

Reactions of the Oxygen Radical Cation

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The atomic oxygen cation, O^+ , is a highly reactive substance important to atmospheric, interstellar, and, combustion chemistry. In fact, it makes up over 90% of the ionic constituents at low-earth orbit elevations.¹ Despite this abundance, the reactions of this ion have not been studied comprehensively.

The experiments were carried out using the flowing afterglow-selected ion flow tube (FA-SIFT). O^+ is generated by ionization of carbon monoxide gas through use of the electron impact ionizer. The oxygen cations are then mass-selected using a quadrupole mass filter and injected into the reaction flow tube where they are thermalized through collisions with He buffer gas, and allowed to react with molecular reagents introduced downstream in the flow tube. The rate constants are measured by monitoring the decrease of the reactant ion signal using a quadrupole mass filter as a function of reaction distance. Branching ratios are determined by plotting the percentage of product ion distribution against the reaction distance and extrapolating back to zero reaction distance.

A preliminary study of the reactions of O^+ with the methyl halogens, and a series of fully fluorinated compounds has been completed in this lab. Reaction rate constants and branching ratios were experimentally determined for each of the halogenated methanes: CH_3F , CH_3Cl , CH_3Br , and CH_3I . Reactions proceed very fast with efficiency above 50% of the collision rates calculated using parameterized trajectory theory. Trends in branching ratio data show a proclivity for the formation of the methyl cation, CH_3^+ . The fluorinated compounds under study includes CF_4 , SF_6 , and SF_5CF_3 . Although fully fluorinated species are very stable, the high internal energy of the oxygen cation prompted these reactions to occur quickly with rate constants on the order of $10^{-9} \text{ cm}^3 \text{ s}^{-1}$. For each reaction, the oxygen atom ended up on the neutral species.

Additionally branching ratios and reaction rate constants were determined for the reactions of O^+ with a series of organic compounds. These systems were studied to get an idea for the general reactivity of the cation with different functional organic groups. Reactions of the oxygen cation with acetaldehyde, acetic acid, acetone, benzene, dimethyl ether, methanol, methyl formate, and pyridine were characterized through this study. Due to the high internal energy of the oxygen cation, high energy ionic products were observed. Additionally, these reactions occurred quickly and proceeded at collision rate for some species.

References

(1) Li, X.; Huang, Y.-L.; Flesch, G.D.; Ng, C.Y. *J. Chem. Phys.* **1997**, 106(3), 928