FUNDAMENTAL STUDIES ON THE CHEMICAL MECHANISM OF FLAME EXTINGUISHMENT BY HALONS

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Presented at:
First Halon Alternative Working Conference
Albuquerque Hilton Hotel
April 30 - May 1, 1991
Albuquerque, New Mexico 87110

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_3Br) as

$$CF_3Br\ (g) + 2H_2O\ (g) - CO,\ (g) + HBr\ (g) + 3\ HF\ (g)$$

where ΔH°_{298} (rxn) = -35.2 kcal mol''.

It has been believed for some time that the mechanism for this reaction involves an initial reaction of atomic hydrogen with CF_3Br 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_3Br^+ and to examine possible implications for flame suppression. Specifically, a molecular beam of cold CF_3Br was prepared by free-jet expansion of a mixture of CF_3Br in Ar. Photoionization efficiency (PIE) functions were determined by mass spectrometric analysis of the parent ion, CF_3Br^+, 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_3Br^+ 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_3Br target molecule were generated by room temperature (23 ± 1 °C) expansions of either neat CF_3Br or premixed CF_3Br 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_3Br produced by ionization of a molecular beam of neat CF_3Br at a nozzle stagnation pressure of 97 torr using 584 ***8,*** (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 ($^{79}Br^+$, $^{81}Br^+$); 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_3Br 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_3Br^+ 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

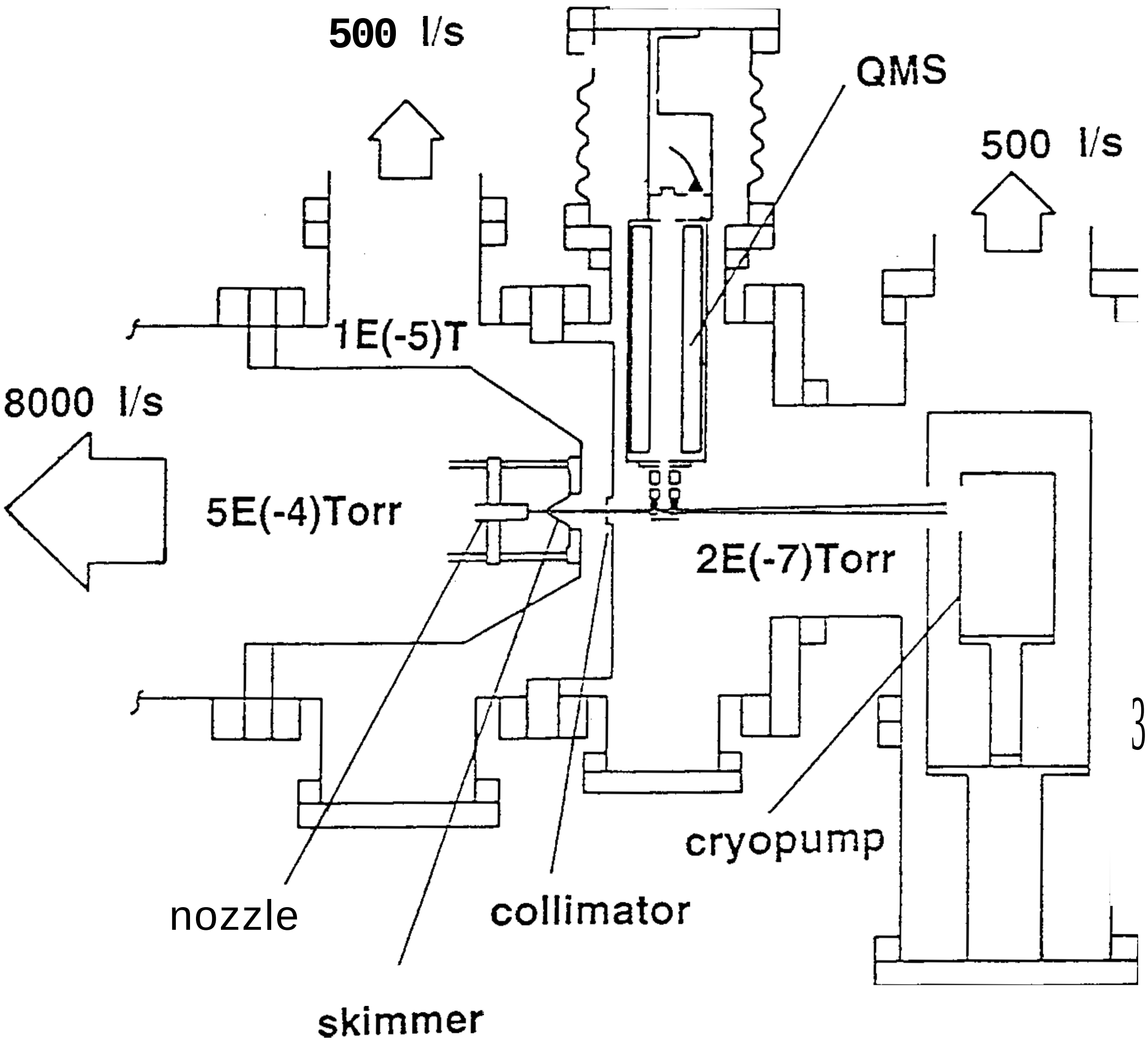

Figure 1. A Schematic Diagram of the Photoionization Mass Spectrometer.

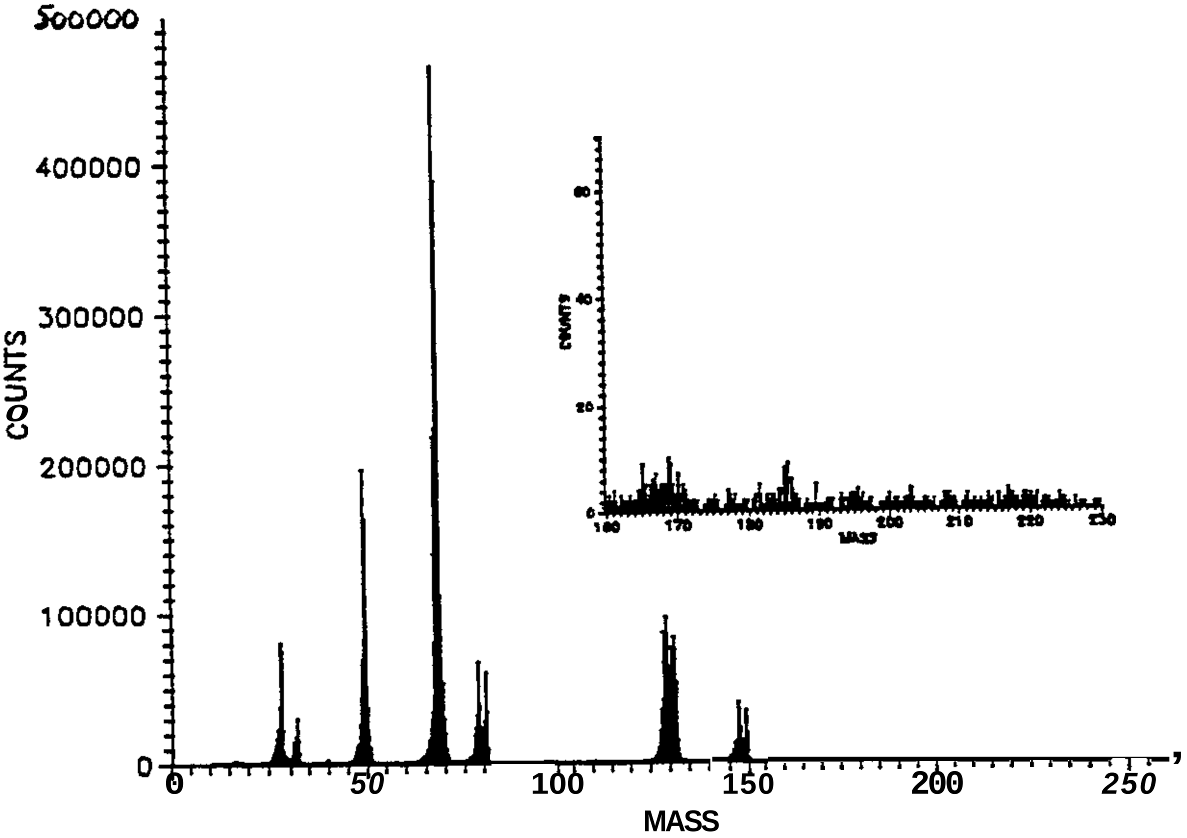

Figure 2. The Mass Spectrum of Neat CF_3Br at **584 Å** (21.22 eV) Taken at a Nozzle Pressure of 97 Torr. The Inset Shows an Expanded Scale of the m/e = 160-230 Region.

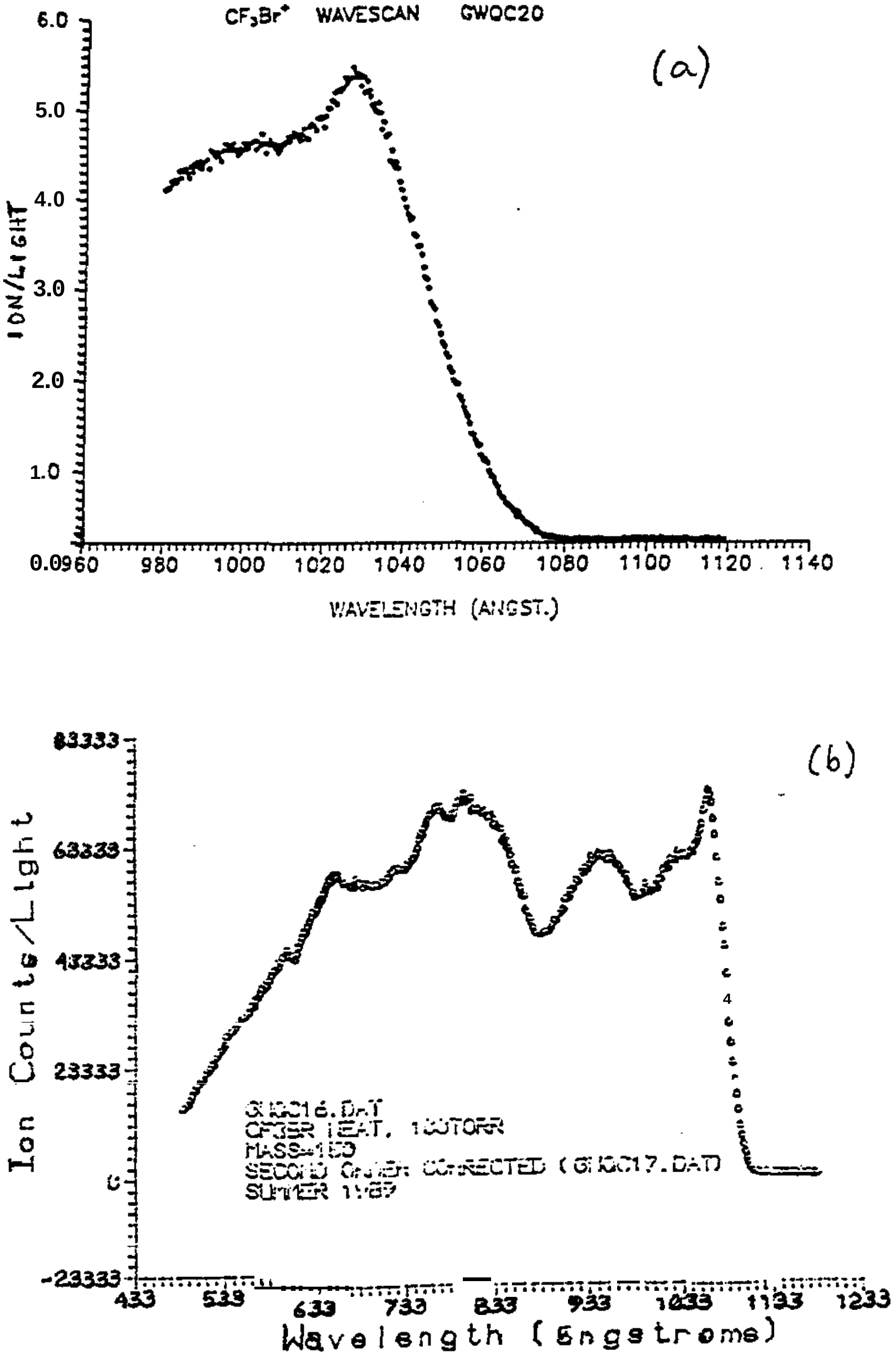

Figure 3. a) CF_3Br^+ Photon Yield Curve Over the Threshold Range of 980-1120 Å. The Observed Intensities are of the Ion CF_3Br^+ Produced by Direct Ionization of Neat CF_3Br at 449 Torr Nozzle Pressure in 0.51 Å Intervals. No LiF Filter was Used and Corrections for Second Order Contributions Have Not Been Applied. b) A Broad Wavelength Scan, 450-1150 Å, of the CF_3Br^+ PIE Taken in 2 Å Intervals.

production of CF_3^+ from CF_3Br is displayed in Figure **4.** The ionization and appearancepotentials and heats of formation derived from them are collected in Table 1

TABLE 1. IONIZATION AND APPEARANCE ENERGIES AND HEATS OF FORMATION FOR NEUTRALS AND IONS IN THE CF_3Br SYSTEM

		Neutral		Ion	
Compound	Ionization Energy, eV	ΔH_{f0}^0 (g) kcal mol-'	ΔH_{f298}^0 (g) kcal mol-'	ΔH_{f0}^0 (g) kcal mol-'	ΔH_{f298}^0 (g) kcal mol-'
CF_3Br	11.36		-155.k0.6 (11)	107.1k0.5	
Br	--	28.189 (12)		300.6 (12)	
CF_3	11.85		-110 (13)		95.4 (13)

DISCUSSION

The PIE wavelength scan of CF_3Br^+ from CF_3Br, 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 CF_3Br^+ should appear on the initial rise from threshold (Reference 4). The reason for the unusual character of the CF_3Br^+ PIE is evident in Figure **4,** which shows the function for

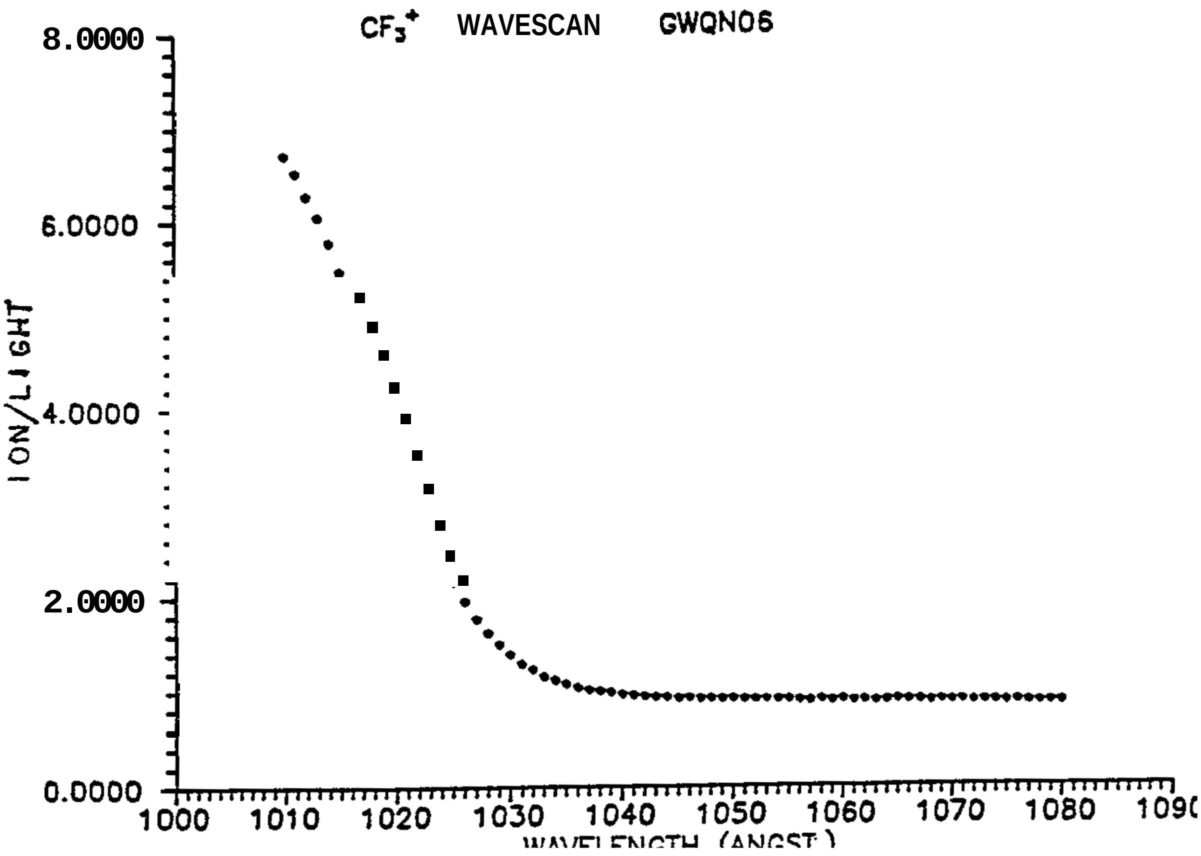

Figure 4. CF_3^+ PIE Curve Over the Range 1010-1080 Å. The Observed Intensities of the Ion CF_3^+ are from Direct Ionization of CF_3Br in a 1:20 Mixture of $CF_3Br + O_2$ at 604 Torr Nozzle Pressure and are Taken in 1 Å Intervals. No LiF Window was Used and the Nozzle Temperature was 1.1°C.

producing CF_3^+ from CF_3Br. The appearance potential of CF_3^+ is at 1046±3 Å = 11.85r0.03 eV, the energy of the first (low energy) peak in Figure 3. From this onset the yield of CF_3^+ increased dramatically, while the production of parent ion CF_3Br^+ ceases to increase further at higher ionization energies. Therefore, the PIE function for CF_3Br^+ is dominated by fragmentation,

$$CF_3Br^+ \rightarrow CF_3^+ + Br$$

The difference

$$AP(CF_3) - IP(CF_3Br) = 0.49\ eV = 11\ kcal\ mol-'$$

is the dissociation energy of the C-Br bond in CF_3Br^+. This value is extremely small and it means that even in the vibrationless state of the radical cation the 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 CF_3Br is 71.7 kcal mol-', based $\Delta H_{f298}^0(CF_3Br)$ = 155.0 kcal mol-', ΔH_{f298}^0 (CF,) = -110 kcal mol-', and ΔH_{f298}^0 (Br) = 26.74 kcal mol-' (Reference 10). This conclusion about the nature of the C-Br bond in CF_3Br^+ is supported by MOPAC (Reference 11) calculations which show that only a very weak association exists between planar CF_3^+ and a neighboring Br atom. Furthermore, the C-Br bond distance has increased enormously from the typical separation of 1.94 8, in covalent molecules to 3.1 8, in CF_3Br^+. In other words, even at the ionization threshold CF_3Br^+ is a free Br atom loosely associated with the stable CF_3^+ cation. When the internal energy of this CF_3^+ • Br complex exceeds the binding energy of 11 kcal mol", rapid dissociation to 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 CF_3Br^+ 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 CF_3Br and a free radical, **R•,** that proceeds with no activation barrier:

$$CF_3Br + R\bullet \rightarrow CF_3^+ + BrR + e$$

The driving force for this reaction would be the stability of CF_3^+. The most likely free radical is atomic hydrogen. Using the standard heats of formation at (298 K) for CF_3Br (-155.0 kcal mol-'), H **(51.626** kcal mol-'), CF, (95.4 kcal mol^{-1}), and HBr (-8.70 kcal mol^{-1}) (Reference 10), we calculate that this reaction is endothermic by 190 kcal mol-'. Therefore, even if no activation barrier is present, this reaction is extremely slow and cannot contribute to radical chain termination. Radicals other than H• give even more highly endothermic heats of reaction.

Another possibility is reaction of CF_3Br with CHO^+, the most abundant cation in flames (Reference 12). CHO^+ is probably formed by chemiionization in the reaction

$$CH + O \rightarrow CHO^+ + e$$

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

$$CHO' + CF_3Br \rightarrow CO + HBr + CF_3^+$$

On the basis of standard heats of formation at **298** K of CHO' (197.3 kcal mol-'), CF_3Br (-155.0 kcal mol-'), CO (-110.52 kcal mol''), HBr (-8.70 kcal mol-'), and CF_3^+ (95.1 kcal mol-'), this reaction is exothermic by 66.1 kcal mol^{-1}. The HBr thus formed may inhibit the branching steps by catalysis of the H-atom recombination process.

$HBr + H \rightarrow H_2 + Br$

$Br + H \rightarrow HBr$

The reaction suggested here is complex, probably proceeding by proton transfer from CHO^+ to CF_3Br, and driven by the high stability of the CO product molecule. This possible mechanism should be examined more carefully.

ACKNOWLEDGEMENTS

This research was carried out at the National Synchrotron Light Source at Brookhaven National Laboratory and supported in part by contract F29601-87-C-0001 with the Engineering and Services Laboratory, Air Force Engineering and Services Center, Tyndall Air Force Base, Florida 32403 and in part by contract DE-AC02-76CH00016 with the U.S. Department of Energy and its Division of Chemical Sciences, Office of Basic Energy Sciences.

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