combustion aids in supersonic combustion, where fuel activation and initiation on fast-flow time scales pose a daunting challenge. However, the information gained from these studies is broadly applicable to a wide range of problems such as spark inhibition, improved engine performance, service life, explosion limits in blended fuels, hydrocarbon molecular growth, and ignition. The oxidation of hydrocarbon ions in these environments is of fundamental interest. For example, C_{4}H_{10}^{+}, C_{8}H_{14}^{+}, and C_{6}H_{12}O_{2}^{+} positive ions have been observed in the flames of a variety of fuels. Although these ions are commonly observed, their formation mechanisms are not fully understood.

One mechanism involves oxidation of hydrocarbon ions in a single step via reactions with oxygen species such as O, O_{2}, O_{3} (a 1^\Delta), and O. As mentioned above, some work has been carried out with regard to O atom reactions, but the other oxidation processes remain relatively unexplored. The reactions of alkyl ions with numerous compounds have been reported previously. However, reactions leading to the oxidation of C_{n}H_{2n+1}^{+} (n = 2−5) species have not been reported. Oxidation of other organic ions with O_{3} has been studied in the gas phase by Mendes et al. using a pentaquadrupole mass spectrometer. The collision energy of the ion−molecule reactions studied in those experiments was ca. 1 eV. Mendes et al. found that neutral ozone transfers an oxygen atom to several positive ions, namely, radical cations of pyridines, alkyl halides, and halogen cations. A
considerable amount of O$_2$ was present in these experiments. However, when the experiments were repeated with pure O$_2$, no O-atom-transfer products were observed, confirming that the oxidation occurs from O$_2$ alone. Ab initio calculations were also performed as part of the work by Mendes et al.\textsuperscript{11} to rationalize the formation of the reaction products observed. An interesting conclusion of that work is that simple nucleophilic addition of ozone followed by O$_2$ loss is the most likely mechanism for O-atom transfer from ozone to radical cations of pyridines, alkyl halides, and halogen cations. This new mechanistic pathway was suggested to be an important pathway for the generation of chemically interesting but difficult-to-generate ionized oxides.

In this paper, the chemistry of ionized hydrocarbons reacting with oxygen and ozone is investigated at 300 K using fast ion flow tube kinetics instrumentation. The measurements are conducted with a selected-ion flow tube (SIFT) instrument at ca. 0.5 Torr helium buffer pressure, and the kinetics are observed over ca. 3–4 ms reaction time. Specifically, rate constants and product ion branching fractions are reported for the reactions of CH$_3$+, C$_2$H$_5$+, s-C$_3$H$_7$+, s-C$_4$H$_9$+, t-C$_4$H$_9$+, and t-C$_5$H$_{11}$+ with O$_2$ and O$_3$ at room temperature. The HCO$_2$+ ion is a major product in many of these reactions, so the reactivity of HCO$_2$+ with O$_2$ and O$_3$ is also investigated. Density functional calculations using the B3LYP functional\textsuperscript{12–14} and 6-31G(d) basis set\textsuperscript{15} are also performed on the electronic ground-state potential surfaces of complexes of O$_2$ and O$_3$ with select hydrocarbon radical cations to elucidate the reaction mechanism leading to the oxidation of these ions. The new experimental findings are discussed in the context of these theoretical calculations and previous work where available.

II. Method

Experimental Details. The measurements were made at 300 K using the SIFT instrument at the Air Force Research Laboratory. This apparatus is described in detail elsewhere,\textsuperscript{16,17} and the modifications required to perform experiments with ozone as a reactant gas have been discussed recently.\textsuperscript{18} The SIFT is shown schematically, with modifications, in Figure 1.

In brief, cationic ions are prepared in a remote, differentially pumped chamber by electron impact ionization of alkyl bromides and alkyl chlorides entrained within a supersonic argon expansion. After a skimmer, all ions are directed into a quadrupole mass filter, where the ionic species of interest is mass-selected. The mass-selected ions are injected via a Venturi-type inlet into a fast flow of helium carrier gas in a meter-long stainless steel flow tube. Reactant gas is introduced into the flow tube through either of two stainless steel reactant gas inlets and allowed to react over a known distance at a known flow velocity. The SIFT operates at ca. 0.5 Torr helium buffer pressure, and the kinetics are observed over ca. 3–4 ms reaction time. A second quadrupole mass spectrometer resolves the reactant and the product ions, which are then detected by an electron multiplier. Extrapolations of product branching fractions to zero reactant flow yield the nascent branching fraction. The decay in the primary reactant ion signal as a function of increasing reactant gas flow rate yields the reaction rate constant. Concentrations are such that [buffer] \gg [reactant neutral] \gg [ions]. Under these conditions, pseudo-first-order kinetics apply, and the rate constant is given by

\begin{equation}
    k = \frac{1}{\tau} \ln \frac{[A_0^\pm]}{[A^\pm]}
\end{equation}

where \( k \) is the rate constant, \( \tau \) is the reaction time, \([B]\) is reactant neutral concentration, and \([A_0^\pm]\) and \([A^\pm]\) are the primary reactant ion concentrations in the absence and in the presence of reactant neutral, respectively. The reaction time, \( \tau \), is the reaction distance divided by the buffer velocity multiplied by a correction factor determined from previous time-of-flight measurements that accounts for the fact that both the ion velocity and the ion concentration are at a maximum along the axis of the flow tube. A typical value for the correction factor is 1.6. The buffer velocity is obtained from the mass flow rate of the buffer, the flow tube cross section, temperature, and pressure in the normal manner.\textsuperscript{19} The absolute uncertainties of the rate constants are 25%, and relative uncertainties are 15%.

An Orec O3V-0 ozonator was interfaced to the SIFT apparatus to produce the ozone reactant gas used in this experiment. A commercial supply of O$_3$ (Airco, 99.9999%) was used to manufacture the ozone. The O$_3$ was produced at a pressure of 3–6 psig using a 0.9-A discharge current. The resulting reactant gas is approximately 5% O$_3$ in O$_2$, which is the same as that reported previously by Fahey et al.\textsuperscript{20} The fraction of O$_3$ was relatively independent of the reactant gas flow rate over a 100 SCCM flow range. The presence of O$_2$ does not affect the measurements, because O$_2$ was found to be unreactive with the positive ions studied here, including the product ions. Flow contamination was less than 0.05%, typically arising from nitrogen and carbon dioxide trace gases in the ozonator and the tubing. Flushing the lines and the ozonator regularly to prevent the buildup of NO, NO$_2$, and CO$_2$ minimized contamination. All fittings and valves used in the O$_3$ delivery system are stainless steel, and the tubing was either stainless steel or Teflon.

A flow controller regulates the O$_3$/O$_2$ reactant mixture flow into a 10.2-cm-long, 1.3-cm-diameter Pyrex absorption cell fitted with quartz windows. The absorption cell is connected to the flow tube stainless steel reactant inlets by approximately 40 cm of 0.25-in.-o.d. Teflon tubing. Varying the length of the Teflon tubing from 40 to 300 cm produced no difference (<5%) in
the results, suggesting that no significant $O_3$ decomposition occurs in the tubing. The absolute concentration of $O_3$ is measured by optical absorption at 248 and 254 nm using a Perkin-Elmer Lambda 10 UV/vis spectrometer. The concentration of the ozone in the flow tube was found using

$$[O_3] = \left( \frac{2.303 A}{\sigma A l} \right) \left( \frac{P_{FT}}{P_{AC}} \frac{F_{AC}}{F_{FT}} \right) \tag{2}$$

where $A$ is the log absorbance (base 10) output from the spectrometer, $\sigma$ (cm$^2$ molecule$^{-1}$) is the absorption cross section for $O_3$ at wavelength $\lambda$, $l$ is the length of the absorption cell in cm, $P_{FT}$ is the flow tube pressure, $P_{AC}$ is the absorption cell pressure, $F_{AC}$ is the total flow through the absorption cell, and $F_{FT}$ is the total flow through the flow tube. The 248- and 254-nm cross sections used were 1.08 $\times$ 10$^{-17}$ and 1.137 $\times$ 10$^{-17}$ cm$^2$ molecule$^{-1}$, respectively.$^{21,22}$ In our previous publication,$^{18}$ results regarding several negative-ion reactions with ozone were compared to literature values regarding the negative-ion chemistry of ozone, which prior to our study lacked sufficient agreement for application to detailed physical models. For the reaction of SF$^-$ with ozone, there is now good agreement between three recent measurements,$^{14}$ indicating reliable delivery and knowledge of the $O_3$ concentrations in the present experiment.

$CH_3^+$ was prepared by ionizing methyl bromide (Aldrich, >99.5%), $C_2H_5^+$ was prepared by ionizing ethyl bromide (Aldrich, >99%), $C_3H_7^+$ was prepared by ionizing isopropyl bromide (Aldrich, >99%), $C_4H_9^+$ was prepared by ionizing propyl bromide (Aldrich, >99%), $C_6H_5^+$ was prepared by ionizing tert-butyl chloride (Aldrich, >99%), $C_6H_6^+$ was prepared by ionizing n-butyl chloride (Aldrich, >99%), and $C_6H_11^+$ was prepared by ionizing 2-chloro-2-methylbutane. $HCO^+$ was formed by ionizing CO (Airco, 99.9%) in the supersonic source and injecting CO$^+$ into the flow tube, which is recombined with 10 SCCM of H$_2$ added 20 cm upstream of the reactant inlet. All source gases were entrained within a supersonic argon (Airco, 99.995%) expansion.

Calculations. Geometry optimizations were carried out using Gaussian's implementation of the B3LYP hybrid density functional$^{12-14}$ using the standard 6-31G(d) basis set of Pople et al.$^{15}$ Open-shell fragments were treated using the spin-unrestricted density functional formalism. Analytical frequency calculations were used to characterize the nature of these stationary points. All of the reaction pathways were verified by intrinsic reaction coordinate (IRC) calculations$^{23-27}$ both forward and backward from the encountered transition states. Standard Mulliken population analysis$^{28-30}$ was employed to analyze electron density and spin density distributions from the B3LYP/6-31G(d) densities.

III. Results

Reaction rate constants and product branching fractions for alkyl ions, $C_4H_{2n+1}^+$ ($n = 1-5$), and $HCO^+$ reacting with $O_3$ measured at 300 K with the SIFT are shown in Table 1. None of the subject cations shows any measurable bimolecular reactivity with $O_2$, $k < 5 \times 10^{-15}$ cm$^3$ s$^{-1}$. In Table 1, the standard reaction enthalpies at 298 K (in kJ mol$^{-1}$) have been calculated and are listed. The heats of formation are taken from the NIST compilation.$^{31,32}$ Note that the tert-butyl ion heat of formation has been recently revised, and a value of $\Delta H_f^{298}$($t$- $C_4H_9^+$) = 711 kJ/mol from recent experimental$^{33-35}$ and theoretical studies$^{36}$ is used, which is 20 kJ/mol higher than previous experimental measurements. Figure 2 shows corrected

![Figure 2](image-url)

Figure 2. Corrected (see text) primary ion decay plots for $CH_3^+$ ( ), $HCO^+$ (A), $C_3H_7^+$ ( ), $C_4H_9^+$ ( ), and $C_6H_5^+$ (*) reacting with $O_3$. The solid lines are nonlinear least-squares fits to the data, performed to determine the rate constants according to eq 1. Experiments are performed with a reactant gas composition of 5% $O_3$ in $O_2$, which is possible since $O_3$ is unreactive.

![Figure 3](image-url)

Figure 3. Normalized $C_4H_9^+$ counts ( ) plotted vs $O_3$ concentration. The dashed line is the result of a single-exponential fit of the data to determine the rate constant according to eq 1. The result of the single-exponential fit is labeled $k_{obs}$. The solid line is the result of a double-exponential fit of the data which yields a fast component ($k_{obs}$) with a rate constant of $(6 \pm 4) \times 10^{-11}$ cm$^3$ s$^{-1}$ and a slow component ($k_{obs}$) with a rate constant $<5 \times 10^{-12}$ cm$^3$ s$^{-1}$.

(see below) primary ion decay plots for the reactions of $CH_3^+$, $HCO^+$, $C_3H_7^+$, $C_4H_9^+$, and $C_6H_5^+$ with $O_3$. The solid lines are linear least-squares fits to the data, performed to determine the rate constants according to eq 1. Sample kinetics data for $C_4H_9^+$, prepared by ionizing n-buty1 bromide, are shown in Figure 3. Electron impact ionization of n-buty1 bromide is expected to produce both $s$-$C_4H_9^+$ and $t$-$C_4H_9^+$. The isomeric composition was determined by exploiting the order of magnitude difference in the hydride-transfer reaction rate constant with 2-methylpentane ($i$-$C_4H_{12}$) for the two isomers, as shown in Figure 4. The specific results for each cation studied are discussed below.

HCO$^+$ Cation. The HCO$^+$ cation is a major product of the primary and secondary carbocation reactions with $O_3$ listed in Table 1. Hence, the reactivity of HCO$^+$ with $O_3$ was included in this study. In these studies, CO$^+$ was injected into the flow tube and reacted with 10 SCCM of H$_2$ added at inlet 1. This provided a source of HCO$^+$, although other ions including H$_2$O$^+$ and O$_2^+$ were present in trace amounts. The SIFT spectrum of CO$^+$ in the absence of added H$_2$ indicated the presence of H$_2$O$^+$.
TABLE 1: Reaction Rate Constants for Reactions of Ozone at 300 K, Measured with the Selected-Ion Flow Tube (SIFT)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products</th>
<th>$k, [k]$ ($\times 10^{-9}$ cm$^3$ s$^{-1}$)</th>
<th>Branching Fractions</th>
<th>$\Delta H$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCO$^+$ + O$_3$ →</td>
<td>HCO$^+$ + CO</td>
<td>1.2, [1.3]</td>
<td>&gt;0.98</td>
<td>-31.5</td>
</tr>
<tr>
<td>CH$_3$ + O$_3$ →</td>
<td>HCO$^+$ + (H$_2$ + O$_2$)</td>
<td>1.7, [1.6]</td>
<td>0.66</td>
<td>-410</td>
</tr>
<tr>
<td></td>
<td>H$_2$CO$^+$ + HO$_2$</td>
<td>0.16</td>
<td>-293</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HO$_2$ + HCO</td>
<td>0.10</td>
<td>-311</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O$_2^+$ + CH$_3$</td>
<td>0.07</td>
<td>-54</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HO$^+$ + CO$_2$</td>
<td>&lt;0.01</td>
<td>-1038</td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_5^+$ + O$_3$ →</td>
<td>HCO$^+$ + (CH$_4$ + O$_2$)</td>
<td>0.59, [1.3]</td>
<td>0.70</td>
<td>-294</td>
</tr>
<tr>
<td></td>
<td>C$_2$H$_5$O$^+$ + (H$_2$ + O$_2$)</td>
<td>0.30</td>
<td>-392</td>
<td></td>
</tr>
<tr>
<td>s-C$_3$H$_7^+$ + O$_3$ →</td>
<td>C$_3$H$_7$O$^+$ + (CH$_4$ + O$_2$)</td>
<td>0.22, [1.2]</td>
<td>0.64</td>
<td>-363</td>
</tr>
<tr>
<td></td>
<td>HCO$^+$ + (CH$_4$ + O$_2$)</td>
<td>0.16</td>
<td>-200</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH$_3$O$^+$ + CH$_4$ + O$_2$</td>
<td>0.14</td>
<td>-186</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH$_3$O$^+$ + CH$_3$COOH</td>
<td>0.05</td>
<td>-670</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH$_3$O$^+$ + 2H$_2$O</td>
<td>0.01</td>
<td>-674</td>
<td></td>
</tr>
<tr>
<td>s-C$_4$H$_9^+$ + O$_3$ →</td>
<td>HCO$^+$ + (C$_2$H$_4$ + O$_2$)</td>
<td>0.08, [1.1]</td>
<td>major (~0.40)</td>
<td>-188</td>
</tr>
<tr>
<td></td>
<td>C$_4$H$_9$O$^+$ + (C$_2$H$_6$ + O$_2$)</td>
<td>major (~0.35)</td>
<td>-339</td>
<td></td>
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<tr>
<td></td>
<td>C$_4$H$_9$O$^+$ + C$_2$H$_4$ + O$_2$</td>
<td>minor (~0.14)</td>
<td>-273</td>
<td></td>
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<tr>
<td></td>
<td>C$_4$H$_9$O$^+$ + CH$_3$COOH</td>
<td>minor (~0.09)</td>
<td>-758</td>
<td></td>
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<tr>
<td></td>
<td>C$_4$H$_9$O$^+$ + C$_2$H$_6$ + HO$_2$</td>
<td>trace (~0.02)</td>
<td>-111</td>
<td></td>
</tr>
<tr>
<td>t-C$_6$H$_9^+$ + O$_3$ →</td>
<td>C$_6$H$_9$O$^+$ + (C$_2$H$_4$ + O$_2$)</td>
<td>&lt;0.005, [1.1]</td>
<td>-284</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C$_6$H$_9$O$^+$ + (C$_2$H$_6$ + O$_2$)</td>
<td>-133</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t-C$<em>7$H$</em>{11}^+$ + O$_3$ →</td>
<td>C$<em>7$H$</em>{11}$CO$^+$ + (C$_2$H$_4$ + O$_2$)</td>
<td>&lt;0.005, [1.1]</td>
<td>-296</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C$<em>7$H$</em>{11}$CO$^+$ + (C$_2$H$_6$ + O$_2$)</td>
<td>-255</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HCO$^+$ + (C$_2$H$_4$ + O$_2$)</td>
<td>-112</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* All of the cations listed showed no reactivity, $k < 5 \times 10^{-13}$ cm$^3$ s$^{-1}$, with O$_3$. The calculated collision rate constant, $k_r$, and the measured rate constant, $k$, are listed in italics. The reaction products and branching fractions are listed under the rate constants. Energetics are taken from the NIST Chemistry WebBook. Neutral products are not resolved in these experiments. Brackets indicate that more than one product channel could contribute to the branching fraction. Products contained in parentheses are estimated on the basis of the mechanism discussed in the text involving O$_2$ loss. Note that the reactions are considerably more exothermic if the reaction products in parentheses are not dissociated.

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![Graph showing normalized counts for i-C$_6$H$_5^+$ plotted vs. 2-methylpentane (i-C$_6$H$_{12}$) concentration.](image)

Figure 4. Normalized C$_7$H$_{11}^+$ counts (●) plotted vs. 2-methylpentane (i-C$_6$H$_{12}$) concentration. The solid line is the result of a double-exponential fit of the data which yields a fast component ($k_{sec}$) with a rate constant of $(4.9 \pm 1.0) \times 10^{-19}$ cm$^3$ s$^{-1}$ and a slow component ($k_{sec}$) with a rate constant of $(4.2 \pm 0.3) \times 10^{-11}$ cm$^3$ s$^{-1}$, and O$_2^+$, which indicates that the source chemistry is responsible for the background levels of H$_2$O$^+$ and O$_2^+$. HCO$^+$ is known to be unreactive with O$_2$ and that finding was confirmed in this study. However, HCO$^+$ is very reactive with O$_3$, which is expected since the isoelectronic hydrogencyanide molecule is known to react with ozone to produce HCNO as a major product. The major product of HCO$^+$ reacting with O$_3$ is HO$_3^+$. The branching fraction reported in Table 1 is >0.98 and is intended to reflect the uncertainty of the source conditions. The measured rate constant of $1.2 \times 10^{-9}$ cm$^3$ s$^{-1}$ is nearly equal to the thermal capture rate constant of $1.3 \times 10^{-9}$ cm$^3$ s$^{-1}$.

**Methyl Cation.** The methyl cation was prepared by ionization of methyl bromide and was selectively injected into the flow tube. However, despite very low injection energies, approximately 12% of the CH$_3^+$ collisionally dissociated to form CH$_3^+$ and CH$_2^+$. While these breakup products do not interfere with the reaction rate constant determination, they do react with O$_3$ to form some of the same products observed in the CH$_3^+$ + O$_3$ reaction. Namely, CH$_3^+$ and CH$_2^+$ react with O$_3$ with rate constants of $9.7 \times 10^{-10}$ and $9.1 \times 10^{-10}$ cm$^3$ s$^{-1}$, respectively, and produce the following products:

- $\text{CH}^+ + \text{O}_3 \rightarrow \text{HCO}^+ + \text{O}$ (major) (3a)
- $\rightarrow \text{O}^+ + \text{HCO}$ (minor) (3b)
- $\rightarrow \text{CO}^+ + \text{OH}$ (minor) (3c)

and

- $\text{CH}_2^+ + \text{O}_3 \rightarrow \text{HCO}^+ + \text{OH}$ (major) (4a)
- $\rightarrow \text{H}_2\text{CO}^+ + \text{O}$ (minor) (4b)

The methyl cation, on the other hand, does not undergo two-
body reactions with O₂ and only exhibits a slow ternary association reaction, k₃₀₀ₓ = 8.6 × 10⁻³⁰ cm⁶ s⁻¹.⁴¹

Therefore, the impurity CH₄⁺ and CH₃⁺ ions were eliminated before entering the reaction zone by addition of a small amount (5 SCCM) of O₂ approximately 20 cm upstream of the first reactant inlet. The O⁺ and CO₂⁺ ions resulting from reactions 3b and 3c are converted to O₂⁺ via charge transfer with O₂, and the H₂CO⁺ from reaction 4b is converted to HCO⁺ (major) and H₂O₂⁺ (minor) via reaction with O₂. After the addition of O₂ at inlet 1, the resulting ion composition in the flow tube at the reactant inlet was observed to be approximately 88% CH₄⁺, 8.5% HCO⁺, 2.5% O₂⁺, and <1% H₂O₂⁺. The O₂⁺ and H₂O₂⁺ ions were accounted for by subtracting their baseline intensities observed at zero O₂/O₃ reactant flow from the appropriate product ion intensities. The HCO⁺ ion counts observed at zero O₂/O₃ reactant flow were corrected for by subtracting the appropriate number of counts at each ozone concentration, on the basis of the reactivity of HCO⁺ with O₂ listed in Table 1.

The methyl cation reacts at the collision rate with O₂, producing HCO⁺ as a major product and H₂CO⁺, H₂O₂⁺, O₂⁺, and H₂O⁺ as minor products. The product ion counts observed for H₂CO⁺, H₂O₂⁺, and O₂⁺ were significantly above the background counts discussed for these ions. Therefore, these ions are confirmed products. The H₂O⁺ product, on the other hand, results either from direct reaction of CH₃⁺ with O₂, which is highly exothermic but involves significant rearrangement, or from secondary reactions of HCO⁺ with the very low level of H₂O present in the flow tube. Secondary chemistry can be accounted for by extrapolating the baseline-corrected product branching fraction back to zero reactant concentration.¹⁸ However, this approach did not fully account for the amount of H₂O⁺ observed. Therefore, H₂O⁺ is listed as a trace product in the reaction of CH₃⁺ + O₂.

Ethyl Cation. The ethyl cation, prepared by ionizing ethyl bromide, reacts with O₂ to form two primary products, HCO⁺ and C₂H₅O⁺. Because C₂H₅⁺ and HCO⁺ are mass-coincident, two separate experiments were performed to determine the reaction rate constant. One experiment involved the addition of CH₃Cl to the flow tube via inlet 1. Methyl chloride reacts with HCO⁺ by proton transfer to form CH₃H₂⁺ and was not intended to react with C₂H₅⁺. However, the addition of methyl chloride did cause a reduction in the C₂H₅⁺ signal and produced several unidentified high-mass ions containing chlorine, so the amount of methyl chloride added was such that only about 20% of the original C₂H₅⁺ signal remained. In a second experiment, C₂H₅⁺ ion was injected into the flow tube. Statistically equal amounts of ¹²CHO⁺ and ¹³CHO⁺ are assumed to be formed, and the intensity of ¹²CHO⁺ is used as a measure of the ¹³CHO⁺ contribution to the m/z = 30 (sum of ¹²C₂H₅⁺ + ¹³CHO⁺). The reaction rate constant was determined by subtracting the intensity monitored at m/z 29 (¹³CHO⁺) from that at m/z = 30 (sum of ¹²C₂H₅⁺ + ¹³CHO⁺) and plotting the decay of the resulting ion signal as a function of O₂ flow. The two different experiments produced the following results. Using the methyl chloride scavenger, three determinations yielded rate constants of 6.3 × 10⁻¹⁰, 6.5 × 10⁻¹⁰, and 5.7 × 10⁻¹⁰ cm³ s⁻¹. The C₂H₅⁺ experiment in a single determination yielded 5.2 × 10⁻¹⁰ cm³ s⁻¹. The reaction rate constant in Table 1 is the average of the four measurements.

The reaction product branching fraction was estimated by reacting the ¹²C form of C₂H₅⁺ with high O₂ concentrations where no intensity at m/z = 29 remained, i.e., C₂H₅⁺ totally reacted and all of the HCO⁺ was converted to H₂O⁺. Approximately 5% of the C₂H₅⁺ dissociated to C₂H₃⁺ upon injection into the flow tube. The reaction products originating from C₂H₅⁺ were not identified or corrected for and constitute no more than a 5 percentage point uncertainty, i.e., the original fraction of the C₂H₅⁺ reactant ion intensity, assuming it yields only a single product in the reported values. Since there are no minor channels, the presence of C₂H₃⁺ has a small effect on the overall reported branching fractions.

sec-Propyl Cation. The propyl radical cation was prepared by ionizing isopropyl bromide in the supersonic source. Approximately 5% of the C₃H₇⁺ dissociated to C₃H₆⁺ upon injection into the flow tube. Because C₃H₆⁺ is a major product of the sec-propyl cation reaction with O₂ and is mass-coincident with C₂H₅⁺, the reaction rate constant was determined by injecting the ¹³C₂H₅⁺ (m/z = 44) form of the reactant ion. Given that the expected C₂H₅O⁺ product distribution is 33% C₂H₅O⁺ (m/z = 43) and 67% C₂H₃O⁺ (m/z = 44), then the I(¹³C₂H₅⁺) = I(m/z = 44) − 2I(m/z = 43). The reaction rate constant was determined using this corrected C₂H₅⁺ intensity. The product branching fractions were determined from the same ¹³C experiments as follows: I(C₂H₅O⁺) = 3I(¹²C₂H₅O⁺), I(HCO⁺) = I(¹²CH₃O⁺) + I(¹³CH₃O⁺), and I(CH₃O⁺) = I(¹²CH₃O⁺) + I(¹³CH₃O⁺), with the remaining C₂ products exhibiting only a single peak. Three determinations were averaged and yielded 16% CHO⁺, 14% CH₂O⁺, 64% C₂H₅O⁺, 5% C₂H₆O⁺, and 1% C₂H₇O⁺. The reaction products originating from C₃H₇⁺ have not been positively identified but can be deduced to be either CHO⁺ and/or C₂H₆O⁺, on the basis of the observed product distributions for the C₂H₅⁺ and s-C₂H₆⁺ (see below) reactant ions. Note that both C₂H₅⁺ and s-C₂H₆⁺ show a small amount of dissociation to C₂H₄⁺ upon injection into the flow tube and that only products common to both reaction systems can be possible reaction products of C₂H₅⁺ and O₂. The influence of the C₂H₅⁺ on the reported branching fractions has not been corrected for but constitutes no more than a 5 percentage point uncertainty (original fraction of the reactant ion intensity yielding a single product) in the reported values of the HCO⁺ and C₂H₅O⁺ product channels.

Previous theoretical studies at the Hartree-Fock and MP2 levels of theory on the character of the potential energy surface of the propyl cation concluded that there exist two global minima, that for the sec-propyl cation and that for the corner-protonated cyclopropane. These calculations showed that a minimum does not exist that corresponds to the n-propyl cation, which appears to be only a transition structure in the interconversion of the sec-propyl cation and the corner-protonated cyclopropane cation. According to these calculations, the n-propyl cation is 80.5 kJ/mol higher and the corner-protonated cyclopropane cation is 30 kJ/mol higher in energy than the sec-propyl cation structure. Our B3LYP/6-31G(d) calculations are consistent with these findings. Furthermore, experimental investigations of the interconversion of the propyl cation structures demonstrate rapid rearrangement to the sec-propyl cation form. A detailed study by Ausloos and co-workers showed that n-propyl cations isomerize intramolecularly to either isopropyl ions or protonated cyclopropane ions within 10⁻¹⁰ s. Rearrangement to the isopropyl ion is favored and increases in importance with increasing internal energy content of the ion. Mass spectrometric investigations suggest that the isomerization of the corner-protonated cyclopropane structure to the isopropyl structure requires 10⁻⁹ to 10⁻⁸ s. All of these isomerization times are much shorter than the approximately 1 ms it takes the ions to leave the source region and travel to the reactant inlet. Therefore, the reactivity shown in Table 1 for the propyl cation has been assigned to the s-C₃H₇⁺ isomer.
Gas-Phase Oxidation of Alkyl Ions C₆H₄₊⁺

To confirm this hypothesis, the propyl cation was also prepared by ionizing n-propyl bromide in the supersonic source. The kinetics measurements were performed using the ¹³C₂H₅⁺ ion and corrected for ¹³CCH₂O⁺ product as described in the experimental details using isopropyl bromide in the source. The product branching distribution was determined from the mass spectrum recorded with 100 SCCM of O₂, where no C₆H₆⁺ remains. As above, no correction for the products originating from C₆H₄⁺ (~5% of the original reactant ion intensity) was made. The reaction rate constants and the product distributions for the C₆H₇⁺ ions generated from n-propyl bromide are found to be nearly identical to those produced from isopropyl bromide. The minor differences observed in the branching ratios can be attributed to statistical deviations in the reproducibility of the measurements and small differences in the source and injection conditions. This result is consistent with the theoretical and experimental studies discussed above regarding the stability and isomerization processes of the C₆H₇⁺ ions, which indicate that only the s-C₆H₄⁺ isomeric form of the ion is present in our experiments.

**tert-Butyl Cation.** In pulsed ion cyclotron resonance (ICR) experiments, Shold and Ausloos observed that C₆H₄⁺ cations formed by electron impact ionization of isobutane, neopentane, 2,2-dimethylbutane, isobutyl halides, and tert-butyl halides all have the tertiary structure. Fragmentation of n-alkanes, 2-methylbutane, 3-methylpentane, n-butyl halides, and sec-butyl halides produce both s-C₆H₄⁺ and t-C₆H₄⁺, with the s-C₆H₄⁺ surviving without rearrangement for at least 0.1 s. However, in the case of the halides, a collision-induced isomerization of the s-C₆H₄⁺ to the t-C₆H₄⁺ was found to occur. The ICR experiments of Shold and Ausloos were conducted at pressures of ca. 10⁻⁶ Torr and observation times ranging from 10⁻³ to 0.5 s. The temperature in the analyzer cell was kept at 320 K, and the electron energy was varied between 10 and 25 eV.

On the basis of the Shold Ausloos results, the tert-butyl cation was prepared by electron impact ionization of tert-butyl chloride in the supersonic argon expansion. The reported reaction rate constant was measured by increasing the flow tube pressure to 0.64 Torr (throttling the roots pump) and providing a measured value of <3.4 × 10⁻¹² cm³ s⁻¹, which is at the detection limit of our experiments and therefore represents an upper limit. No reactivity of t-C₆H₄⁺ with O₂ was observed either, i.e., k < 3 × 10⁻¹¹ cm³ s⁻¹.

**sec-Butyl Cation.** The sec-butyl cation was prepared by ionizing n-butyl bromide in the supersonic source. Injection of C₆H₄⁺ into the flow tube yielded approximately 93% C₆H₅⁺, 5% C₆H₆⁺, and 2% C₆H₇⁺. The electron impact ionization of n-butyl bromide produces both s-C₆H₄⁺ and t-C₆H₄⁺, and collisions with halide molecules in the source region can convert s-C₆H₄⁺ to t-C₆H₄⁺. The kinetics plots with the C₆H₄⁺ cation exhibited curvature indicating the presence of more than one form of C₆H₄⁺. Using a large number of flow points and fitting the data as a double exponential with a nonlinear least-squares analysis program provides an estimate of the relative amounts of the two types of C₆H₄⁺ and a measure of the rate constant for the fast-reacting species. Figure 3 shows the normalized counts of the C₆H₄⁺ reactant ion plotted as a function of the ozone reactant concentration. The result of a single-exponential fit to the data yielded the dashed line associated with the rate constant designated kₒₐₒₒ. The single-exponential fit reproduces the data very poorly. However, a double-exponential fit provides a much better representation of the data. Free fitting several sets of data for the two rate constants yields a fast component with a rate constant of 8 × 10⁻¹¹ cm³ s⁻¹ and a slow component with a rate constant <4 × 10⁻¹² cm³ s⁻¹. No reactivity of either form of C₆H₄⁺ with O₂ was observed, i.e., k < 3 × 10⁻¹² cm³ s⁻¹, which is the detection limit of the experiment. It is assumed that the slower reacting component is the tert-butyl cation (ca. 67%) and the faster reacting component is sec-butyl cation (ca. 33%).

Additional insight into the relative amounts of the different forms of C₆H₄⁺ was explored using 2-methylbutane as the neutral reactant in hydride-transfer reactions, as done by Shold and Ausloos and Meot-Ner and Field. The tertiary and secondary forms of C₆H₄⁺ have markedly different rates for hydride transfer from 2-methylbutane (i-C₆H₁₃). On the basis of previous results, the hydride-transfer rate constants for the reactions

\[
\text{t-C₆H₄⁺ + (CH₃)₂CHCH₂CH₃ \rightarrow i-C₆H₁₀H + t-C₆H₁₁⁺ ,}
\]

\[
k_{298} = 2 \times 10⁻¹¹ \text{ cm}³ \text{ s}⁻¹ (5a)
\]

and

\[
\text{s-C₆H₄⁺ + (CH₃)₂CHCH₂CH₃ \rightarrow n-C₆H₁₀H + t-C₆H₁₁⁺ ,}
\]

\[
k_{298} = 4 \times 10⁻¹⁰ \text{ cm}³ \text{ s}⁻¹ (5b)
\]

differ by over an order of magnitude. Figure 4 shows a plot of the total C₆H₄⁺ reaction ion concentration as a function of 2-methylbutane reactant concentration. A biexponential fit of the data plotted in Figure 4 yields two rate constants of (4.9 ± 1.9) × 10⁻¹⁰ (35%) and (4.2 ± 1.4) × 10⁻¹¹ cm³ s⁻¹ (65%). These hydride-transfer rate constants are in good agreement with those reported previously, and this experiment confirms that approximately 35% of the ions formed under our conditions are s-C₆H₄⁺.

The product branching measurements are considerably more difficult than those of the reaction rate constant because most of the C₆H₄⁺ is the nonreactive tertiary form. Hence, the contributions of contaminant ions produced on breakup during injection, C₆H₄⁺ and C₆H₅⁺, are considerably larger compared to the products of the s-C₆H₄⁺ primary ion. The major products observed are HCO⁺ and C₅H₅O⁺, and C₅H₆O⁺ and C₅H₇O⁺ are minor products. As shown in Table 1, the reaction of C₆H₄⁺ with O₂ produces HCO⁺ and C₅H₅O⁺, and C₅H₆O⁺ is unreactive with O₂. Since C₅H₅O⁺ and C₅H₆O⁺ were not observed in the experiments discussed above that contain the C₅H₅⁺ impurity ion, these products most likely originate from the reaction of s-C₆H₄⁺ with O₂. Given this level of uncertainty, the only conclusions that can be drawn are that HCO⁺ and C₅H₅O⁺ are major products and that C₅H₆O⁺ and C₅H₇O⁺ are minor products produced in the reaction of s-C₆H₄⁺ with O₂.

The production of C₅H₇O⁺ in the reaction of s-C₆H₄⁺ with O₂ is exothermic and is a conceivable product channel. The reaction for such a process is given below:

\[
\text{s-C₆H₄⁺ + O₂ \rightarrow C₅H₆O⁺ + CH₄ + O₂ ,}
\]

\[
\Delta H = -393 \text{ kJ/mol (6)}
\]

Since C₅H₇O⁺ is mass-coincident with C₆H₄⁺, the ¹³C₂H₅⁺ (m/z = 58) form of the reactant ion was injected into the flow tube. Assuming a statistical ¹³C product distribution, approximately 25% of the C₅H₅O⁺ product ion produced should be C₅H₅O⁺ (m/z = 57). Product branching fraction measurements taken at high resolution resulted in barely detectable amounts of C₅H₆O⁺ (m/z = 55), ¹³C₅H₆O⁺ (m/z = 56), and C₅H₇O⁺ (m/z = 57) produced in the reaction. Trace amounts of ions at m/z = 31 and m/z = 32 were also observed and have
been assigned to CH$_3$O$^+$ (m/z = 31) and CH$_2$OH$^+$ (m/z = 32). Note that the CH$_3$O$^+$, CH$_2$OH$^+$, and CH$_2$O$^+$ product ions could also originate from reaction of the C$_2$H$_5^+$ breakup ion (5%) reacting with O$_2$. Therefore, the CH$_3$O$^+$, CH$_2$OH$^+$, and CH$_2$O$^+$ product ions are listed as trace product ions in Table 1.

C$_2$H$_5^+$ Cation. The C$_2$H$_5^+$ radical cation was prepared by ionizing 2-chloro-2-methylbutane. The reported reaction rate constant for the C$_2$H$_5^+$ ion formed after reaction with O$_2$ is $3 \times 10^{-13}$ cm$^3$ s$^{-1}$ and with O$_3$ is $4 \times 10^{-12}$ cm$^3$ s$^{-1}$. The tertiary form of the C$_2$H$_5^+$ cation is the most stable form of this carbocation, and electron impact ionization of the 2-chloro-2-methylbutane ion precursor is expected to produce this ion exclusively. The t-C$_2$H$_5^+$ cation is the most stable cation studied in this series, and, like the exceptionally stable t-C$_4$H$_9^+$ cation, it is not oxidized by either O$_2$ or O$_3$, even though several very exothermic products are available.

IV. Discussion

Cacace and co-workers first experimentally detected the elusive protonated ozone molecule, HO$_2^+$, in 1994 by reacting ozone with CH$_4^+$. The present study shows that protonated ozone is produced efficiently by the reaction of HCO$^+$ with O$_2$ via a fast proton-transfer reaction, as listed in Table 1. The high efficiency is expected because the reaction is exothermic and spin-allowed, with singlet reactants forming singlet products. There are several other examples of efficient exothermic proton-transfer reactions in the literature which have been discussed in detail.

In the early stages of combustion, O$_2$ is in large abundance, and even limited reactivity of hydrocarbon ions with O$_2$ could prove to be an important mechanism in these environments. However, none of the C$_n$H$_{2n+1}^+$ ($n = 1–5$) alkyl ions exhibited any appreciable reactivity with O$_2$. All of these cations are closed-shell singlet molecules, and O$_2$ is triplet in its ground state. The production of the OH radical is spin-allowed and is exothermic by over 90 kJ/mol for the C$_n$H$_{2n+1}^+$ ($n = 1–4$) alkyl ions. For example,

$$s$-C$_2$H$_5^+$($^1\text{A}$) + O$_2$(($^3\Sigma$) $\rightarrow$ CH$_2$C(OH)CH$_3^+$($^2\text{A}^\prime$) + OH($^2\Pi$)\hspace{1cm} (7)$$

is spin-allowed and exothermic by 99 kJ. The reaction products listed in reaction 7 require significant rearrangement, possibly through a strongly attractive intermediate complex. Several other exothermic reaction channels, requiring less rearrangement, are available but are spin-forbidden, namely,

$$s$-C$_2$H$_7^+$ + O$_2$ $\rightarrow$ CH$_3$O$^+$ + C$_2$H$_4$O, $\Delta H = -267$ kJ/mol \hspace{1cm} (8a)$$

$$\rightarrow$ C$_2$H$_5$O$^+$ + CH$_3$OH, $\Delta H = -249$ kJ/mol \hspace{1cm} (8b)$$

$$\rightarrow$ HCO$^+$ + C$_2$H$_6$O, $\Delta H = -209$ kJ/mol \hspace{1cm} (8c)$$

It is not necessary that a reaction proceed in a manner that allows for spin conservation. There are several ion–molecule reactions that have been observed to be fast despite violating spin conservation. Examples include

$$O^+$($^3\Sigma$) + CO$_2$(($^\Sigma$) $\rightarrow$ O$_2^+$($^1\Pi$) + CO($^\Sigma$)\hspace{1cm} (9)$$

which proceeds at the collision rate,\(^{49,50}\) the reaction of CH$_3^+$ with oxygen atoms,\(^{1,47}\)

$$\text{CH}_3^+($^1\text{A}) + O_2($^3\Sigma$) $\rightarrow$ HCO$^+($^1\text{A}$) + \text{H}_2($^3\Sigma$)\hspace{1cm} (10)$$

with a measured rate constant of $4.4 \times 10^{-10}$ cm$^3$ s$^{-1}$, a number of positive-ion charge-transfer reactions where the rate constant exceeds the spin-conserving weighted collision rate constant,\(^{51}\) as well as a number of hydrocarbon ion reactions with N($^3\Sigma$) atoms.\(^{52}\)

Ab initio calculations regarding C$_2$H$_5^+$ and s-C$_2$H$_7^+$ reacting with O$_2$ at the B3LYP/6-31G(d) level of theory set suggest that these alkyl ions yield relatively weak complexes with O$_2$ with elongated C–O bond distances, namely,

$$s$-C$_2$H$_5^+$($^1\text{A}$) + O$_2$(($^3\Sigma$) $\rightarrow$ [OOC$(_2$H$_2^+$)$^*$($^2\text{A}^\prime$)], $\Delta H = -24$ kJ/mol \hspace{1cm} (11)$$

and

$$s$-C$_2$H$_7^+$($^1\text{A}$) + O$_2$(($^3\Sigma$) $\rightarrow$ [OOCH(CH$_3$)CH$_3^+$)$^*$($^2\text{A}^\prime$)], $\Delta H = -13$ kJ/mol \hspace{1cm} (12)$$

The minimum calculated C–O bond distance for these complexes is ca. 2.6 Å with further C–O approach being repulsive, independent of the orientation of O$_2$ relative to the cation. These calculations suggest that no C–O bond can be formed on the triplet surface in these complexes, and that the singlet state required for bond formation is about 109 kJ/mol higher in energy. In addition, hydrogen atom and proton abstraction, which are spin-allowed, are not at all favorable processes due to large endothermicities. For example, the reactions involving the ethyl cation are

$$C_2H_5^+($^1\text{A}$) + O_2($^3\Sigma$) $\rightarrow$ OOH($^2\text{A}^\prime$) + C$_2$H$_4^+($^2\text{B}$_2$g$)$, $\Delta H = 166$ kJ/mol \hspace{1cm} (13a)$$

and

$$C_2H_7^+($^1\text{A}$) + O_2($^3\Sigma$) $\rightarrow$ OOH($^2\text{A}^\prime$) + C$_2$H$_6^+($^2\text{B}$_2$g$)$, $\Delta H = 248$ kJ/mol \hspace{1cm} (13b)$$

Therefore, no appreciable O$_2$ oxidation chemistry can be foreseen at 300 K for these species because our quantum chemical calculations predict that the approach of the triplet oxygen molecule toward the hydrocarbon cation is strongly repulsive and that the singlet/triplet crossing is not likely to be an important factor at thermal energy. This theoretical picture is consistent with the present experimental observations, which places an upper bound to the reactivity of O$_2$ with hydrocarbon ions at <5 $\times$ 10$^{-12}$ cm$^3$ s$^{-1}$. Scott et al.\(^{7}\) observed that C$_2$H$_4^+$ also did not react with triplet atomic oxygen, even though the product channel HCO$^+$ + CH$_3$ is exothermic by 399 kJ/mol. These authors suggested that the barriers on the potential energy surface are too high for the extensive rearrangement required. Ozone, on the other hand, is able to produce these products in its reaction with C$_2$H$_5^+$, where this channel is exothermic by 294 kJ/mol (Table 1).

Ozone is a singlet in its ground state, and ab initio calculations at the B3LYP/6-31G(d) level of theory indicate that reactant complexes can be formed, decreasing in stability with the size
Gas-Phase Oxidation of Alkyl Ions \( \text{CH}_n\text{H}_{2n+1}^+ \)

**Figure 5.** Initial reactant complexes for alkyl cations with ozone. Geometries were optimized at the B3LYP/6-31G(d) level of theory, bond distances are in Å, and bond angles are in degrees. Interaction energies are in kJ mol\(^{-1}\) with respect to isolated alkyl cations and ground-state ozone.

![Image of alkyl cation complexes](image)

\[
\begin{align*}
\text{CH}_3\text{O}^+ & \quad \text{O}_2^+ \quad \rightarrow \quad \text{[CH}_3\text{O}_2]^+ \\
\Delta H &= -248 \text{ kJ mol}^{-1} \quad (1a)
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{H}_3^+ & \quad \text{O}_2\text{(1A)} \quad \rightarrow \quad \text{[CH}_2\text{CH}_2\text{O}_2]^+ \quad (1a')
\Delta H &= -144 \text{ kJ mol}^{-1} \quad (1b)
\end{align*}
\]

\[
\begin{align*}
s-\text{C}_3\text{H}_7^+ & \quad \text{O}_2\text{(1A)} \quad \rightarrow \quad \text{[CH}_3\text{CH}_2\text{O}_2\text{CH}_3]^+ \quad (1a'')
\Delta H &= -60 \text{ kJ mol}^{-1} \quad (1c)
\end{align*}
\]

\[
\begin{align*}
s-\text{C}_3\text{H}_7^+ & \quad \text{O}_2\text{(1A)} \quad \rightarrow \quad \text{[CO}_3\text{(CH}_3)^2]^+ \quad (1a''')
\Delta H &= -55 \text{ kJ mol}^{-1} \quad (1d)
\end{align*}
\]

\[
\begin{align*}
t-\text{C}_3\text{H}_7^+ & \quad \text{O}_2\text{(1A)} \quad \rightarrow \quad \text{[CO}_3\text{(CH}_3)_2]^+ \quad (1a''''')
\Delta H &= -10 \text{ kJ mol}^{-1} \quad (1e)
\end{align*}
\]

All of these systems form a complex with a C–O distance of about 1.5 Å with no activation energy required (see Figure 5). From these complexes, rearrangement can occur, leading to several different spin-conserving products. In addition, the large exothermicity of the available reaction channels permits breaking of C–H/C–C bonds, favoring the production of smaller fragments, consistent with the experimental observations. These complexes are characterized by weak O–H–\(\beta\)-hydrogen interactions; \(\alpha\)-hydrogens are not in the position to interact with the terminal oxygen atom in the initial complexes. The presence of \(\alpha\)-hydrogens is therefore not a factor in the relative stabilities of these complexes. Drastic energetic destabilization of these initial complexes occurs when additional alkyl groups are added to the cationic carbon atom, leaving the tert-butyl cation/ozone complex with only a small binding energy of 10 kJ/mol.

A major product for all of the primary and secondary alkyl cations is HCO\(^+\). The reaction pathway for this product channel could be traced computationally for the methyl cation. In the case of \(\text{CH}_3^+\), a straightforward mechanism evolved involving nucleophilic addition of ozone to \(\text{CH}_3^+\), early O–O \(\text{C}_2\text{H}_4\) cleavage in the transition state with a low barrier of only 50 kJ/mol, and subsequent hydrogen elimination to yield the highly exothermic products HCO\(^+\) + \(\text{H}_2 + \text{O}_2\). The calculations indicate that \(\text{H}_2\text{O}_2\) is not formed in this channel and that the ethyl, sec-propyl, and sec-butyl cations proceed via a similar mechanism, as illustrated in Figure 6. For \(\text{C}_2\text{H}_3^+\), HCO\(^+\) and \(\text{C}_2\text{H}_4\text{O}^+\) are produced from the elimination of \(\text{CH}_2\text{H}_4\) and \(\text{H}_2\text{H}_4\) respectively, from the \[\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3\] intermediate. Similarly, HCO\(^+\) and \(\text{C}_2\text{H}_4\text{O}^+\) are produced from the elimination of \(\text{C}_2\text{H}_4\) and \(\text{CH}_2\text{H}_4\) respectively, from the \[\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3\text{CH}_2\text{H}_4\] intermediate. On the basis of the same mechanism, the \[\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3\text{CH}_2\text{H}_4\] intermediate produced in the reaction of \(\text{C}_2\text{H}_4^+\) is expected to produce HCO\(^+\), \(\text{C}_2\text{H}_4\text{O}^+\), and \(\text{C}_2\text{H}_5\text{O}^+\) with the elimination of \(\text{C}_2\text{H}_5\), \(\text{C}_2\text{H}_6\) and \(\text{CH}_4\), respectively. This mechanism is in qualitative agreement with the branching fractions observed in these reactions, as shown in Table 1, although only a barely detectable amount of \(\text{C}_2\text{H}_5\text{O}^+\) reaction product is observed in the sec-butyl cation reaction with ozone, perhaps due to steric constraints. This mechanism is similar to that proposed by Mendes et al.\(^{11}\) on the basis of their ab initio calculations of O-atom-transfer reactions of ozone with radical cations of pyridines, alkyl halides, and halogen cations.
A possible explanation for the apparent lack of reactivity of $\text{r-C}_2\text{H}_5^+$ and $\text{r-C}_3\text{H}_7^+$ is that the initial complex with ozone is not formed. The calculations find that the stability of the complex decreases from 248 to 10 kJ/mol on going from $\text{CH}_3^+$ to $\text{r-C}_2\text{H}_5^+$. Therefore, it seems likely that the lack of reactivity of the alkyl ions involving a tertiary carboxation may be attributed to a greatly reduced O$_3$ binding energy.

V. Summary

Numerous alkyl cations and HCO$^+$ reacting with O$_2$ and O$_3$ were studied at 300 K in a selected-ion flow tube coupled to a novel ozone source. The HCO$^+$ cation exhibits no reactivity with O$_2$, but the reaction of HCO$^+$ with O$_3$ proceeds at the collision rate via proton transfer to produce HCO$_2^+$. None of the alkyl carboxations studied showed any measurable bimolecular reactivity, $k < 5 \times 10^{-13}$ cm$^3$ s$^{-1}$, with O$_3$, despite the availability of reaction channels with exothermicities of several hundred kilojoules per mole. The ab initio calculations indicate that the O$_2$ reaction systems form weak complexes with large C–O bond distances on the lowest energy triplet potential energy surface which are repulsive at smaller distances. Access to the singlet surface is required for bond formation; however, this surface is not accessible at thermal energies.

For reactions with O$_3$, the total reaction rate constants for the alkyl carboxations decrease dramatically as the order of the reactant carboxations increases, as shown in Figure 2 and listed in Table 1. This finding is consistent with ab initio calculations which show that the initial alkyl cation/ozone complexes are largely destabilized when alkyl groups are added to the cationic center. The primary carboxations CH$_3^+$ and C$_2$H$_5^+$ react at 100% and 46% of the collision rate given by the Su–Chesnavich equation, respectively. The secondary s-C$_3$H$_7^+$ and s-C$_4$H$_9^+$ carboxations react with O$_3$ at 19% and 7% of the collision rate, respectively. The tertiary carboxations t-C$_4$H$_9^+$ and t-C$_5$H$_7^+$ were found to be unreactive with O$_3$, $k < 5 \times 10^{-12}$ cm$^3$ s$^{-1}$, which is the detection limit of our apparatus using this ozone source. A straightforward mechanism was discussed involving initial complex formation involving the primary or secondary alkyl cation with O$_3$, followed by early O–O$_2$ cleavage in the transition state, and finally hydrogen and alkane elimination to yield the highly exothermic products listed in Table 1. An explanation for the lack of reactivity of $\text{t-C}_4\text{H}_9^+$ and $\text{t-C}_5\text{H}_7^+$ is that the initial complex with ozone is not formed because of a much reduced O$_3$ binding energy. Details of theoretical studies of the potential energy surfaces of the present systems will be published separately.

The only other positive organic ions reactions with ozone previously studied used a pentagonal quadrupole mass spectrometer at nonthermal (ca. 1 eV) collision energies, and thermal rate constants were not reported as done here. In addition, alkyl ions were not part of that study. Therefore, the values reported in Table 1 represent the most self-consistent and complete set of reaction rate and branching fraction data reported to date and, on the basis of the above considerations, are recommended for use in modeling applications requiring thermal rate data near 300 K.

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References and Notes

Gas-Phase Oxidation of Alkyl Ions C\textsubscript{n}H\textsubscript{2n+1}^+ 
