FUNDAMENTAL STUDIES ON THE CHEMICAL MECHANISM OF FLAME EXTINGUISHMENT BY HALONS


Center for Global Environmental Technologies
New Mexico Engineering Research Institute
The University of New Mexico
Albuquerque, New Mexico 87131-1376

J. R. Grover
Chemistry Department
Brookhaven National Laboratory
Upton, NY 11973

*Also, Department of Chemistry
The University of New Mexico
Albuquerque, NM 87131

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INTRODUCTION

Although halon fire extinguishants have been in use for many years because of their favorable properties of effectiveness, cleanliness, and low toxicities, little is known about the detailed chemical mechanisms of their flame extinguishment. The overall reaction of a halon in flames can be illustrated with Halon 1301 (CF$_3$Br) as

$$\text{CF}_3\text{Br} \ (g) + 2\text{H}_2\text{O} \ (g) \rightarrow \text{CO}_2 \ (g) + \text{HBr} \ (g) + 3 \text{HF} \ (g)$$

where $\Delta H^{\circ \text{rxn}} = -35.2$ kcal mol$^{-1}$.

It has been believed for some time that the mechanism for this reaction involves an initial reaction of atomic hydrogen with CF$_3$Br to give HBr, which then catalyzes recombination of H, thus removing chain branching radicals from the flame. These conclusions were based on a wide range of experimental and theoretical studies (Reference 1). Furthermore, the implication of halons in stratospheric ozone depletion and consequent mandatory phaseout under the Montreal Protocol and the Clean Air Act Amendments of 1990 dictates searches for alternative extinguishing agents that are effective, clean, nontoxic, and environmentally sound (Reference 2).

The purpose of this paper is to report the low stability of the radical cation CF$_3$Br$^+$ and to examine possible implications for flame suppression. Specifically, a molecular beam of cold CF$_3$Br was prepared by free-jet expansion of a mixture of CF$_3$Br in Ar. Photoionization efficiency (PIE) functions were determined by mass spectrometric analysis of the parent ion, CF$_3$Br$^+$, and fragments under collisionless conditions. From the observed thresholds, onsets and other distinct features of the PIE curves, detailed information on ionization potentials, appearance potentials, heats of formation, bond energies, modes of dissociation, and involvement of excited states was determined (Reference 3). The results call attention to some striking properties of CF$_3$Br$^+$ which may contribute to the desirable extinguishment features of halons.
EXPERIMENTAL

The experimental apparatus and the techniques for determining cluster distributions have been presented elsewhere (References 4 through 9). The apparatus, shown in Figure 1, is a photoionization mass spectrometer equipped with a skimmed and further collimated jet source for the molecular beam. It uses the tunable photon beam available from line U11 of the 750 MeV storage ring at the National Synchrotron Light Source at Brookhaven National Laboratory. The optical resolution of the monochromator was set at 3 Å over the wavelength range of 450 to 1350 Å used in these experiments.

Molecular beams containing the CF$_3$Br target molecule were generated by room temperature (23 ± 1 °C) expansions of either neat CF$_3$Br or premixed CF$_3$Br and Ar in a 9:100 ratio. The mixtures were prepared quantitatively in large steel cylinders and were mixed thoroughly before use. These samples were expanded sufficiently low stagnation pressures that cluster formation was insignificant.

RESULTS

A mass spectrum of CF$_3$Br produced by ionization of a molecular beam of neat CF$_3$Br at a nozzle stagnation pressure of 97 torr using 584 Å (21.22 eV) light is shown in Figure 2. The parent ion peak appears weakly at m/e 148, 150 (CF$_3$$_{79}$Br$^+$, CF$_3$$_{81}$Br$^+$) and fragments at m/e 129, 131 (CF$_2$$_{79}$Br$^+$, CF$_2$$_{81}$Br$^+$); 79, 81 (79Br$^+$, 81Br$^+$); 69 (CF$_3$$^+$), and 50 (CF$_2$$^+$) are also found. The inset in Figure 3 shows only background signal in the range of m/e 160-230 amu, indicating that CF$_3$Br clusters were not formed. It is evident that production of CF$_3$$^+$ dominates the mass spectrum at this ionization energy.

The PIE function for production of CF$_3$Br$^+$ in the threshold region (980 - 1120 Å, 11.0-7-12.65 eV) and over a broad energy range (450-1150 Å, 10.78-27.55 eV) is given in Figure 3. The PIE curve for the threshold region (1018-1080 Å, 11.48-12.18 eV) for
Figure 1. A Schematic Diagram of the Photoionization Mass Spectrometer.
Figure 2. The Mass Spectrum of Neat CF$_3$Br at 584 Å (21.22 eV) Taken at a Nozzle Pressure of 97 Torr. The Inset Shows an Expanded Scale of the m/e = 160-230 Region.
Figure 3. a) CF$_3$Br$^+$ Photon Yield Curve Over the Threshold Range of 980-1120 Å. The Observed Intensities are of the Ion CF$_3$Br$^+$ Produced by Direct Ionization of Neat CF$_3$Br at 449 Torr Nozzle Pressure in 0.51 Å Intervals. No LiF Filter was Used and Corrections for Second Order Contributions Have Not Been Applied. b) A Broad Wavelength Scan, 450-1150 Å, of the CF$_3$Br$^+$ PIE Taken in 2 Å Intervals.
production of \( \text{CF}_3^+ \) from \( \text{CF}_3\text{Br} \) is displayed in Figure 4. The ionization and appearance potentials and heats of formation derived from them are collected in Table 1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ionization Energy, eV</th>
<th>( \Delta H^0_{\text{m}} ) (g)</th>
<th>( \Delta H^0_{\text{f}} ) (g)</th>
<th>( \Delta H^0_{\text{r}} ) (g)</th>
<th>( \Delta H^0_{\text{r}} ) (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CF}_3\text{Br} )</td>
<td>11.36</td>
<td>-155 k0.6 (11)</td>
<td>107 k0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>--</td>
<td>28.189 (12)</td>
<td></td>
<td>300.6 (12)</td>
<td></td>
</tr>
<tr>
<td>( \text{CF}_3 )</td>
<td>11.85</td>
<td>-110 (13)</td>
<td></td>
<td>95.4 (13)</td>
<td></td>
</tr>
</tbody>
</table>

**DISCUSSION**

The PIE wavelength scan of \( \text{CF}_3\text{Br}^+ \) from \( \text{CF}_3\text{Br} \), Figure 3, is striking. The ion yield rises sharply from threshold at 1091 Å = 11.36 eV to peak near 1050 Å as the wavelength decreases. From here to 450 Å, the shortest wavelength used in this study, the PIE function remains low while exhibiting a few structured features. This behavior is highly atypical. Much more common is a sharp rise at threshold followed shortly by a plateau to shorter wavelengths, then a large increase in ion yield reaching a maximum near 700 Å, then gradually decreasing with decreasing wavelength. Even with the optical resolution in this experiment, some evidence of vibrational structure in \( \text{CF}_3\text{Br}^+ \) should appear on the initial rise from threshold (Reference 4). The reason for the unusual character of the \( \text{CF}_3\text{Br}^+ \) PIE is evident in Figure 4, which shows the function for...
Figure 4. CF$_3^+$ PIE Curve Over the Range 1010-1080 Å. The Observed Intensities of the Ion CF$_3^+$ are from Direct Ionization of CF$_3$Br in a 1:20 Mixture of CF$_3$Br + O$_2$ at 604 Torr Nozzle Pressure and are Taken in 1 Å Intervals. No LiF Window was Used and the Nozzle Temperature was 1.1°C.
producing $\text{CF}_3^+$ from $\text{CF}_3\text{Br}$. The appearance potential of $\text{CF}_3^+$ is at $1046 \pm 3 \, \text{Å} = 11.85 \pm 0.03 \, \text{eV}$, the energy of the first (low energy) peak in Figure 3. From this onset the yield of $\text{CF}_3^+$ increased dramatically, while the production of parent ion $\text{CF}_3\text{Br}^+$ ceases to increase further at higher ionization energies. Therefore, the PIE function for $\text{CF}_3\text{Br}^+$ is dominated by fragmentation,

$$\text{CF}_3\text{Br}^+ \rightarrow \text{CF}_3^+ + \text{Br}$$

The difference

$$\Delta P(C\text{F}_3) \cdot \Delta P(\text{CF}_3\text{Br}) = 0.49 \, \text{eV} = 11 \, \text{kcal mol}^{-1}$$

is the dissociation energy of the C-Br bond in $\text{CF}_3\text{Br}^+$. This value is extremely small and it means that even in the vibrationless state of the radical cation the $\text{CF}_3^+$ and Br are not held together by a chemical bond, but only by ion-induced dipole attractions. In contrast, the C-Br bond in neutral $\text{CF}_3\text{Br}$ is 71.7 kcal mol$^{-1}$, based $\Delta H_{f,298}^{0}(\text{CF}_3\text{Br}) = 155.0 \, \text{kcal mol}^{-1}$, $\Delta H_{f,298}^{0}(\text{CF}_3) = -110 \, \text{kcal mol}^{-1}$, and $\Delta H_{f,298}^{0}(\text{Br}) = 26.74 \, \text{kcal mol}^{-1}$ (Reference 10). This conclusion about the nature of the C-Br bond in $\text{CF}_3\text{Br}^+$ is supported by MOPAC (Reference 11) calculations which show that only a very weak association exists between planar $\text{CF}_3^+$ and a neighboring Br atom. Furthermore, the C-Br bond distance has increased enormously from the typical separation of 1.94 Å, in covalent molecules to 3.1 Å, in $\text{CF}_3\text{Br}^+$. In other words, even at the ionization threshold $\text{CF}_3\text{Br}^+$ is a free Br atom loosely associated with the stable $\text{CF}_3^+$ cation. When the internal energy of this $\text{CF}_3^+ \cdot \text{Br}$ complex exceeds the binding energy of 11 kcal mol$^{-1}$, rapid dissociation to $\text{CF}_3^+$ and Br occurs and very few complexes survive long enough to reach the detector. That is, their lifetimes are less than 10 μs. These features strongly suggest that $\text{CF}_3\text{Br}^+$ radical cations be considered as a possible source of traps for O, OH, or H free radicals in flames, or as the catalyst for recombination reactions.
At least two possible routes to involvement of ions exist. First, consider a chemiionization reaction between $\text{CF}_3\text{Br}$ and a free radical, $\text{R}^\cdot$, that proceeds with no activation barrier:

$$\text{CF}_3\text{Br} + \text{R}^\cdot \rightarrow \text{CF}_3^+ + \text{BrR} + e$$

The driving force for this reaction would be the stability of $\text{CF}_3^+$. The most likely free radical is atomic hydrogen. Using the standard heats of formation at (298 K) for $\text{CF}_3\text{Br}$ (-155.0 kcal mol$^{-1}$), $\text{H}$ (51.626 kcal mol$^{-1}$), $\text{CF}_3$ (95.4 kcal mol$^{-1}$), and $\text{HBr}$ (-8.70 kcal mol$^{-1}$) (Reference 10), we calculate that this reaction is endothermic by 190 kcal mol$^{-1}$. Therefore, even if no activation barrier is present, this reaction is extremely slow and cannot contribute to radical chain termination. Radicals other than $\text{H}^\cdot$ give even more highly endothermic heats of reaction.

Another possibility is reaction of $\text{CF}_3\text{Br}$ with $\text{CHO}^+$, the most abundant cation in flames (Reference 12). $\text{CHO}^+$ is probably formed by chemiionization in the reaction

$$\text{CH} + \text{O} \rightarrow \text{CHO}^+ + e$$

which is exothermic by 4.6 kcal mol$^{-1}$ at 298 K. One reaction that can ultimately lead to interference with the chain branching step in flames is

$$\text{CHO}^+ + \text{CF}_3\text{Br} \rightarrow \text{CO} + \text{HBr} + \text{CF}_3^+$$

On the basis of standard heats of formation at 298 K of $\text{CHO}^+$ (197.3 kcal mol$^{-1}$), $\text{CF}_3\text{Br}$ (-155.0 kcal mol$^{-1}$), $\text{CO}$ (-110.52 kcal mol$^{-1}$), $\text{HBr}$ (-8.70 kcal mol$^{-1}$), and $\text{CF}_3^+$ (95.1 kcal mol$^{-1}$), this reaction is exothermic by 66.1 kcal mol$^{-1}$. The $\text{HBr}$ thus formed may inhibit the branching steps by catalysis of the H-atom recombination process.
\[ \text{HBr} + \text{H} \rightarrow \text{H}_2 + \text{Br} \]
\[ \text{Br} + \text{H} \rightarrow \text{HBr} \]

The reaction suggested here is complex, probably proceeding by proton transfer from \( \text{CHO}^+ \) to \( \text{CF}_3\text{Br} \), and driven by the high stability of the \( \text{CO} \) product molecule. This possible mechanism should be examined more carefully.

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