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PHOTOIONIZATION STUDIES OF ORGANOSULFUR TRANSIENT SPECIES

B. Ruscic and J. Berkowitz

Chemistry Division, Argonne National Laboratory

Photoionization mass spectrometric studies of the transient species CH_2SH , CH_3S , CH_2S , and HCS have established the heats of formation of these species and their cations, thereby resolving a serious discrepancy between other recent experiments and ab initio calculations in favor of the latter. The isomers CH_2SH (CD_2SH) and CH_3S (CD_3S) were prepared in situ by reaction of F atoms with CH_3SH (CD_3SH). Similar successive abstractions, as well as pyrolysis of suitable precursors, were used to generate CH_2S and HCS . The adiabatic ionization potentials obtained, together with relevant appearance potentials and some auxiliary data, were sufficient to establish the heats of formation for the cited species.

Drs. B. Ruscic and J. Berkowitz at Argonne National Laboratory used the above method, together with confirmatory data obtained from the dissociative ionization of CH_3SSCH_3 into various fragments, to derive the thermochemical properties of these important intermediates occurring in the combustion of sulfur-containing hydrocarbon fuels. Their work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences.

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B. Ruscic and J. Berkowitz

Chemistry Division, Argonne National Laboratory

Recently there has been a flurry of activity directed at the determination of thermochemical properties of simple organosulfur species. The interest has been at least partly motivated by the need to better understand the combustion of sulfur-containing fuels and the concomitant emission of atmospheric pollutants. The transient species CH_3S , CH_2SH , CH_2S , and HCS are believed to play important roles as intermediates in these processes.

We have prepared these transient species in situ by hydrogen abstraction, pyrolysis, or a combination of both methods, and have succeeded in studying them by photoionization mass spectrometry.

The species CH_3S and CH_2SH are isomers. Both can be formed as abstraction products during the reaction of F atoms with methyl mercaptan (CH_3SH), and in photoionization experiments they appear at the same $m/e = 47$ channel (see Fig. 1). The two isomers can be further distinguished by selective isotopic studies, e.g., using CD_3SH , where CD_3S appears at $m/e = 50$, and CD_2SH at $m/e = 49$ (see Figs. 2 and 3). Our values for the adiabatic ionization potentials are: CH_2SH , 7.536 ± 0.003 eV; CD_2SH , 7.522 ± 0.003 eV; CH_3S , 9.262 ± 0.005 ; CD_3S , 9.268 ± 0.005 eV.

For CH_3S , our value is an improvement on a prior measurement. For the other three species, our measurements represent the first direct detection in photoionization mass spectrometric experiments. From the adiabatic ionization potentials, and other auxiliary data (appearance potentials, an independent ΔH_f° of CH_3S), we have determined the heats of formation of these species and of their cations. We find that CH_3S is more stable than CH_2SH by 6.3 ± 2 kcal/mol. Hence, $D_0(\text{H}-\text{CH}_2\text{SH}) = 92.4 \pm 2.0$ kcal/mol ($\leq 94.0 \pm 0.1$ kcal/mol) is stronger than $D_0(\text{H}_3\text{CS}-\text{H}) = 86.1 \pm 0.6$ kcal/mol by the same quantity. However, CH_2SH^+ is more stable than CH_3S^+ by 33.5 ± 2.0 kcal/mol. This latter value is in agreement with a recent ab initio calculation, but in disagreement with other recent experiments. The a posteriori analysis of the latter experiments shows that ΔH_f° (CH_3S) and ΔH_f° (CH_3S^+) were placed too high by about 3-4 kcal/mol, whereas ΔH_f° (CH_2SH^+) was placed too low by 5-7 kcal/mol.

It is interesting to compare the behavior of CH_2SH and CH_3S with their oxygen analogs, CH_2OH and CH_3O . These analogs, extremely important in combustion processes, were also studied by us recently. There, unlike the case of the sulfur analogs, CH_2OH is more stable than CH_3O by $\geq 8.0 \pm 1.2$ kcal/mol. Thus $D_0(\text{H}-\text{CH}_2\text{OH}) = 95.0 \pm 0.7$ kcal/mol, close to $D_0(\text{H}-\text{CH}_2\text{SH})$, whereas $D_0(\text{H}_3\text{CO}-\text{H}) = 103.1 \pm 1.0$ kcal/mol, is significantly larger than $D_0(\text{H}_3\text{CS}-\text{H})$. However, CH_2OH^+ is significantly more stable than CH_3O^+ , paralleling the situation for the sulfur analogs. Therefore, both CH_3S^+ and CH_3O^+ are metastable. However, whereas both CH_3S^+ and CD_3S^+ seem relatively long-lived, CH_3O^+ is very short-lived even in its ground vibrational state (less than 10 μs) and decomposes to $\text{HCO}^+ + \text{H}_2$ through a triplet-singlet surface crossing. Its isotopomer, CD_3O^+ , shows some marginal stability in its ground vibrational state, presumably due to lower zero point energy and barrier tunneling probability.

Thioformaldehyde, CH_2S , was observed as a successive abstraction product from the $\text{F} + \text{CH}_3\text{SH}$ reaction, and was also prepared by pyrolytic decomposition of two different precursors: methanesulfuryl chloride, CH_3SCl , and methyl disulfide, CH_3SSCH_3 . The photoionization spectrum of CH_2S is shown in Fig. 4. The ionization potential of CH_2S was found to be 9.376 ± 0.003 eV, which is a slight improvement over two prior photoelectron spectroscopic studies. The general shape of the photoionization curve is reminiscent of that of its oxygen analog, CH_2O . In both cases the threshold is very abrupt, indicating very little change in geometry upon ionization. In fact, a Franck-Condon analysis of the threshold region in CH_2S indicates that the C-S bond length changes by about 0.03 Å, in very good agreement with recent ab initio calculations. During these experiments we also observed the formation of the HCS^+ fragment from CH_2S . Its appearance potential, reduced to 0 K, was found to be $\leq 11.533 \pm 0.021$ eV.

HCS was observed as a successive abstraction product from the $\text{F} + \text{CH}_3\text{SH}$ reaction, and also by the reaction of F atoms with CH_2S , which was prepared by pyrolysis. Curiously, the former method (nominally three-step) yielded more intensity than the latter, almost certainly due to a very efficient surface reaction. To our knowledge, this study was the first detection of HCS in the gas phase. The photoion yield curve, representing a transition from bent HCS to linear HCS^+ , has a very extended Franck-Condon progression, with almost vanishing ionization probability at the adiabatic threshold (see Fig. 5). Upon a careful Franck-Condon analysis of the observed progression, we con-

cluded that the adiabatic ionization potential of HCS is $\leq 7.499 \pm 0.005$ eV, and possibly 7.412 ± 0.007 eV.

The measurements performed on CH_2S and HCS, together with those on CH_2SH and CH_3S , enabled us to derive the heats of formation of each of these species. An additional valuable check of internal consistency was provided by examining the photodissociative ionization of methyl disulfide, CH_3SSCH_3 . The possible alternative pairs of products, $\text{CH}_2\text{S}^+ + \text{CH}_3\text{SH}$, $\text{CH}_2\text{SH}^+ + \text{CH}_3\text{S}$, $\text{CH}_3\text{SH}^+ + \text{CH}_2\text{S}$, and $\text{CH}_3\text{SH}_2^+ + \text{HCS}$, each having a different m/e as signature, have appearance potentials that are close to one another. By carefully measuring these differences, the individual heats of formation could be confirmed. Thus, $\Delta H_{\text{f}}^\circ (\text{CH}_2\text{S}) = 28.3 \pm 2.0$ kcal/mol ($\leq 29.9 \pm 0.9$ kcal/mol) and $\Delta H_{\text{f}}^\circ (\text{HCS}) = 71.7 \pm 2.0$ kcal/mol ($\leq 73.3 \pm 1.0$ kcal/mol, $\geq 69.7 \pm 2.0$ kcal/mol).

Our heats of formation of the CH_nS species discussed above, together with auxiliary data, enable us to calculate various C-H, S-H, and C-S bond energies and observe some trends. For example, the values for the C-S bond energies clearly indicate that while in CH_3SH and CH_3S this bond energy has a single-bond character (72.6 ± 0.7 and 70.0 ± 0.6 kcal/mol, respectively), it has a double-bond character in CH_2S ($\geq 129.4 \pm 1.1$ kcal/mol, $\leq 131.0 \pm 2.0$ kcal/mol) and HCS (135.9 ± 2.0 kcal/mol), whereas in CS it acquires a triple-bond character (169.8 ± 0.6 kcal/mol). In CH_2SH , the C-S bond (89.7 ± 2.0 kcal/mol) has a bond order slightly higher than one, but it can still be considered as essentially a single bond. Also, it is readily apparent that C-H bond energies in CH_3S (48.5 ± 2.0 kcal/mol) and HCS (45.7 ± 2.0 kcal/mol) are significantly lower than those in CH_3SH (92.4 ± 2.0 kcal/mol) and CH_2S (94.0 ± 1.0 kcal/mol). The reason for this behavior is obvious: the C-H bond dissociations are accompanied by a strengthening of the C-S bond in the former two cases, but not in the latter two. A similar reasoning applies also to the S-H bond strengths in CH_3SH and CH_2SH . As a consequence, the sequence $D_{\text{O}}(\text{H-CH}_n\text{S})$, $n = 2, 1, 0$ oscillates between a high and a low value. These effects are similar to those observed previously by us in the C_2H_n and Si_2H_n systems.

All of the heats of formation and ionization potentials of the CH_nS transient species determined here experimentally are in excellent agreement with recent ab initio calculations, and provide a necessary and valuable input for combustion calculations involving organosulfur species.

Fig. 1. The photoion yield at $m/e = 47$, corresponding to parent ionization from the isomeric species CH_3S and CH_2SH . The wavelength region between the onset at $1645 \text{ \AA}$ and $\sim 1340 \text{ \AA}$ is attributable to ionization of CH_2SH . The growth in the region below $\sim 1340 \text{ \AA}$ is attributable to ionization of CH_3S .

Fig. 2. (a) The photoion yield curve of pure CD_3S . (b) An expanded portion of the photoion yield curve from Fig. 1, in the region where ionization from CH_3S begins to contribute to $m/e = 47$. Note the great similarity in structure between curves (a) and (b). In curve (b), the photoion yield from CH_3S "rides" on top of an essentially featureless "background" belonging to CH_2SH .

Fig. 3. The photoion yield curve of pure CD_2SH . Note the similarity to the curve from Fig. 1, and the absence of growth in the region $\sim 1340 \text{ \AA} - 1300 \text{ \AA}$.

Fig. 4. The photoion yield curve of CH_2S , obtained by pyrolysis of CH_3SCl . Note the sharp threshold at 1322 Å, and the presence of autoionization peaks in the shorter wavelength region.

Fig. 5. The photoion yield curve of HCS, obtained by successive hydrogen abstraction reactions from CH_3SH . The region is replete with autoionizing structure. The underlying growth from threshold to shorter wavelength is a consequence of a broad Franck-Condon distribution consistent with a bent-to-linear transition.

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