Photodissociation dynamics of the methyl perthiyl radical at 248 nm via photofragment translational spectroscopy

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Photofragment translational spectroscopy was used to study the photodissociation of the methyl perthiyl radical CH₃SS at 248 nm. The radical was produced by flash pyrolysis of dimethyl disulfide (CH₃SSCH₃). Two channels were observed: CH₃ + S₂ and CH₂S + SH. Photofragment translational energy distributions indicate that CH₃ + S₂ results from C–S bond fission on the ground state surface. The CH₃S + SH channel can proceed through isomerization to CH₂SSH on the ground state surface but also may involve production of electronically excited CH₂S. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4789485]

I. INTRODUCTION

The disulfide bond plays a key role in diverse areas of chemistry ranging from chemical biology, where it plays a critical role in protein folding and structure as the cysteine bond,1 to atmospheric chemistry, where it is found in atmospherically relevant species that take part in the sulfur cycle.2 These considerations have motivated fundamental studies of the gas-phase chemistry and photochemistry of alkyl disulfides, with dimethyl disulfide (DMDS) at the forefront of many investigations.3–17 Depending on the wavelength used, the competing dissociation pathways for DMDS are as follows:15

\[
\text{CH}_3\text{SSCH}_3 + hv \rightarrow 2\text{CH}_3\text{S} (\tilde{X}^2E) \quad \Delta H_0 = 70 \text{ kcal/mol}, \quad (1)
\]

\[
\text{CH}_3\text{SSCH}_3 + hv \rightarrow \text{CH}_3\text{SS} (\tilde{X}^2A'^v) + \text{CH}_3 (\tilde{X}^2A'^v) \\
\Delta H_0 = 55 \text{ kcal/mol}. \quad (2)
\]

Channel (2) has been of special interest due to the CH₃SS (methyl perthiyl) radical produced. Callear and Dickson studied this pathway at ca. 195 nm, and observed CH₃ and S₂ photoproducts.4 Pressure dependence studies for this channel demonstrated that internally excited CH₃SS from channel (2) decayed spontaneously to produce the S₂ fragment. Subsequently, Ng and co-workers14 observed both the methyl perthiyl radical and S₂ fragments from the 193 nm photodissociation of DMDS and attributed the S₂ signal to absorption of a second photon rather than a secondary process. Additional studies at 193 nm by Lee et al.15 and Martínez-Haya et al.16 showed that spontaneous decay of hot CH₃SS was the primary source of S₂, but that there was a smaller contribution from photoexcitation of CH₃SS. Kumar et al.18 studied the 248 nm photodissociation of DMDS via transient absorption spectroscopy in a static cell. They reported several UV absorption bands that they assigned to CH₃S and S₂ photofragments. The more recent work by Lee et al.15 showed that the collisionless photodissociation of DMDS at 248 nm exclusively occurs via channel (1). They attributed the exclusivity to a σ → n_e electronic excitation, resulting in a rapid, bond-specific dissociation.

In this work, we investigate the photodissociation of the methyl perthiyl radical itself at 248 nm. Several experimental and theoretical studies of CH₃SS have been reported previously. Moran and Ellison19 measured the electron affinity of CH₃SS via negative-ion photoelectron spectroscopy. Ma et al.20 measured the photoionization efficiency of the methyl perthiyl radical in a supersonic beam and carried out ab initio calculations to explore possible isomerization on its ground state surface. Subsequent theoretical work by Cheung et al.21 found several stable conformers of the methyl perthiyl radical with CH₃SS as the most stable. More recently, Maofa et al.22 studied the ionization of CH₃SS using photoelectron spectroscopy and Martin-Diaconescu and Kennepohl23 measured its X-ray absorption spectrum. While the above studies were concerned with the energetics and spectroscopy of the methyl perthiyl radical, none probed the specific photochemistry of the radical itself. The only previous study of perthiyl photodissociation was performed by Mikhailik et al. on the tert-buty1 perthiyl radical in a hydrocarbon matrix at 365 nm.24 Appearance of the tert-buty1 radical was monitored using EPR, and the group concluded that the tert-buty1 perthiyl radical was undergoing C–S bond fission to produce S₂ and the tert-buty1 radical. The methyl perthiyl radical is of further interest as an isovalent analog to the methyl peroxy radical (CH₃OO), an important atmospheric and combustion intermediate.25–27

The ultraviolet absorption spectrum of CH₃SS has not been characterized. By analogy to CH₃O₂,28 excitation at 248 nm may access the B (2A′) state of the radical.
II. EXPERIMENTAL

A molecular beam of CH$_3$SS was produced by flash pyrolysis of DMDS and photodissociated; the photoproducts were mass-analyzed using a rotatable detector. Details about this instrument have been described elsewhere.$^{30, 31}$ A piezoelectric valve produced a pulsed beam of 0.5% DMDS seeded in 2 atm of 10% N$_2$ in He. The N$_2$ was added to slow the molecular beam in order to facilitate detection of slower photofragments and to achieve better temporal separation of photofragments (see Sec. III). Methyl perthiyl radicals were generated using a resistively heated SiC flash pyrolysis source based on the design of Kohn et al.$^{32}$ and previously used by our laboratory to study the phenyl and tert-butyl radicals.$^{33, 34}$ The radical beam was collimated by two skimmers that separate the source and main chambers of the machine. The beam was then crossed at 90° with the 248 nm output of a GAM EX100/500 excimer laser focused into a 3 × 1 mm$^2$ beam spot. Typical pulse energies were around 20 mJ/pulse. The laser and pulsed valve were operated at repetition rates of 100 Hz and 200 Hz, respectively, to allow for background subtraction. The scattered photofragments were detected as a function of laboratory scattering angle, $\theta_{\text{lab}}$, relative to the molecular beam in the plane defined by the molecular and laser beams. After entering the detector, photofragments were ionized by an electron impact ionizer, mass selected with a quadrupole mass filter, and detected with a Daly style ion detector.$^{35}$ Ion counts were recorded as a function of time relative to the laser pulse. The resulting time-of-flight (TOF) spectra were collected using a multichannel scaler interfaced to a computer. Typical TOF spectra were averaged over 100 000 to 200 000 laser shots. An iterative forward convolution program was used to simulate the TOF spectra for photoproducts over all angles, resulting in a photofragment translational energy distribution in the center-of-mass frame of reference.

The radical beam was characterized using a rotating, slotted chopper disk. Typical beam velocities were around 1500 m/s with speed ratios between 5 and 6. The beam was further characterized by taking mass spectra at $\theta_{\text{lab}} = 0$ as the SiC tube temperature was increased. Intensities of the CH$_3$SSCH$_3^+$ ($m/z = 94$) and CH$_3$SS$^+$ ($m/z = 79$) signals were monitored as a function of current passing through the tube.

While complete removal of the precursor ion signal at $m/z = 94$ was possible, the remaining CH$_3$SS$^+$ signal at $m/z = 79$ was insubstantial under these very hot source conditions and the only photodissociation signal observed was $m/z = 32$ (S$^+$) from S$_2$ produced in the pyrolysis source; this signal was not observed under any other source conditions. As such, photodissociation data were taken under a variety of pyrolysis source conditions while monitoring the $m/z = 64$ photoproduction signal. Since $m/z = 64$, corresponding to the S$_2$ photoprotuct, is not produced from the photodissociation of DMDS,$^{15}$ ion signal at this mass was assumed to be from the methyl perthiyl radical. This assumption was tested experimentally and will be discussed in Sec. IV. Because of incomplete precursor depletion from the beam and the large absorption cross section of dimethyl disulfide at 248 nm,$^{12}$ DMDS photodissociation experiments (pyrolysis source off) at 248 nm were also performed.

III. RESULTS

TOF spectra were taken for $m/z = 64$ (SS$^+$), $m/z = 47$ (CH$_3$S$^+$), $m/z = 46$ (CH$_2$S$^+$), $m/z = 45$ (CHS$^+$), $m/z = 33$ (SH$^+$), $m/z = 32$ (S$^+$), and $m/z = 15$ (CH$_3^+$), representing possible photofragments from channels (3)–(5) and daughter ions from dissociative ionization in the electron impact ionizer. Figure 2 shows sample TOF spectra for $m/z = 64$ at $\theta_{\text{lab}}$
TOF spectra taken at $m/z = 33$ (SH\textsuperscript{+}) were inconclusive due to low signal levels, while $m/z = 32$ spectra were unusable due to contributions from DMDS photodissociation and high background gas signal.

IV. ANALYSIS

The results in Sec. III suggest that CH\textsubscript{2}SS undergoes photodissociation via channels (3) and (5). In this section, we first analyze our data based on this assumption and then consider alternative interpretations. Center-of-mass photofragment translational and angular distributions, $P(E\textsubscript{T},\Theta)$, were obtained by simulating the TOF spectra of the photoproducts. For each channel, this distribution can be written as a product of uncoupled center-of-mass translational energy and angular distributions,

$$P(E\textsubscript{T}, \Theta) = P(E\textsubscript{T}) I(E\textsubscript{T}, \Theta),$$  

where $I(E\textsubscript{T},\Theta)$ is the angular distribution and $P(E\textsubscript{T})$ is the translational energy distribution. The PHOTRAN\textsuperscript{36} forward convolution program was used to simulate all TOF spectra using assumed $P(E\textsubscript{T})$ distributions. The input $P(E\textsubscript{T})$ was adjusted point-wise until a satisfactory TOF simulation was achieved for all spectra. The experimental configuration used in this study has the detector rotating in the plane defined by the molecular and laser beams, so an anisotropic distribution is possible with unpolarized laser light. However, satisfactory agreement between simulation and experimental data was achieved by assuming isotropic distributions for all $E\textsubscript{T}$.

By conservation of energy, the total $E\textsubscript{T}$ available is given by

$$E\textsubscript{T} = h\nu + E\textsubscript{a} - E\textsubscript{int} - D\textsubscript{\nu},$$

where $h\nu$ is the photon energy, $E\textsubscript{a}$ is the initial internal energy of the methyl perthyl radicals, $E\textsubscript{int}$ is the internal energy of the photoproducts, and $D\textsubscript{\nu}$ is the bond dissociation energy. In the limit of cold radicals ($E\textsubscript{int} = 0$), the maximum translational energy $E\textsubscript{T,max}$ is given by $h\nu + D\textsubscript{\nu}$. For channel (3), $E\textsubscript{T,max} = 67.5$ kcal/mol whereas for channel (5), $E\textsubscript{T,max} = 69.1$ kcal/mol.

The best TOF simulations for channels (3) and (5) are shown in Figures 4 and 5, respectively. The $P(E\textsubscript{T})$ distribution shown in Fig. 4, used to simulate channel (3), peaks at 6.1 kcal/mol and extends to 34 kcal/mol, 33.5 kcal/mol below the maximum allowable translational energy. The distribution has an average translational energy $\langle E\textsubscript{T}\rangle = 10.4$ kcal/mol. The
The interpretation of our TOF data in terms of channels (3) and (5) is based on the observation of only a single fragment from each channel, rather than momentum-matched pairs of fragments as would be preferred when carrying out radical photodissociation experiments. Consideration must be given to sources of signal other than perthiyl photodissociation contributing to an observed TOF spectrum. In particular, owing to incomplete elimination of DMDS from the molecular beam, the 248 nm photodissociation of this species must be accounted for in all TOF spectra. As DMDS exclusively undergoes dissociation by channel (1) at 248 nm, the pyrolysis source-dependent peak at \( m/z = 64 \) is a strong indication of methyl perthiyl production and dissociation via channel (3).

The assignment of channel (5) is not as straightforward, especially in light of its best-fit \( P(E_T) \) distribution (see Sec. V). Dissociative ionization of CH\(_3\)S from DMDS channel (1) yields daughter ions in the \( m/z = 46 \) and 45 spectra in Fig. 3, partly obscuring the slower features. However, since the slower peaks in those spectra were not observed in the 248 nm photodissociation of DMDS (both in the present work and by Lee et al.\(^{15} \)), these slower features are not from direct dissociation of the precursor. Another possibility is that this signal is from secondary photodissociation of CH\(_3\)S produced from DMDS via channel (1). While H-atom loss from CH\(_3\)S is energetically allowed at 248 nm,\(^{37} \) the slower peaks in Fig. 3 were not observed in the DMDS photodissociation experiments where further photodissociation would have been obvious. Finally, it is possible that the signal in question could be from photodissociation of other DMDS pyrolysis products generated in the source, such as CH\(_3\)S or CH\(_2\)S. Attempts to simulate the signal as H + CH\(_3\)S from the photodissociation of CH\(_3\)S were unsuccessful. Trial \( P(E_T) \) functions ranged from low translational energy distributions similar to the work by Zheng et al.\(^{38} \) to a distribution peaking at the maximum available translational energy of 67.5 kcal/mol. All of these yielded TOF simulations with photofragment arrival times later than the slower peak in the experimental spectra, particularly at larger laboratory angles. It thus appears that CH\(_3\)S photodissociation is an unlikely explanation for the slower feature in the \( m/z = 46 \) and 45 TOF spectra. If this signal were from CH\(_2\)S photodissociation, then there would only be signal at \( m/z = 45 \) and not \( m/z = 46 \). Overall, the slower peaks in Fig. 3 are most reasonably assigned to methyl perthiyl radical photodissociation via channel (5).

V. DISCUSSION

The primary objectives of this study were (a) to probe the primary photochemistry of the methyl perthiyl radical and (b) to gain insight into the photodissociation mechanism at 248 nm. A key question is whether photodissociation occurs on an excited state surface or if the excited radical undergoes internal conversion to the ground state followed by statistical dissociation. This issue can be addressed by examining the translational energy distributions for the observed channels to see if they are consistent with statistical decay on the ground state surface.

Based on the schematic for the ground state surface in Fig. 1, no exit barriers are involved in the simple bond fission channels (3) and (4). In a statistical picture, the resulting \( P(E_T) \) distributions should be most intense at low translational energy with most of the energy distributed among the internal degrees of freedom. While channel (4) was not observed, channel (3) does peak at low translational energy, consistent with the high degree of internal excitation expected with ground state dissociation. To further test the hypothesis that channel (3) is statistical, a prior distribution was calculated using the functional form\(^{39} \)

\[
P(E_T | E_{\text{avail}}) \propto E_T^{1/2} \rho_{\text{rot}}(E_{\text{avail}} - E_T),
\]

where \( E_T \) is the translational energy and \( \rho_{\text{rot}}(E_{\text{avail}} - E_T) \) is the rotational-vibrational density of states for the pair of fragments. To implement Eq. (8) for channel (3), five total rotational degrees of freedom and seven total vibrational degrees of freedom (treated as classical harmonic oscillators) were used. The resulting prior distribution for channel (3), shown in Fig. 4 as the dashed grey line, agrees reasonably well with the experimentally derived \( P(E_T) \), suggesting that dissociation for this channel occurs statistically on the ground state surface.
The $P(E_T)$ distribution for channel (5) falls off more rapidly as $E_T \to 0$ than the distribution for channel (3), a result suggesting ground state dissociation over a small exit barrier. Such a result can be rationalized with reference to Fig. 1, which shows that the lower energy pathway to channel (3) involves isomerization over TS2 and then passage through a shallow well (19.8 kcal/mol with respect to products) corresponding to the CH$_2$SSH structure. Under these circumstances, energy randomization in this well may not occur, with the overall $P(E_T)$ distribution still reflecting the effect of TS2. However, the form of this distribution is still unusual, as it implies a significant degree of product internal energy confined within a narrow range of only a few kcal/mol. It is possible that this signal corresponds to CH$_2$S in its first electronic excited state ($\tilde{A}^1\tilde{A}_2$), which lies only 47 kcal/mol above the thioformaldehyde ground state with a corresponding $E_{T_{\text{max}}}$ of 22 kcal/mol. Full elucidation of the dissociation mechanism requires more information than is presently available. Observation of the SH photofragment and a determination of the translational energy (or internal energy distribution via techniques such as laser induced fluorescence) would provide further insight into the exact dynamical process. Calculation of the excited state potential energy surfaces for CH$_3$SS would also provide valuable insight.

The results for the methyl perthiyl radical can be compared to the 248 nm photofragmentation of the methyl peroxo (CH$_3$O$_2$) radical by Hartmann et al. In that experiment, ground state OH and CH$_3$O products were seen by laser-induced fluorescence, and emission from electronically excited OH($\tilde{A}^2\Sigma^+$) was also observed. These are the analogues to channels (4) and (5) in CH$_3$SS photodissociation. Although Hartmann et al. were not set up to detect CH$_1$ + O$_2$ products, the analogue to channel (3), they proposed, based on quantum yield measurements, that this was in fact the dominant channel (74%), followed by CH$_3$O + O (20%) and CH$_3$O + OH (6%). However, the asymptotic energetics for CH$_3$O dissociation are very different than for CH$_3$SS; the lowest energy channel is production of CH$_3$O + OH, which lies 21 kcal/mol below CH$_3$O$_2$, 52 kcal/mol below CH$_3$ + O$_2$ and 80 kcal/mol below CH$_3$O + O. The observation of OH($\tilde{A}^2\Sigma^+$) indicates that at least some dissociation of CH$_3$O$_2$ occurs on an excited state surface. Direct characterization of the CH$_3$ + O$_2$ channel would be of considerable interest to see if that channel is indeed dominant and if so, whether its dynamics are consistent with ground state dissociation.

VI. CONCLUSIONS

The photodissociation dynamics of the methyl perthiyl radical has been explored at 248 nm using photofragment translational spectroscopy. Two channels were observed, CH$_3$ + SS and CH$_3$S + SH. The translational energy distribution for channel (3), CH$_3$ + SS, is similar to that expected for a simple statistical distribution, suggesting that the methyl perthiyl radical undergoes internal conversion to the ground state prior to dissociation to these products. Channel (5), CH$_3$S + SH, can occur via isomerization on the ground state surface but could also involve production of electronically excited CH$_3$S.

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