

Photoionization Study of Supersonically Cooled Polyatomic Radicals: Heat of Formation of CH_3S^+

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The stabilities of the mercaptomethyl ion, $\text{CH}_2=\text{SH}^+$ (1), and the thiomethoxy ion, CH_3-S^+ (2), have been subjects of numerous experimental¹⁻¹⁶ and theoretical^{11,17-21} studies. A collisional activation experiment¹ indicates that both these isomers are stable and that 1 is more stable than 2. This conclusion is supported by a high-level ab initio study,¹⁷ predicting that the singlet $\text{CH}_2=\text{SH}^+(\text{}^1\text{A}')$ lies >27 kcal/mol below the triplet $\text{CH}_3-\text{S}^+(\text{}^3\text{A}_1)$. Despite all these studies, the value for $\Delta H_{\text{f}}(\text{CH}_3\text{S}^+)$ has not been measured. In this communication, we report a photoionization study of supersonically cooled CH_3S , which yields a value of 9.225 ± 0.014 eV for the ionization energy (IE) of $\text{CH}_3\text{S}(\text{}^2\text{E})$ ²² to 2 and a corresponding value of 244.1-247.7 kcal/mol for $\Delta H_{\text{f}}(\text{CH}_3\text{S}^+)$.

The molecular beam photoionization apparatus used has been described in detail.^{23,24} A pulsed beam of CH_3SCH_3 (vapor pressure ≈ 400 Torr) seeded in Ar is produced by supersonic expansion through a pulsed valve with a nozzle diameter of 0.5 mm and a total stagnation pressure of 1150 Torr. The pulsed valve is operated at 40 Hz. The ArF excimer laser beam is mildly

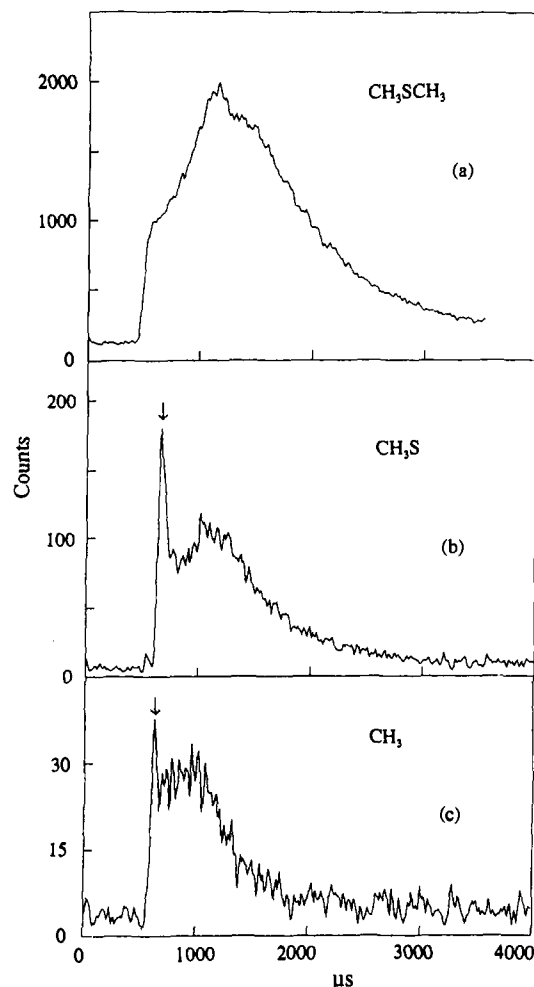


Figure 1. (a) Temporal profile of the CH_3SCH_3 beam pulse observed at a photoionization wavelength of 1280 Å. (b and c) Temporal profiles of the CH_3S and CH_3 beam pulses observed at a photoionization wavelength of 1250 Å and laser energies of 60 and 35 mJ, respectively. These spectra are measured by using a multichannel scaler with a channel width of 10 μs . Time zero of the spectrum corresponds to the initiation of the trigger pulse for opening the pulsed valve. For b and c, the firing of the excimer laser is delayed by 500 μs . The accumulation time for each spectrum is 5 min. Total stagnation pressure = 1150 Torr.

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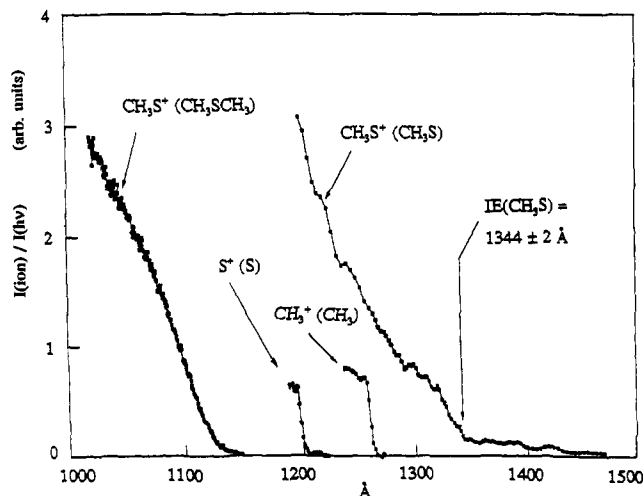


Figure 2. PIE spectra for CH_3S^+ from CH_3S and CH_3SCH_3 , for CH_3^+ from CH_3 , and for S^+ from S. CH_3S , CH_3 , and S result from the 193-nm laser (pulse energy = 60 mJ) photolysis of CH_3SCH_3 .

focused and intersects the CH_3SCH_3 free jet at 90° and ≈ 2 mm from the nozzle tip. The gas beam is skimmed by a conical skimmer before entering the photoionization region of a quadrupole

mass spectrometer located ≈ 8 cm from the nozzle tip. The photoionization wavelength resolution used is 1.5 Å [full width at half-maximum (FWHM)].

Figure 1a shows the temporal profile of the CH_3SCH_3 beam pulse observed by photoionization at 1280 Å using a multichannel scaler with a channel width of 10 μs . Time zero of the spectrum corresponds to the initiation of the trigger pulse for opening the pulse valve. The triggering pulse for firing the excimer laser is delayed by 500 μs with respect to time zero.²⁵ The temporal profiles for the CH_3S and CH_3 beam pulses observed at 1250 Å and laser pulse energies of 60 and 35 mJ are shown in Figure 1b,c, respectively. The accumulation time for each spectrum is 5 min. The vertical scale indicates the actual counts of various channels. The peaks indicated by arrows in Figure 1b,c are identified as background ions caused by the excimer laser alone.²⁶ In order to avoid the background due to the excimer laser, the CH_3S^+ (CH_3^+) ion counts resulting from photoionization of CH_3S (CH_3) radicals are measured by gating the scaler in the temporal range of 0.9–2.9 ms.

The observed widths [≈ 800 μs (FWHM)] of the CH_3S and CH_3 beam pulses are lower than that [≈ 1500 μs (FWHM)] of the CH_3SCH_3 beam pulse, but are greater than that expected based on the spacial distribution (≈ 6 mm) of the photodissociation region and the laser pulse width [≈ 8 ns (FWHM)]. Since the radicals initially formed by photodissociation have substantial kinetic energies, the greater than expected width may be attributed to the expansion effect of translationally hot radicals and to their collisions with Ar and CH_3SCH_3 molecules in the free jet. This interpretation implies that the density of the free jet has to be sufficiently high and the pulse width sufficiently wide for complete trapping and cooling of the internally and translationally hot radicals produced by photodissociation. With use of similar experimental procedures and conditions, photoionization efficiency (PIE) spectra for SO^{27} and CS^{28} prepared by 193-nm laser photodissociation^{29,30} of SO_2 and CS_2 , respectively, show that SO and CS sampled at the photoionization region are in the $v = 0$ states.

The PIE spectra for CH_3S^+ from CH_3S and for CH_3S^+ from CH_3SCH_3 in the ranges of 1200–1470 and 1020–1150 Å are depicted in Figure 2. The threshold for the formation of CH_3S^+ (or CH_2SH^+) from CH_3SCH_3 is determined to be ≈ 1049 Å.^{16,31,32} Therefore, the CH_3S^+ ions observed at wavelengths > 1200 Å are due to the photoionization of CH_3S . The PIE spectra for CH_3^+ from CH_3 and for S^+ from S^{33} near their thresholds are also shown in the figure. The observed IEs of CH_3 and S are consistent with the literature values.^{34,35} Since the photoionization of CH_3S involves the removal of an essentially nonbonding electron from S , the IE of CH_3S is expected to be sharp. As the photon energy is increased, the PIE for CH_3S^+ is found to rise rapidly from 1344

± 2 Å, which is interpreted as the IE for CH_3S to form **2**. On the basis of the energy release measurements, $\Delta H_{\text{f}}(\text{CH}_3\text{S})$ is determined to be 35.0 ± 1.0 kcal/mol.^{16,36} Most recently, a value $\Delta H_{\text{f}}(\text{CH}_3\text{S}) = 31.4 \pm 0.5$ kcal/mol has been obtained by Wine and co-workers³⁷ using a chemical kinetics bromination method. These values, together with the IE for CH_3S to **2**, yield a value of 244.1–247.7 kcal/mol for $\Delta H_{\text{f}}(\text{CH}_3\text{S}^+)$. The literature value for $\Delta H_{\text{f}}(\text{CH}_2\text{SH}^+)$ is in the range of 206–209 kcal/mol.^{4,9,15} The finding that $\Delta H_{\text{f}}(\text{CH}_3\text{S}^+)$ is greater than $\Delta H_{\text{f}}(\text{CH}_2\text{SH}^+)$ by 35–42 kcal/mol is consistent with the theoretical prediction of > 27 kcal/mol.¹⁷ The PIE of CH_3S in the range of 1344–1470 Å is small and decreases slowly toward lower photon energy, indicating that the Franck-Condon factor for photoionization to **1** is unfavorable.

(36) On the basis of energy release measurements of the processes, $\text{CH}_3\text{SSCH}_3 + h\nu(193 \text{ nm}) \rightarrow 2\text{CH}_3\text{S}$, $\text{CH}_3\text{SCH}_3 + h\nu(193 \text{ nm}) \rightarrow \text{CH}_3\text{S} + \text{CH}_3$, and $\text{CH}_3\text{SH} + h\nu(193 \text{ nm}) \rightarrow \text{CH}_3\text{S} + \text{H}$. See ref 16.

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Distorted Amides: Correlation of Their Enhanced Solvolysis with Local Charge Depletions at the Carbonyl Carbon

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Recently, Bennet et al. studied a series of tertiary amides in which the rate of base hydrolysis was compared with structural characteristics determined by X-ray diffraction.¹ They observed that distortion of the amide group away from planarity led to enhanced rates of hydrolysis. The distortion, resulting in the pyramidalization of the amide nitrogen, is obtained by rotation about the C–N bond. The hydrolysis rates demonstrated that the greater the distortion, the greater the susceptibility of the carbonyl carbon to attack. The geometric observations agree with theoretical predictions which demonstrated that the resonance model fails to satisfactorily predict the consequences of rotation about the C–N bond.² This leaves open the origin of the enhanced rate of hydrolysis in the apparent absence of an accompanying loss in amidic resonance.

The Laplacian of the electronic charge density ($\nabla^2\rho$) predicts the sites of electrophilic and nucleophilic attack, as well as their relative propensity toward reaction,³ the structures and geometries of hydrogen-bonded complexes,⁴ the directing abilities of substituents in aromatic electrophilic substitution,⁵ the relative susceptibility of activated double bonds to Michael addition,⁶ and the relative kinetic reactivity of the syn and anti faces of the carboxylate anion.⁷ This note presents such a study of the relative reactivities of planar and pyramidalized formamide to nucleophilic attack by comparing the relative magnitudes of $\nabla^2\rho$ at the critical points in the valence-shell charge concentration (VSCC) of the carbonyl carbon. These are the holes in the VSCC which locate the sites of local charge depletion ($\nabla^2\rho > 0$), the predicted sites for nucleophilic attack.³ These predictions, together with the predicted direction of approach of the nucleophile, agree with both experiment^{8a} and theory.^{8b}

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