Photoionization Study of the Heat of Formation of HCS^+

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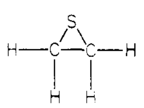
Abstract: The heat of formation of HCS^+ was determined by a dissociative photoionization study of three saturated cyclic sulfur molecules: thiirane (C_2H_4S), thietane (C_3H_6S), and tetrahydrothiophene (C_4H_8S). The HCS^+ appearance energies from the latter two precursors gave a $\Delta H_f{}^\circ{}_0 \leq 233$ kcal/mol. However, the derived heat of formation of HCS^+ from thiirane was 12 kcal/mol higher, a discrepancy ascribed to a reverse activation barrier. Kinetic energy release as a function of the thiirane internal energy measured by photoion–photoelectron coincidence indicated that at the dissociation threshold only 0.03 eV of the reverse activation energy is released as kinetic energy of the HCS^+ and CH_3 products, considerably less than the statistically expected 0.1 eV.

The HCS^+ ion is an abundant ion in the mass spectra of many organosulfur compounds.[1] In addition HCS^+ has been postulated[2a] and very recently found to exist in interstellar clouds through its microwave spectrum.[2] What is singular about this simple ion is the lack of a reliable experimentally determined value for its heat of formation. This is probably a result of the fact that the HCS^+ ion is often formed by a high-energy fragmentation process in competition with several lower-energy decomposition pathways. This shifts the observed onset to higher energies, an effect termed the kinetic shift. Gallegos and Kiser determined the heat of formation at 298 K of HCS^+ by measuring the HCS^+ onsets in the electron-impact ionization of several neutral precursors. They obtained a value of 271 kcal/mol from thiirane[3] and thietane[4] and 278 kcal/mol from tetrahydrothiophene.[4] Butler and Baer measured a much lower value of ≤251 kcal/mol at 298 K in a photoionization (PI) study of thiophene.[5] The $\Delta H_f{}^\circ$ was reported as an upper limit because of the possible presence of a kinetic shift. The heat of formation has also been investigated by Dewar and Rzepa,[6] who calculated a theoretical value of 245.3 kcal/mol by using MINDO/3.

We have undertaken this study of the HCS^+ ion in order to determine a reliable experimental value for its heat of formation by the technique of dissociative photoionization. The HCS^+ ion was generated as a first-generation fragment ion from three saturated sulfur heterocycles: thiirane (I), thietane (II), and tetrahydrothiophene (III). Kinetic energy released in the dissociation of thiirane to HCS^+ and CH_3 was measured by photoion–photoelectron coincidence (PIPECO).



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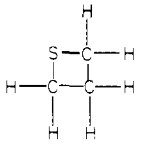

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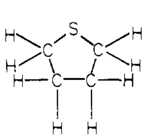

III

Experimental Section

The photoionization apparatus has been described previously.[5] A 1-m normal-incidence monochromator was used to disperse the vacuum UV light from a hydrogen many-line light source with a resolution of 17 meV at 120 nm. The ions were mass analyzed by a quadrupole mass filter.

The kinetic energy release distributions (KERDS) of thiirane ions in selected internal energy states were measured by photoion–photoelectron coincidence (PIPECO). The PIPECO experiment and the technique of extracting KERDS from the time-of-flight (TOF) distributions have been described in detail previously.[7,8] In summary, the ion internal energy is selected by detecting zero-energy electrons in coincidence with their corresponding ions. The coincidence of zero-energy electrons with ions is obtained by using the electron and ion signals as start and stop pulses in the TOF spectrum. Dissociating parent ions produce fragment ion TOF distributions which are approximately symmetric, the widths of which are due primarily to thermal broadening and kinetic energy released in the dissociation. KERDS can therefore be extracted from these symmetric TOF distributions from which the average kinetic energy release is calculated.

Results

A. Photoionization Efficiency Curves. The photoionization efficiency (PIE) curves for the HCS^+ fragment ions from thiirane, thietane, and tetrahydrothiophene are shown in Figure 1. Appearance energies (AE) at 298 K for the formation of HCS^+ from these precursors were obtained by linear extrapolation of the PIE curves near their onsets. The portions below 12 eV for the four- and five-membered ring compounds are shown on an expanded scale in Figure 2. Although the noise in the data is considerable, onsets can be discerned at the indicated energies. These onsets were converted to 0 K onsets by the method outlined by Monteiro et al.[9] The $\Delta H_f{}^\circ{}_0$ is then obtained from eq 1, where AB, A^+,

$$\Delta H_f{}^\circ{}_0(AB) + AE_0 = \Delta H_f{}^\circ{}_0(A^+) + \Delta H_f{}^\circ{}_0(B) \qquad (1)$$

and B are the molecular precursor, the ionic fragment, and the neutral fragment, respectively. Table I summarizes the AE's and derived heats of formation at 0 and 298 K while Table II lists the heats of formation of the neutral precursor molecules and fragments used to obtain the $\Delta H_f{}^\circ$ of CHS^+. The conversion between 298 and 0 K was done by the method outlined by Monteiro et al.[9]

All the $\Delta H_f{}^\circ(HCS^+)$ in Table I are listed as upper limits because a number of factors such as kinetic shifts and reverse activation barriers cause measured values to be too high. A kinetic shift clearly affects the HCS^+ AE from thiophene because this dissociation has an activation energy of 4 eV and it is 1 eV above the onset for $C_2H_2S^+$. This shift appears to be less in thietane and tetrahydrothiophene, although here also the HCS^+ fragment is the third and eighth one to be formed, respectively. This results in very slowly rising HCS^+ signals in the PIE curves of Figure 1. The fact that thietane and tetrahydrothiophene give similar HCS^+ heats of formation suggests that the 0 K value of 233 ± 2 kcal/mol is close to the true one.

It is remarkable how much too high the electron-impact appearance energies of Gallegos and Kiser[3,4] are. Even for the HCS^+ ion from thiirane, which has a sharp onset at 11.07 eV in the PIE spectrum, the reported EI onset was 12.3 eV. The other onsets are over 3 eV too high.

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Table I. HCS$^+$ Appearance Energies and Heats of Formation

precursor	AE$_{298}$, eV	AE$_0$, eV	$\Delta H_f{}^\circ{}_{298}$, kcal/mol	$\Delta H_f{}^\circ{}_0$, kcal/mol	ref
thiirane (C_2H_4S)	11.07 ± 0.04	11.13 ± 0.04	≤245 ± 2[a]	245 ± 2	this work
	12.3 ± 0.2		271[b]		3
thietane (C_3H_6S)	10.4 ± 0.1	10.5 ± 0.1	≤233 ± 2[a]	233 ± 2	this work
	13.9 ± 0.2		271[b]		4
tetrahydrothiophene (C_4H_8S)	11.0 ± 0.1	11.1 ± 0.1	≤233 ± 2[a]	233 ± 2	this work
	13.8 ± 0.2		278[b]		4
thiophene (C_4H_4S)	13.19 ± 0.04		≤251 ± 2		5

[a] The following vibrational frequencies were used to convert the 0 K to 298 K $\Delta H_f{}^\circ$: 3440, 1810, 1010, 1010 cm^{-1}. [b] These values were derived by assuming that several neutral products were formed.

Table II. Auxiliary Heats of Formation of Neutral Molecules and Fragments (kcal/mol)

molecule or fragment	$\Delta H_f{}^\circ{}_{298}$	ref	$\Delta H_f{}^\circ{}_0$	ref for vib freq
thiirane	19.6	21	22.4	22
thietane	14.5	21	19.1	23
tetrahydrothiophene	−8.15	21	−1.48	24
CH_3	34.0	20	34.8	20[a]
C_2H_5	25.7	20	28.5	25[b]
i-C_3H_7	17.6	20	22.0	26[b]

[a] This is the reference for the $\Delta H_f{}^\circ{}_0$ value. [b] These frequencies were estimated from those of stable products.

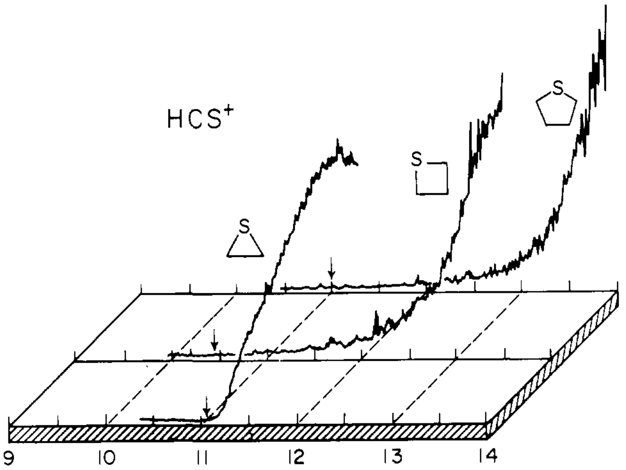

Figure 1. Photoionization efficiency (PIE) curves for HCS$^+$ from thiirane, thietane, and tetrahydrothiophene. The 298 K appearance energies are marked by arrows in each curve.

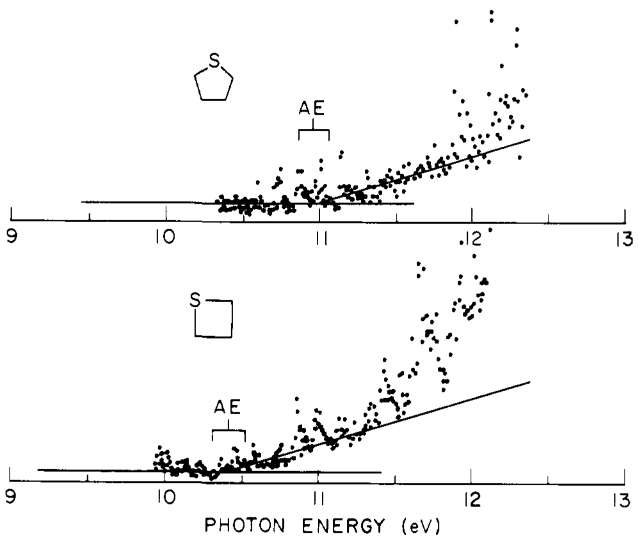

Figure 2. Photoionization efficiency (PIE) curves for HCS$^+$ from thietane and tetrahydrothiophene in the vicinity of the HCS$^+$ onset.

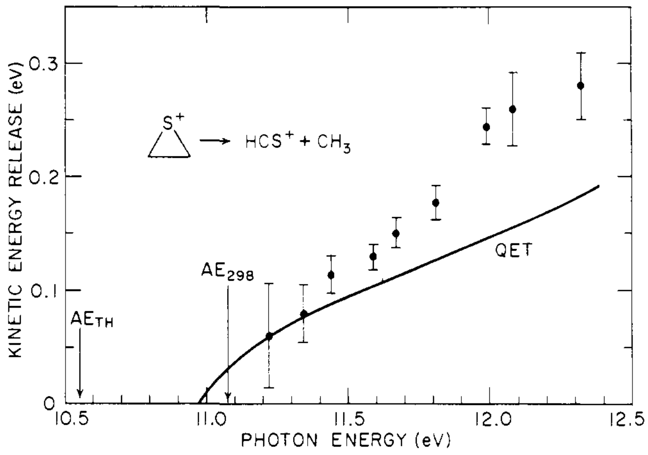

Figure 3. Average kinetic energy released vs. photon energy for the dissociation of thiirane to HCS$^+$ and CH$_3$. The solid line is the result of a QET calculation assuming a bent structure for HCS$^+$. AE$_{th}$ is the thermochemical onset.

B. Average Kinetic-Energy Release. Figure 2 is a plot of the average kinetic energy released for the dissociation of thiirane to HCS$^+$ and CH$_3$ as a function of the thiirane internal energy. These average release values were determined from an analysis of the whole KERD, whose shape appears to be rather statistical, as well as from an analysis of the full width half maximum in which a Maxwellian KERD is assumed.[10] The two methods gave similar results.

The solid line in Figure 2 is a theoretical calculation of the average kinetic energy using the quasiequilibrium theory (QET) as formulated by Klots.[11-13] The calculation was performed by assuming a bent HCS$^+$ structure because, as will become evident later, the HCS$^+$ is formed with a considerable amount of vibrational energy in the bending mode. The major effect is that three rotational degrees of freedom were assumed to be active. The vibrational frequencies for HCS$^+$ were obtained from those of HCO$^+$,[14] while the CH$_3$ frequencies were those reported by Snelson.[15] The measured kinetic energy release is greater than that calculated by the statistical theory. Similar discrepancies have been found for C$_2$H$_2$S$^+$ from thiophene,[5] CH$_3$O$^+$ from acetone,[7] and C$_3$H$_6$O$^+$ from dioxane.[9] For the purpose of this study, the significant result of Figure 2 is that the kinetic energy release extrapolates to about 30 meV at the HCS$^+$ appearance energy.

Discussion

Table I exhibits a range of HCS$^+$ heats of formation that extends over 2 eV. The old values of Gallegos and Kiser[3,4] are understandably high because they were done by electron impact. A combination of kinetic shift and the inherent difficulty in determining the onset by non-monoenergetic electron impact generally causes derived heats of formation to be high in these ex-

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periments. In thiophene the HCS^+ fragment must compete with the lower-energy formation of $C_2H_2S^+$ via a loose transition state. We attempted to calculate the kinetic shift by RRKM/QET calculations, but could not fit satisfactorily the HCS^+ onset and shape of the PIE curve. However, it was clear that the onset is shifted to higher values.

The striking result in Table I is that the derived HCS^+ heat of formation from thiirane is too high. We could perhaps attribute this to a kinetic shift because of the H-loss reaction whose onset is 0.8 eV below that of the CH_3-loss reaction. However, this is very unlikely because the measured kinetic energy release drops to near zero at the HCS^+ AE. Because thiirane is strained and highly reactive, we considered the possibility that it isomerized to the more stable thioacetaldehyde prior to photoionization. However, this was ruled out because our measured thiirane ionization energy of 9.04 ± 0.01 eV is identical with the 9.05 eV PES value.[16] The IE of thioacetaldehyde by contrast is 8.98 ± 0.02 eV.[17]

The formation of HCS^+ in higher-energy isomeric forms or higher-energy electronic states was considered and rejected. Bruna et al.[2] calculated both HCS^+ and CHS^+ energies and found the latter to be 110 kcal/mol higher that that of HCS^+. A CNDO/2 calculation[18] yielded an energy difference of 124 kcal/mol. These values are far too large to account for the 12-kcal/mol difference we observe. Similarly Bruna et al.[2] calculated the first excited state of HCS^+ to be 102 kcal/mol above the ground state.

The above considerations all point to a reverse activation barrier in the HCS^+ production from thiirane. This rather puzzling result is unexpected in that a portion of the reverse activation energy is normally released as kinetic energy in dissociation reactions. The statistically expected release energy at an excess energy of 0.5 eV is about 0.1 eV for this reaction. this is 3 times higher than the observed 0.03 ± 0.01 eV. However, the energy available from a reverse activation barrier need not be statistical. In fact the fraction released as kinetic energy is very much a function of the potential energy surface governing this dissociation. This negligible kinetic energy release near the onset of the HCS^+ ion can be explained if the transition state for the dissociation is a tight and "early" one, in which the bond angle of HCS^+ is constrained to a value far from its equilibrium position. Such a situation would arise if the transition state had the thiirane ring structure. Upon dissociation, the HCS^+ fragment could be formed in a bent configuration and would retain virtually all of the 12-kcal/mol reverse activation barrier as vibrational energy in the bending mode.

Support for such an energy partitioning comes from theoretical calculations of Bruna et al.[2] in which the total energy of HCS^+ was calculated as a function of the HCS^+ bond angle. An HCS^+ bond angle of 143° corresponds to an ion energy of about 13 kcal/mol above the HCS^+ linear ground-state structure. This 143° is precisely the HCS bond angle in thiirane.[19] Although this correspondence is most likely fortuitous because some of the internal energy must also reside in the neutral CH_3 fragment, it does point out that energy partitioning in which 95% remains in the vibrational modes is very reasonable for the dissociation of thiirane.

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