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Journal

Journal of Physical Chemistry, 104(45)

Author

Mcgovern, W. Sean

Publication Date

2000-03-29

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Chemical Sciences Division

March 2000

Submitted to
Journal of Physical Chemistry

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**Primary and Secondary Processes
in the Photodissociation of CHBr_3**

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Primary and Secondary Processes in the Photodissociation of CHBr_3

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Abstract

The photodissociation of CHBr_3 at 193 nm has been investigated using photofragment translational spectroscopy with VUV ionization detection. The only primary process observed was the loss of bromine atom. The translational energy distribution for this channel suggests a direct dissociation from an excited electronic state, and the anisotropy parameter, $\beta=0.0$, is consistent with a transition dipole moment aligned perpendicular to C_{3v} axis. The majority of nascent CHBr_2 fragments undergo secondary dissociation *via* two competing channels. The elimination of HBr and C-Br bond cleavage in CHBr_2 occur with comparable yields. We also provide *ab initio* calculations on the relevant photochemical species and RRKM estimates of the product branching ratios that are consistent with the experimental observations.

Submitted to *J. Phys. Chem.*, January 25, 2000
Revisions submitted: March 29, 2000

1 Table, 9 Figures

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I. INTRODUCTION

The role of anthropogenic and natural sources of chlorine-containing molecules in stratospheric ozone depletion has been well established.¹ The influence of bromine and its chemistry on the atmosphere, however, has received considerably less attention.

Bromine in the stratosphere depletes ozone *via* a chain reaction mechanism analogous to the well-known ClO_x cycle,

Although the concentration of bromine in the stratosphere is much lower than chlorine, the reservoir species which temporarily confine reactive bromine are photochemically labile and, therefore, inefficient. As a result, bromine is far more destructive to stratospheric ozone than chlorine on an atom for atom basis.² Recent estimates by Garcia and Solomon report that this factor could be as high as 100, suggesting that bromine may be as important in stratospheric ozone depletion as chlorine.³ In addition to catalytic bromine cycles, the coupling of BrO and ClO cycles to produce free bromine and chlorine atoms *via* the reaction,

can enhance the depletion of ozone by chlorofluorocarbons by up to 20 percent for even moderate mixing ratios of bromine in the stratosphere. Despite the influence of the solar ultraviolet photolysis that both bromine sources and reservoir species have on the reactive bromine budget of the atmosphere, there is a severe lack of experimental data regarding the photodissociation of these molecules.

Bromoform is one of several volatile halocarbon compounds that contribute active bromine to the atmosphere. It is primarily of biogenic origin and is produced in the Arctic by both kelp and ice algae as a byproduct of photosynthetic processes.⁴ Other natural sources include emissions from oceanic microalgae that result in large concentrations of bromocarbons in the marine boundary layer.⁵ Of the bromomethane derivatives, bromoform has been found to be the greatest contributor of bromine to the Arctic atmosphere⁶ with an atmospheric lifetime of approximately two weeks.⁷ Despite its importance, relatively few studies of its photochemistry have been performed. At

wavelengths near 200 nm there are several energetically accessible dissociation pathways, including both two-body and three-body processes,

Simons and Yarwood have studied the photodissociation of CHBr_3 using flash photolysis near 200 nm.⁸ Spectral features corresponding to vibronic transitions associated with CBr were observed following photolysis. The authors asserted that the origins of CBr involved the primary loss of bromine atom followed by the spontaneous decomposition of the energized CHBr_2 radical. Power dependence studies indicated that the CBr was the result of a single photon process. Stern-Volmer experiments varying buffer gas pressures at several different excitation energies and RRK calculations provided information on the threshold for CBr formation from CHBr_2 . Sears and co-workers have subsequently used CHBr_3 photolysis at 193 nm as a means to prepare CBr for infrared spectroscopic studies.⁹ The authors were also able to obtain the CHBr radical from CHBr_3 at this wavelength and determined that the products also resulted from a single photon process, suggesting an additional fate of the energized CHBr_2 radicals.^{10,11}

In the present paper we have examined the photodissociation of CHBr_3 at 193 nm. We find that the dissociation involves both primary and secondary fragmentation channels resulting in bromine atom quantum yields greater than unity and the release of HBr. The primary step in the dissociation is the rapid loss of atomic bromine resulting in a CHBr_2 radical with sufficient internal energy to dissociate *via* the loss of Br and HBr with comparable yields. The use of VUV ionization as opposed to electron impact for product detection is ideally suited for studying complex multichannel dissociation processes, where excessive dissociative ionization can significantly complicate the analysis. Analysis of such data, in addition to RRKM calculations using *ab initio* energies and geometries, permits a precise determination of the photofragment quantum yields and

provides valuable thermodynamic information, including the barrier height for HBr elimination from CHBr_2 .

II. EXPERIMENTAL

The fixed detector-rotating source molecular beam apparatus has been described in detail previously.¹² A continuous molecular beam of <1% bromoform seeded in helium was collimated with conical skimmers and intersected at 90° with the output of a Lambda Physik LPX-200 excimer laser operating on the ArF transition (193 nm). There was no change in the shape of any of the TOF spectra over a laser fluence range of 60-500 mJ/cm^2 providing strong evidence that all of the observed signals are the result of single photon absorption. Neutral photodissociation products traveled 15.1 cm where they were ionized by tunable VUV undulator radiation, mass selected, and counted as a function of time. The characteristics of the VUV undulator radiation used for product photoionization have also been previously described.¹³ The nozzle was heated to 100°C to minimize clustering in the beam and no evidence for clusters was observed. A pile-of-plates polarizer, consisting of 8 quartz plates at Brewster's angle, was used to polarize the excimer beam, resulting in >85% linear polarization. Rotation of the linear polarized beam was achieved using a half-wave plate (Karl Lambrecht).

Bromoform 99% was obtained from Aldrich Chemical Co. and used without further purification.

III. RESULTS AND ANALYSIS

Center-of-mass translational energy, $P(E_T)$, distributions were obtained from the time of flight (TOF) spectra using the forward convolution technique.¹⁴ For all of the TOF spectra presented, the circles represent the data and the lines represent the forward convolution fit.

TOF spectra were obtained for several masses: CHBr^+ (m/z 92), Br^+ (m/z 79, 81), HBr^+ (m/z 80 82), and CBr^+ (m/z 91). No signal was observed for CHBr_2^+ (m/z 173) at VUV ionization energies from 15 eV to 8 eV. Although the ionization energy for CHBr_2 is 8.13 eV¹⁵ it is formed with an average internal energy (*vide infra*) which exceeds the threshold for CHBr^+ upon ionization above threshold.¹⁶ As a result this species only

contributes to the m/z 92 (CHBr^+) TOF spectra. The ionization energy dependence of both Br^+ and HBr^+ signals showed no change in shape as the energy was varied from 15 eV to 12 eV, indicating that there is no contribution from dissociative ionization to these TOF spectra. No CBr_2^+ was detected (ionization energy of 10.1 eV), and no evidence of this fragment at lower masses was observed.

A. Primary Dissociation and Product Identification

TOF spectra for m/z 92 (CHBr^+) at laboratory angles of 10° , 15° and 20° are shown in Figure 1. There are two contributions to the CHBr spectra. The first contribution, indicated by the solid line, results from the dissociative ionization of CHBr_2 fragments. The second contribution (dashed line) is from CHBr fragments that arise from the spontaneous dissociation of CHBr_2 . Figure 2 shows the ionization dependence of the CHBr TOF spectra which confirms the identity of the contributions. As the VUV energy is decreased to 11 eV the contribution attributed to CHBr_2 daughter fragments shows a significant decrease relative to the CHBr fragments. The ionization energy of CHBr is 8.94 eV¹⁷ and signals associated with this fragment persist near threshold although the overall signal is greatly reduced. Figure 3 shows Br^+ (m/z 79) TOF spectra at laboratory angles of 15° and 30° and a photoionization energy of 15 eV. There are also two contributions to the m/z 79 spectra; a fast contribution near the leading edge of the profile (solid line) and a contribution at longer times (dashed line). The fast component can be attributed to primary loss of Br from CHBr_3 and has been fitted using the $P(E_T)$ distribution shown in the top panel of Figure 4. The $P(E_T)$ distribution is nearly Gaussian in shape with a maximum at 13 kcal/mol and a FWHM of 8 kcal/mol. The CHBr_2 internal energy corresponding to the total translational energy is indicated on the top axis, assuming that the bromine atom is formed in its ground spin-orbit state, $\text{Br}(^2\text{P}_{3/2})$. Only the fastest Br signal can be momentum-matched to the features assigned to CHBr_2 fragments in Figure 1. The $P(E_T)$ distribution used to fit the primary CHBr_2 is shown in the bottom panel of the figure corresponding to a threshold for secondary dissociation near 68 kcal/mol.¹⁸ The fits to the m/z 92 TOF spectra are extremely sensitive to changes in the leading edge of the CHBr_2 $P(E_T)$ distribution, providing a good estimate of the threshold energy. Although HBr fragments are detected, they cannot be attributed to a

primary dissociation channel. Therefore, we find that the only observed primary channel is the loss of bromine atom and the remaining products are the result of secondary processes.

Photofragment angular distributions were recorded as a function of laser polarization using the leading edges of the Br^+ and CHBr^+ signals at a laboratory angle of 10° . The laboratory angular distributions, $I(\theta)$ are,

$$I(\theta) = \frac{1}{4\pi} [1 + \beta P_2(\cos \theta)]$$

where β is the anisotropy parameter and $P_2(x)$ is the second Legendre polynomial. For prompt dissociation in the axial recoil limit the anisotropy parameter is given by $\beta = 2P_2(\cos \chi)$ where χ is the angle between the recoil velocity vector and the transition dipole moment. No polarization dependence was observed for either mass, corresponding to an anisotropy parameter of $\beta = 0.0 \pm 0.1$.

B. Secondary Dissociation of the CHBr_2 Radical

The lack of momentum matching between the Br and CHBr_2 fragments is strong evidence for secondary dissociation. Only the Br loss channel (5) and the HBr elimination channel (6) are energetically accessible at 193 nm, and we see evidence for both channels in the TOF spectra. The forward convolution fitting of secondary dissociation processes has been discussed in detail previously.^{19,20} A primary $P(E_T)$ distribution is first chosen to represent the translational energy of those primary fragments which undergo secondary decomposition. In principle, this can be determined by subtracting the $P(E_T)$ distribution derived from fitting the CHBr_2 fragment from the $P(E_T)$ distribution for the Br fragment. There are two secondary channels, however, each with a different energetic threshold. As a consequence the leading edge of the distribution in the lower panel of figure 4 corresponds only to the lowest threshold process. We have relied on *ab initio* and RRKM calculations to provide additional information for assigning these thresholds. We find that the threshold for HBr loss is lower in energy (68.0 kcal/mol) than for Br elimination (73.6 kcal/mol), and therefore the abrupt truncation point in the CHBr_2 $P(E_T)$ distribution corresponds to the onset of HBr loss. Based on RRKM calculations, discussed in detail below, once the Br loss channel is

energetically accessible, it becomes the dominant dissociation pathway for CHBr_2 . Therefore, primary CHBr_2 fragments with internal energy greater than the HBr loss threshold but less than the Br loss threshold contribute to channel 5 while the CHBr_2 fragments with internal energy greater than the Br loss threshold contribute only to channel 6. The resulting primary $P(E_T)$ distributions for each secondary channel are shown in Figure 5 and provide very good fits to the data. It should be noted that initial attempts to iteratively fit the data without the *ab initio* constraints resulted in quantitatively similar distributions providing additional support for the locations of the secondary thresholds.

The secondary dissociation lifetimes for both channels were assumed to exceed the rotational period resulting in a forward-backward symmetric secondary angular distribution.^{21,22} Fits to the TOF spectra for each secondary channel were obtained by iteratively adjusting the secondary angular distribution, maintaining forward-backward symmetry, and the secondary $P(E_T)$ distribution. Fragments associated with the Br loss channel appear as the central feature in the CHBr^+ spectra and the slow feature in the Br^+ spectra. The best fit secondary $P(E_T)$ distribution for this channel is shown in the top panel of Figure 7. Fragments arising from the HBr elimination channel represent the sole contributions to the HBr^+ and CBr^+ TOF spectra shown in Figure 6. The secondary $P(E_T)$ for the HBr loss channel is shown as the bottom panel in Figure 7. Both distributions peak at low translational energies suggesting almost no barrier to recombination. On average there is little energy available (<19 kcal/mol) for the fragments of secondary dissociation. The sensitivity of the fits to the secondary $P(E_T)$ distributions is modest and depends on the choice of each corresponding primary $P(E_T)$. However, the qualitative result that both are peaked near zero is robust.

IV. DISCUSSION

A. Primary Dissociation Mechanism

The measured isotropic spatial distribution of the photofragments could be the result of several factors. If the dissociation is not prompt on the time-scale of parent rotation,

the correlation between the direction of the electric dipole moment and the relative velocity will be diminished by parent rotation. Based on previous work on halogenated methane derivatives²³ and the observed translational energy distribution, however, we believe that the primary dissociation is direct, involving excitation to a repulsive state. The impulsive model, which provides an adequate description of direct dissociation, predicts an average translational energy of 16 kcal/mol in reasonable agreement with the measured value. A fast dissociation can also produce an isotropic velocity distribution if the angle between the recoil direction and the transition dipole moment, χ , is 54.7° . In C_{3v} symmetry an $A_1 \leftarrow A_1$ transition requires that the transition dipole moment lies along the three-fold axis and gives $\chi = 72.7^\circ$ resulting in an anisotropy parameter of $\beta = -0.73$, based on an *ab initio* geometry optimization of CHBr_3 . The dipole moment for an $E \leftarrow A_1$ transition is perpendicular to this axis and yields $\beta = -0.05$ after averaging over the azimuthal orientation of the bromine atoms. This result is consistent with our observations.

Although there is no direct experimental evidence, we do not expect that spin-orbit excited bromine, $\text{Br}(^2P_{1/2})$, is formed in significant yield. The truncation of the primary $P(E_T)$ distribution required to fit the CHBr_2 contribution shown in Figure 1 is very abrupt. The formation of substantial excited state bromine would result in stable CHBr_2 with translational energies approaching zero which is not observed. In addition, the quantum yields for primary and secondary Br are more consistent with the absence of excited Br. We are unable, however, to rule out a minor contribution of excited state bromine. State-selected experiments could provide a definitive determination of the spin-orbit branching in the dissociation.

B. Ab initio and RRKM Calculations on the dissociation of CHBr₂

In order to understand more about the photodissociation of CHBr_3 , and in particular, the competition between secondary dissociation channels, we have performed *ab initio* and RRKM calculations. All *ab initio* calculations were performed using Gaussian 94²⁴ on an Origin 2000 Supercomputer and an SGI Power Challenge workstation. Geometries and frequencies for the ground state species were calculated at the MP2/6-311+G* level, and vibrational frequencies were left unscaled for the zero-point

corrections and RRKM calculations. The transition state for the HBr loss channel was optimized at the MP2/6-31+G* level, and single-point energies were calculated at the MP2/cc-pVtz level. Relevant geometries for the secondary dissociation products and transition state are shown in Figure 9. Recently, a methodology has been developed to correct carbon-halogen bond energies for basis set effects beyond the triple-zeta level and correlation effects beyond the MP2 approximation by applying corrections to MP2/cc-pVtz energies.²⁵ Using this methodology, we have calculated final zero-point corrected C-Br bond energies of 63.8 kcal/mol and 73.6 kcal/mol for CHBr₃ and CHBr₂ respectively. The former value was calculated previously²⁵ and is in good agreement with previous theoretical²⁶ (62.7 ± 0.9 kcal/mol) and experimental²⁷ (66 ± 4 kcal/mol) results. The HBr loss channel is endothermic with a reaction energy of 67.4 kcal/mol, very close to previous reports²⁸, and a barrier height of 68.0 kcal/mol. Calculated energies are shown schematically in Figure 8. The very small exit barrier from the three-center elimination of HBr is consistent with previous reports of three-center hydrogen halide elimination. Riehl and Morokuma have examined the three-center elimination of HCl from vinyl chloride.²⁹ The calculated transition state is qualitatively similar to the HBr transition state of the present study with an elongated carbon-halogen bond length and a modestly lengthened C-H bond (Figure 9). The exit barrier for HCl loss was calculated to be only 2.6 kcal/mol above the asymptotic products. In the present study, the HBr loss channel from CHBr₂ is found to be only 0.6 kcal/mol higher than the asymptotic product energy. The smaller barrier found for CHBr₂ is not surprising given that bromine atom can interact with the hydrogen more readily in the present system due to its larger size and relative proximity to the reacting hydrogen in a tetrahedral geometry.

Microcanonical unimolecular rates, $k(E, J)$, have been evaluated using and RRKM and variational RRKM calculations³⁰ to describe the HBr and Br loss channels respectively. For consistency all frequencies and energies used in the RRKM calculations, including reactant and product species, were obtained from *ab initio* theory. A direct count algorithm was used to determine the sum of states using the harmonic oscillator approximation for both sets of calculations. The rate of HBr loss was calculated using the optimized *ab initio* transition state geometries and frequencies.

The unimolecular rates for the Br elimination channel were performed using variational RRKM theory,³⁰ minimizing the sum of states along the reaction coordinate,

$$\frac{dN^\ddagger(E, J, R^\ddagger)}{dR} = 0.$$

The frequencies of the transitional modes were assumed to change smoothly according to

$$\nu_i(R) = \nu_i(R_e) \exp(-aR),$$

where R_e is the equilibrium C-Br bond length, and a is a constant taken to be 1.2.^{31,32} The sum of a Morse function and a centrifugal barrier was used to model the potential along the C-Br stretching coordinate. The centrifugal barrier was derived using the average rotational energy of the CHBr_2 corresponding to $J = 111$ derived from the soft fragment impulsive model³³ following primary loss of bromine. Moments of inertia at each fixed geometry were obtained by changing only the C-Br bond length. One rocking mode and one wagging mode were treated as transitional modes. The remaining modes were assumed to be well-represented by the product frequencies.

RRKM and variational RRKM calculations were performed at a series of energies above the respective threshold energies for HBr and Br channels corresponding to the measured CHBr_2 internal energy distribution. Table 1 summarizes the results as a function of the internal energy of the CHBr_2 fragment after the initial Br loss from CHBr_3 . Rates for Br loss increase from $1 \times 10^{12} \text{ s}^{-1}$ to $2 \times 10^{13} \text{ s}^{-1}$ for energies above threshold up to 10 kcal/mol. Rates for HBr elimination range from $1.5 \times 10^9 \text{ s}^{-1}$ near threshold to $7 \times 10^{11} \text{ s}^{-1}$ at the maximum energies available. Clearly for CHBr_2 internal energies above the threshold for Br loss, the rate of Br loss exceeds the rate for HBr elimination by more than an order of magnitude. As a result, CHBr_2 fragments with internal energies above 73.6 kcal/mol will predominately form $\text{CHBr} + \text{Br}$. The collision frequency at ambient tropospheric conditions at 300 K is on the order of 10^9 s^{-1} suggesting that CHBr_2 radicals with internal energies above the Br threshold will not be collisionally stabilized. However, CHBr_2 fragments with internal energies near the HBr elimination threshold may be quenched prior to reaction. This is consistent with the work of Simons and Yarwood⁸, who observed pressure dependent-quantum yields for the CBr products in CHBr_3 dissociation near 200 nm. Given that the peak of the $P(E_T)$ distribution for CHBr_2 is near this threshold, a significant fraction of CHBr_2 fragments would be

expected to be stabilized in the atmosphere in contrast to the collisionless conditions present in a molecular beam experiment.

C. Product Branching Ratios

We can estimate the branching ratio for the secondary dissociation channels and obtain Br and HBr quantum yields based on the primary $P(E_T)$ distributions used to fit the TOF spectra. Assuming that the quantum yield for the primary bromine atoms is unity, the quantum yields for secondary Br and HBr can be determined by integrating the normalized $P(E_T)$ distribution in the top panel of Figure 4 over the limits illustrated in Figure 5 for each secondary channel. This analysis gives quantum yields for the secondary Br and HBr channels of 0.3 and 0.4 respectively. Therefore, the total yield for bromine atoms is 1.3 using this procedure. A quantum yield for Br atoms based on the relative contributions of primary and secondary channels to the Br TOF spectra is consistent with this value, although slightly higher value is obtained than from the $P(E_T)$ distributions. The observation of bound CHBr_2 in the m/z 92 (CHBr^+) TOF spectra and the location of the lower threshold to secondary dissociation provides an upper limit of 1.7 to the Br quantum yield. Since Br loss *via* a barrierless dissociation from CHBr_2 dominates HBr elimination above threshold and significant secondary HBr is observed, it is unlikely that the Br quantum yield is close to this upper bound. We, therefore, assign a quantum yield of 1.5 ± 0.2 , which reflects the upper and lower bounds of analysis. Accordingly we assign a final HBr quantum yield of 0.2 ± 0.2 .

Based on our calculated thresholds we can also comment on the wavelength dependence on the Br quantum yield. At wavelengths longer than 209 nm there is insufficient energy for the formation of secondary Br and the Br quantum yield should be unity. Above 218 nm there is insufficient energy for the secondary dissociation of CHBr_2 towards HBr elimination and only primary C-Br bond cleavage will occur. Of course, the precise quantum yields of Br and HBr at wavelengths shorter than these limits will depend intimately on the partitioning of the available in the primary dissociation step and will be more difficult to predict *a priori*. We note that Br loss from CHBr_2 should become increasingly dominant over HBr loss as the internal energy of the CHBr_2 radicals increases.

IV. CONCLUSIONS

The photodissociation of CHBr_3 has been investigated at 193 nm using photofragment translational spectroscopy with VUV ionization for product detection. We have identified and characterized both primary and secondary dissociation channels in the dissociation. The primary dissociation involves prompt C-Br bond fission. A fraction of the CHBr_2 radicals formed in the primary step contain sufficient energy to undergo spontaneous secondary dissociation *via* the elimination of both HBr and Br to a comparable extent. *Ab initio* calculations have provided important thermochemical information on the fragmentation of CHBr_2 including the transition state associated with HBr elimination. RRKM calculations have shown that significant secondary HBr may be formed in addition to secondary bromine fragments; however, under ambient tropospheric conditions, CHBr_2 fragments with internal energies below the Br-loss threshold may be collisionally stabilized prior to reaction.

V. ACKNOWLEDGMENTS

Work by SWN and WSM was partially supported by a Research Enhancement from Texas A&M University. The work by AGS and OS was supported by the Director, Office of Energy Research, Office of Basic Energy Science, Chemical Sciences Division of the U. S. Department of Energy under contract No. DE-AC03-76SF00098. The experiments were conducted at the Advanced Light Source, Lawrence Berkeley National Laboratory which is supported by the same source. Hardware and software support for the *ab initio* calculations was given by the Texas A&M University Supercomputing Facility and Texas A&M University Laboratory for Molecular Simulations under National Science Foundation grant CHE-9528196.

Figure Captions:

- Figure 1: Unpolarized TOF spectra for m/e 92 (CHBr^+) photoproducts at a scattering angle of 10° , 15° , and 20° and a photoionization energy of 15.0 eV. The circles are the experimental data, and the solid lines are the forward convolution fits using the $P(E_T)$ distributions in figure 4.
- Figure 2: Experimental TOF spectra for m/e 92 (CHBr^+) at 15° and a photoionization energy of 15.0 eV (top trace) and 8 eV (bottom trace).
- Figure 3: Unpolarized TOF spectra for m/e 79 (Br^+) at scattering angles of 15° and 30° and a photoionization energy of 15.0 eV. The circles are the experimental data, the solid line is the forward convolution fit using the $P(E_T)$ distribution shown in top panel of figure 4, and the dashed line is the contribution from secondary Br loss from the CHBr_2 radical.
- Figure 4: The upper panel shows the primary $P(E_T)$ used to fit the fastest Br contribution in the TOF spectra in figure 3. The internal energy of the CHBr_2 radical, formed in coincidence with ground state bromine, is indicated on the top axis. The lower panel shows the primary $P(E_T)$ distribution used to fit the CHBr_2 contribution to the m/z 92 TOF spectra in figure 1.
- Figure 5: The upper panel shows the primary $P(E_T)$ distribution used to model the secondary Br loss from CHBr_2 . The lower panel shows the primary $P(E_T)$ distribution used to model the HBr elimination from CHBr_2 . The thresholds for secondary Br and HBr loss are indicated by the arrows in the upper panel.

- Figure 6: The upper panel shows the secondary $P(E_T)$ distribution corresponding to the Br loss from the CHBr_2 radical. The lower panel shows the secondary $P(E_T)$ distribution for HBr elimination from CHBr_2 .
- Figure 7: Experimental TOF spectra for m/e 91 (CBr^+) at 15° (upper panel) and for m/e 82 (HBr^+) at 20° (lower panel) for a photoionization energy of 15.0 eV. The circles are the experimental data and the solid lines are the forward convolution fits to the data using the primary $P(E_T)$ distribution in the lower panel of figure 5 and the secondary $P(E_T)$ distribution in the lower panel of figure 6.
- Figure 8: Schematic energy diagrams for the secondary dissociation of the CHBr_2 radical. The energies are the result of *ab initio* calculations as described in the text.
- Figure 9: Optimized geometries of CHBr_2 , CHBr , CBr , and the transition state for the HBr loss channel. Lengths are in Angstroms, and angles are in degrees. The CHBr_2 radical shows a slight nonplanarity with an angle of 33.0° between the two HCBBr planes.

Table 1: RRKM and var-RRKM microcanonical rates for the dissociation of CHBr_2

E^* (kcal/mol)	E_T (kcal/mol) ^a	$k(\text{CHBr}_2 \rightarrow \text{CBr} + \text{HBr})$ [s^{-1}]	$k(\text{CHBr}_2 \rightarrow \text{CHBr} + \text{Br})$ [s^{-1}]
84	0.2	6.95×10^{11}	1.94×10^{13}
83	1.2	5.70×10^{11}	1.56×10^{13}
81	3.2	3.69×10^{11}	1.02×10^{13}
79	5.2	2.24×10^{11}	6.01×10^{12}
77	7.2	1.25×10^{11}	3.01×10^{12}
75	9.2	6.18×10^{10}	1.26×10^{12}
73	11.2	2.59×10^{10}	-
71	13.2	8.25×10^9	-
69	15.2	1.47×10^9	-

^aTotal translational energy for the CHBr_2 and Br fragments following 193 nm photodissociation of CHBr_3 .

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Fig 1

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Fig 9

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