An Experimental Study of the Gas-Phase Bond Energies and Structures of $[c\text{-}C_4H_8S\therefore c\text{-}SC_4H_8]^+$, $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_4H_8]^+$, and $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_5H_{10}]^+$ and of Reactions of $[c\text{-}C_4H_8S]^+$ and $[c\text{-}C_5H_{10}S]^+$

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Experimental gas-phase high-pressure equilibrium determinations of ΔH^o_{rxn} and ΔS^o_{rxn} for the reactions: $c\text{-}C_4H_8S^+ + c\text{-}C_4H_8S \rightleftharpoons [c\text{-}C_4H_8S\therefore c\text{-}SC_4H_8]^+$, $c\text{-}C_5H_{10}S^+ + c\text{-}SC_4H_8 \rightleftharpoons [c\text{-}C_5H_{10}S\therefore c\text{-}SC_4H_8]^+$ and $c\text{-}C_5H_{10}S^+ + c\text{-}SC_5H_{10} \rightleftharpoons [c\text{-}C_5H_{10}S\therefore c\text{-}SC_5H_{10}]^+$ have been carried out. The product ions of these reactions are examples of species which may contain two-center three-electron (2c−3e) sulfur−sulfur bonds. The heats of reaction result in the following bond enthalpies for the 2c−3e bonded adducts: 115 kJ/mol for $[c\text{-}C_4H_8S\therefore c\text{-}SC_4H_8]^+$, 108 kJ/mol for $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_4H_8]^+$, and 106 kJ/mol for $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_5H_{10}]^+$ while the entropies of reaction are −119, −109, and −112 J/mol K, respectively. Metastable and collision induced dissociation (CID) spectra provide experimental evidence of the atomic connectivity and of the 2c−3e bonds. Metastable cleavage of the $S\therefore S$ 2c−3e bonds appear to occur with no reverse activation barriers and to result in small average kinetic energy releases. In the unsymmetric ion $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_4H_8]^+$, both ionic moieties are observed but the intensity is greater for retention of the charge on the larger ring, $c\text{-}C_5H_{10}S^+$. Cleavage of the $S\therefore S$ 2c−3e bonds by CID of the adducts yields the most intense product ions. Reaction of $[c\text{-}C_4H_8S]^+$ with $c\text{-}C_2H_4S$ entailed a ring expansion with incorporation of a sulfur atom to produce $[c\text{-}C_4H_8S_2]^+$. However, in a similar experiment, no expansion occurred when $c\text{-}C_5H_{10}S^+$ and $c\text{-}C_2H_4S$ reacted. In addition, no expansion reaction was observed for either $[c\text{-}C_4H_8S]^+$ or $[c\text{-}C_5H_{10}S]^+$ reacting with $c\text{-}C_3H_6S$.

I. Introduction

Gas-phase strained cyclic sulfur-containing cations have been shown to undergo ring expansions upon reaction with strained cyclic sulfur-containing neutral molecules.[1,2] The ring expansion steps proceed through sulfur−sulfur two-center three-electron (2c−3e) intermediates. These 2c−3e interactions where two electrons occupy a σ orbital and one electron occupies a σ^* orbital, both of which are localized between two atoms, were first described by Linus Pauling in 1931.[3] Acyclic gas-phase sulfur-containing cations $[R_2S]^+$ undergo ion−molecule association reactions forming stable products containing 2c−3e sulfur−sulfur bonds $[R_2S\therefore SR_2]^+$.[4−9] These association products often undergo metastable reactions by cleavage of the $S\therefore S$ bond and by loss of an R group.[6,8] The loss of an R group is analogous to the first step in the ring expansion mechanism for the strained rings.[1,2]

In gas-phase studies of ion−molecule reactions of methyl halide radical cations with methyl halides, formation of 2c−3e bonds were implicated.[10−13] Both direct metastable fragmentation of the 2c−3e bonds as well as unimolecular rearrangements followed by metastable fragmentation were observed.

In this article, a study of the association reactions of $[c\text{-}C_5H_{10}S]^+$ and $[c\text{-}SC_4H_8]^+$ with $c\text{-}C_5H_{10}S$ and $c\text{-}SC_4H_8$ is presented. A short discussion of some of the reactions of $[c\text{-}C_5H_{10}S]^+$ and $[c\text{-}SC_4H_8]^+$ neutral cyclic three- to six-membered sulfur-containing rings is also presented.

II. Experimental Methods

The experimental methods have been reported in detail and only those which pertain to these experiments will be described. Ion−molecule equilibrium experiments were carried out using a highly modified DuPont 491B mass spectrometer.[6] The ion source used resembles a small drift tube with coaxial ionizing electron entrance and ion exit apertures. Drift guard rings provide a controlled uniform electric field gradient which extracts the ions through the source; however, the electric field is small compared to kT and the ions are not translationally heated. Nevertheless, all experiments are conducted as a function of electric field strength and equilibrium constants are extrapolated to zero electric field strength. Equilibrium experiments were conducted at numerous total ion source pressures, up to 2 Torr, and varying compositions. The temperature ranged from 457 to 559 K.

The equilibrium experiments were carried out *without* a restriction to prevent arcing between the ion source, which was maintained at 1800 V, and ground.[14] The metal inlet was insulated from the ion source by 0.8 m of Pyrex tubing with a 4 mm i.d. With this arrangement, no arcing of the source was observed from 0.5 to 2 Torr. Removal of the restriction simplifies the gas flow into the source and minimizes discrimination of the heavier molecules due to molecular flow. Experimental entropies are determined from the extrapolated intercept in the van't Hoff equation. The form of the intercept for these reactions is:

$$\ln \{[P_{ap}^{\ +}]/[P_{ri}^{\ +}][P_{rn}]\} \qquad \text{(I)}$$

where $[P_{ap}^{\ +}]$ is the association product ion pressure, $[P_{ri}^{\ +}]$ is the reactant ion pressure, and $[P_{rn}]$ is the reactant neutral pressure. Ionic pressures are never measured; rather ion intensities are measured. Since an ion appears in both the numerator and the denominator, experimental errors due to ion discrimina-

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tion cancel as long as the instrument function is the same for both ions, as is the case with the DuPont sector instrument. However, errors in the determination of the neutral gas pressure do not cancel and will affect the determined values for the entropies of reaction. Restrictions, such as capillaries or glass wool in the gas inlet lines to prevent electrical arcing,[14] could affect the pressure determinations for heavier gases; hence, as stated, the present data were collected without any restrictions or glass wool in the inlet lines. There should be no systematic error due to the measurement of the neutral gas pressures.

It is imperative in these types of equilibrium studies that the reactions in question attain true thermodynamic equilibrium. Ion residence time distributions (RTD's) are routinely collected using time-resolved methods to ensure that all ions collected in continuous experiments are in dynamic equilibrium.

Mass spectrometry/mass spectrometry (MS/MS) experiments were also carried out with a VG ZAB-1F.[8,12] In the MS/MS experiments described in this article, the source pressure was near 1 Torr using a CI slit, and the temperature was near 323 K. Metastable spectra were recorded in the second field-free region at a base pressure of 2×10^{-8} Torr using multiple scanning methods. The source and collector slits were adjusted so that no detectable product ion peak narrowing resulted from decreasing the resolution. The practice of defining a main beam energy resolution has been questioned;[15] however, for convenience we note that this resolution was 4000. Product peaks were collected with peaks being at least 250 channels wide and 10,000 counts at the peak maxima. Kinetic energy release distributions (KERD) were obtained from the product peak shapes by standard methods.[16] Collision induced dissociation (CID) spectra were also recorded using multiple scanning methods with 40% beam reduction using helium as a collision gas.

Samples purchased from Aldrich were outgassed and dried on molecular sieve which had been baked out under vacuum at 500 °C for 24 h.

III. Results and Discussion

Equilibrium Studies. The high-pressure mass spectra of $c\text{-}C_4H_8S$ in a N_2O bath gas obtained at low ionizing electron energies contained major peaks corresponding to $[c\text{-}SC_4H_8]^+$ and $[c\text{-}C_4H_8S\therefore c\text{-}SC_4H_8]^+$. The spectra of $c\text{-}C_5H_{10}S$ had major peaks corresponding to $[c\text{-}SC_5H_{10}]^+$ and $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_5H_{10}]^+$. The ion−molecule reactions responsible for these peaks are

$$[c\text{-}SC_4H_8]^+ + c\text{-}C_4H_8S + M \rightleftharpoons [c\text{-}C_4H_8S\therefore c\text{-}SC_4H_8]^+ + M \quad (1)$$

$$[c\text{-}SC_5H_{10}]^+ + c\text{-}C_5H_{10}S + M \rightleftharpoons [c\text{-}C_5H_{10}S\therefore c\text{-}SC_5H_{10}]^+ + M \quad (2)$$

Mixtures of $c\text{-}C_4H_8S$ and $c\text{-}C_5H_{10}S$ had peaks corresponding to $[c\text{-}SC_4H_8]^+$, $[c\text{-}SC_5H_{10}]^+$, $[c\text{-}C_4H_8S\therefore c\text{-}SC_4H_8]^+$, $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_4H_8]^+$, and $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_5H_{10}]^+$. These ions are linked by reactions 1 through 4.

$$[c\text{-}SC_5H_{10}]^+ + c\text{-}C_4H_8S + M \rightleftharpoons [c\text{-}C_5H_{10}S\therefore c\text{-}SC_4H_8]^+ + M \quad (3)$$

$$[c\text{-}SC_4H_8]^+ + c\text{-}C_5H_{10}S + M \rightleftharpoons [c\text{-}C_5H_{10}S\therefore c\text{-}SC_4H_8]^+ + M \quad (4)$$

Equilibrium reactions 1 through 3 were studied as a function of temperature. Reaction 1 was studied with $c\text{-}C_4H_8S$ in N_2O while reaction 2 was studied with $c\text{-}C_5H_{10}S$ in N_2O. The tests for attainment of equilibrium, described in the Experimental Section and in previous publications, show that with these samples it was easy to attain equilibrium for reactions 1 and 2, and hence, to obtain reliable equilibrium constants.

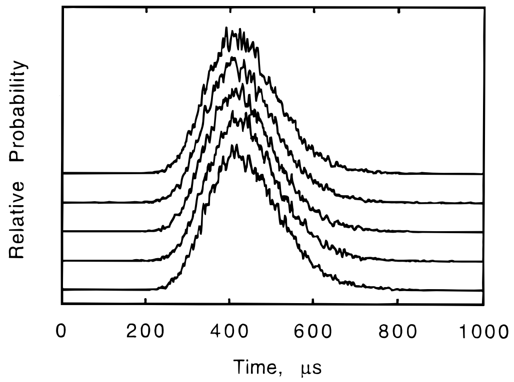

Figure 1. Residence time distributions for all ions in reactions 1 to 3. From top to bottom the distributions correspond to $[c\text{-}SC_4H_8]^+$, $[c\text{-}SC_5H_{10}]^+$, $[c\text{-}C_4H_8S\therefore c\text{-}SC_4H_8]^+$, $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_4H_8]^+$, and $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_5H_{10}]^+$. The distributions demonstrate that reactions 1−3 attained equilibrium simultaneously.

Reactions 1 through 4 were studied in the mixtures of $c\text{-}C_4H_8S$ and $c\text{-}C_5H_{10}S$ in N_2O bath gas. When these reactions were studied simultaneously in the mixtures, the experiments became more challenging. In this case, all five ions involved in the reactions had to achieve equilibrium simultaneously. RTDs for such a case are shown in Figure 1. All five RTDs in this figure have the same average residence time. When these RTDs are superimposed upon each other, they also clearly have the same shape. This experimental finding suggests that all four equilibrium reactions could be studied simultaneously. In practice, however, it was very difficult to study reaction 4 in the mixtures due to the low ion intensity for $[c\text{-}SC_4H_8]^+$. The low intensity for $[c\text{-}SC_4H_8]^+$ may indicate that the charge-transfer reaction 5 channels $[c\text{-}SC_4H_8]^+$ into $[c\text{-}SC_5H_{10}]^+$ as follows:

$$[c\text{-}SC_4H_8]^+ + c\text{-}SC_5H_{10} \rightarrow [c\text{-}C_5H_{10}S\therefore c\text{-}SC_4H_8]^+ \rightarrow [c\text{-}SC_5H_{10}]^+ + c\text{-}SC_4H_8 \quad (5)$$

This reaction is consistent with the ionization potentials (IPs) of the neutral molecules which are 8.38 eV for $c\text{-}SC_4H_8$ and 8.28 for $c\text{-}C_5H_{10}S$.[17]

The experimental van't Hoff plots for reactions 1 through 3 are shown in Figure 2. The scatter is low for all the data. In addition, the agreement for both sets of experiments on $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_5H_{10}]^+$ gives great confidence in the experimental enthalpies and entropies of reaction. These enthalpies and entropies for all three reactions are presented in Table 1; the temperatures reported in the table are the mid-temperatures for the ranges studied.

For ion−molecule association reactions, the association reaction enthalpies are the negative of the bond enthalpies for the bond formed in the reaction, eq II

$$\Delta H_{\text{rxn}} = -\Delta H_{\text{bond}} \quad \text{(II)}$$

The values for the bond enthalpies are presented in Table 1 and can be compared to the S−S 2c−2e bond energy of 272.8 kJ/mol in CH_3SSCH_3.[18] The bond enthalpies reported in Table 1 are less than half that for the bond in CH_3SSCH_3 and are in accord with previous published results on $S\therefore S$ bonds in dialkyl

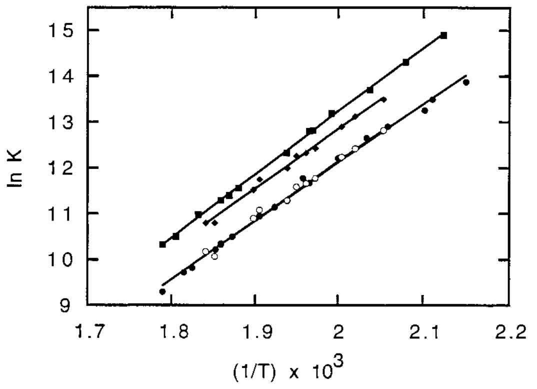

Figure 2. van't Hoff plots for reactions 1−3. The symbols represent ■ reaction 1 forming $[c\text{-}C_4H_8S\therefore c\text{-}SC_4H_8]^+$ with $c\text{-}SC_4H_8$ in N_2O, ◆ reaction 2 forming $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_4H_8]^+$ with mixtures of $c\text{-}SC_4H_8$ and $c\text{-}C_5H_{10}S$ in N_2O, ● reaction 3 forming $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_5H_{10}]^+$ with $c\text{-}C_5H_{10}S$ in N_2O, and ○ reaction 3 with $c\text{-}SC_4H_8$ and $c\text{-}C_5H_{10}S$ in N_2O.

TABLE 1: Bond Enthalpies and Reaction Entropies for the Adducts Formed in Reactions 1−3

	ΔH^o_{bond} (kJ/mol)	ΔS^o_{rxn} (J/K mol)	T (K)[a]
$[c\text{-}C_4H_8S\therefore c\text{-}SC_4H_8]^+$	115 ± 1	−119 ± 2	515
$[c\text{-}C_5H_{10}S\therefore c\text{-}SC_4H_8]^+$	108 ± 2	−109 ± 3	513
$[c\text{-}C_5H_{10}S\therefore c\text{-}SC_5H_{10}]^+$	106[b] ± 2	−111[b] ± 3	512
$[c\text{-}C_5H_{10}S\therefore c\text{-}SC_5H_{10}]^+$	107[c] ± 4	−113[c] ± 7	512

[a] The temperatures are those for the midpoints in the van't Hoff plots. [b] For reaction 2 forming $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_5H_{10}]^+$ with $c\text{-}C_5H_{10}S$ in N_2O. [c] For reaction 2 forming $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_5H_{10}]^+$ with $c\text{-}SC_4H_8$ and $c\text{-}C_5H_{10}S$ in N_2O.

sulfides.[5−7,9] The bond enthalpies reported in this article decrease in the order $[c\text{-}C_4H_8S\therefore c\text{-}SC_4H_8]^+$, $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_4H_8]^+$, and $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_5H_{10}]^+$. This trend may be due to steric hindrance across the 2c−3e bond. In previous studies[5,7] we found that steric hindrance did not play a major role in the S∴S 2c−3e bonding interaction; however, it was noted that computationally the energy minimum for the $[Et_2S\therefore SEt_2]^+$ product ion had C_2 symmetry rather than C_{2v} as did $[Me_2S\therefore SMe_2]^+$. The difference in the geometries was attributed to steric hindrance across the S∴S bond in the case of $[Et_2S\therefore SEt_2]^+$; however, the effect of the hindrance on the S∴S 2c−3e bond energy was minimal when the computed energies for the C_{2v} and C_2 structures were compared. In a paper submitted for publication on dialkyl sulfide systems, Nibbering et al. also suggested that steric hindrance played a role across S∴S bonds.[19]

The experimental entropies of reaction from Table 1 are −119, −109, and −112 J/mol K for reactions 1 through 3, respectively (errors are given in Table 1). The magnitude of these values are also in accord with those expected for gas-phase entropies of association and previous results on similar reactions.[5−7,9] As discussed in the Experimental Section, we are confident in these numerical results; the fact that both experiments for reaction 3 yield the same entropy of reaction lends support to this finding. The entropy for reaction 1 is the highest of the three reactions. This is in synergy with the bond enthalpies; the strongest interaction has the largest change in the entropy of reaction since it is least like the reactants. The differences between the numerical values for the enthalpies and entropies of reaction reactions 2 and 3 are much smaller.

MS/MS Studies. Metastable and CID MS/MS experiments on the three adduct ions were carried out using the ZAB mass spectrometer. Only one product ion corresponding to cleavage of the S∴S bond is observed in the metastable spectra of the two symmetric adducts $[c\text{-}C_4H_8S\therefore c\text{-}SC_4H_8]^+$ and $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_5H_{10}]^+$. This single fragmentation path can be contrasted to published metastable spectra of dialkyl sulfide cases $[R_2S\therefore SR_2]^+$, where both cleavage of the S∴S bond and loss of R groups were observed.[6,8] The loss of R groups was observed when the R groups were larger than Me (i.e., for Et, *n*-Pr, and *i*-Pr). In those adducts, loss of a R group results from cleavage of a single C−S 2c−3e bond. An energy "trade off" was proposed allowing for the competition between cleavage of a S∴S bond with a bond order of $^1/_2$ and a C−S bond with a bond order of 1.[6,8] The adducts being discussed here, $[c\text{-}C_4H_8S\therefore c\text{-}SC_4H_8]^+$ and $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_5H_{10}]^+$, cannot lose an R group by simple cleavage of only one bond if the rings are intact. Hence, the single peaks observed in the metastable spectra support the notion that the association products contain intact rings.

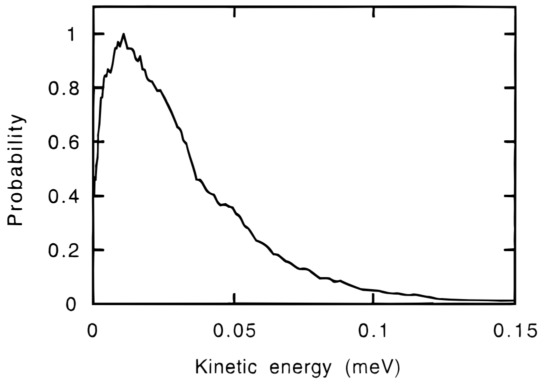

Figure 3. KERD for reaction 6; the average KER is 34 meV.

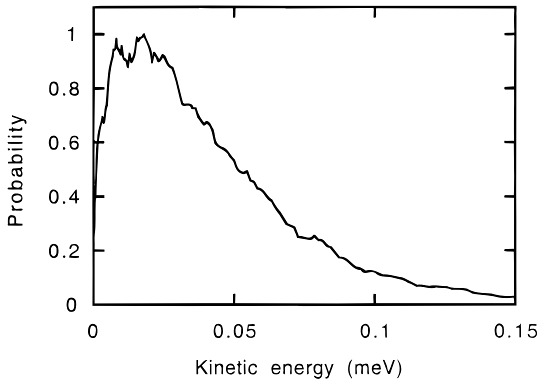

Figure 4. KERD for reaction 7; the average KER is 42 meV.

The kinetic energy release distributions, KERDs, derived from the product ion peak shapes for reactions 6 and 7 are shown in

$$[c\text{-}C_4H_8S\therefore c\text{-}SC_4H_8]^+ \rightarrow [c\text{-}SC_4H_8]^+ + c\text{-}C_4H_8S \quad (6)$$

$$[c\text{-}C_5H_{10}S\therefore c\text{-}SC_5H_{10}]^+ \rightarrow [c\text{-}SC_5H_{10}]^+ + c\text{-}C_5H_{10}S \quad (7)$$

Figures 3 and 4.

The average KERs are 34 meV for reaction 6 and 42 meV for reaction 7. The larger average KER for fragmentation of $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_5H_{10}]^+$ relative to $[c\text{-}C_4H_8S\therefore c\text{-}SC_4H_8]^+$ is consistent with the weaker S∴S bond in the former ion. In both cases, the KERD peak shapes are very similar to published shapes for fragmentations involving S∴S bonds[6,8] and suggest that the reactions proceeds via a process that does not involve a substantial reverse activation barrier.

The CID spectra of $[c\text{-}C_4H_8S\therefore c\text{-}SC_4H_8]^+$ and $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_5H_{10}]^+$ also provide evidence for the 2c−3e bonded cyclic

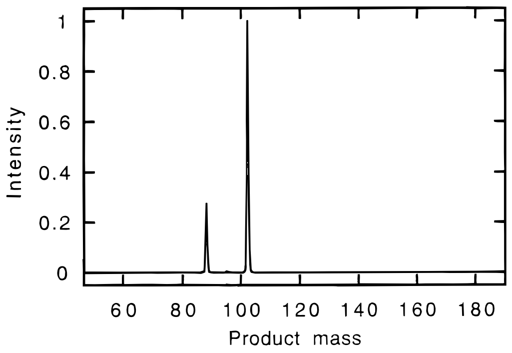

Figure 5. Metastable spectrum of $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_4H_8]^+$.

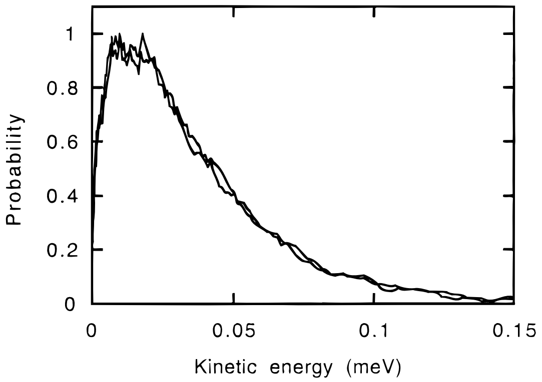

Figure 6. Kinetic energy release distributions for reactions 8 and 9; the average KER for both reactions is 36 meV.

adducts with intact rings. The spectra have very intense peaks for fragmentation of the S∴S bond while all other product peaks are substantially weaker. In fact, it was difficult to distinguish between the metastable and CID spectra, the convincing difference between the two processes were the peak widths at the base line (the CID spectra were broader than the metasable spectra) and the absence of the very weak peaks in the metastable spectra.

The metastable spectrum of $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_4H_8]^+$ is shown in Figure 5. It differs from those of $[c\text{-}C_4H_8S\therefore c\text{-}SC_4H_8]^+$ and $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_5H_{10}]^+$, in that two peaks are observed, corresponding to $[c\text{-}C_5H_{10}S]^+$ and $[c\text{-}C_4H_8S]^+$. This result is reasonable since the IPs of the two neutral moieties are similar.[17] As expected the metastable intensity is strongest for $[c\text{-}C_5H_{10}S]^+$ the ion which originates from the neutral with the lowest IP. In fact, this result can be interpreted by the kinetic method[20] to definitively show that the IP of c-$C_5H_{10}S$ is lower than that of c-C_4H_8S. It is interesting to note that both ions are observed in comparable intensity in the metastable spectra which result from energized adducts but that the intensity is weaker for $[c\text{-}C_4H_8S]^+$ than that for $[c\text{-}C_5H_{10}S]^+$ in the equilibrium studies which involve thermal ions.

The KERDs for reactions 8 and 9

$$[c\text{-}C_5H_{10}S\therefore c\text{-}SC_4H_8]^+ \rightarrow [c\text{-}SC_5H_{10}]^+ + c\text{-}C_4H_8S \quad (8)$$

$$[c\text{-}C_5H_{10}S\therefore c\text{-}SC_4H_8]^+ \rightarrow [c\text{-}SC_4H_8]^+ + c\text{-}C_5H_{10}S \quad (9)$$

are shown in Figure 6. The distributions are nearly identical and have the same general shape as those shown above for the metastable reactions of $[c\text{-}C_4H_8S\therefore c\text{-}SC_4H_8]^+$ and $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_5H_{10}]^+$. The average KER for both fragmentation process is 36 meV. The same general peak shape and average KER for both reactions very strongly suggests similar fragmentation processes and energy requirements for the reactions. One could argue that the reaction coordinate for reactions 8 and 9 are almost identical, the only difference being which moiety retains the charge.

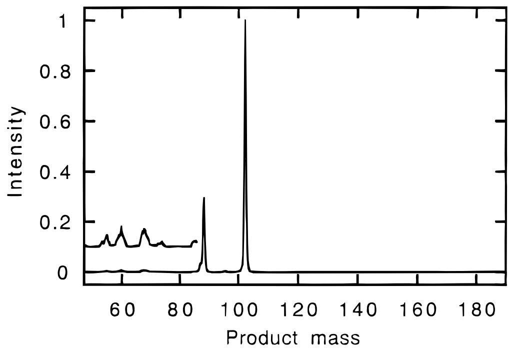

Figure 7. The collision induced dissociation spectrum $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_4H_8]^+$. The inset is ×10.

The CID spectrum of $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_4H_8]^+$ is shown in Figure 7. As expected, intense peaks are observed for $[c\text{-}C_5H_{10}S]^+$ and $[c\text{-}C_4H_8S]^+$ and only very weak peaks for other processes corresponding to fragmentations which must involve ring opening reactions.

In this study, both the metasable and CID spectra of all three ions were very similar. This provides strong evidence for intact rings, since if one or both of the rings were open, loss of the dangling R groups might take place in the metastable time frame and would be facile following collisional activation.

Ring Expansion reactions. When small cyclic sulfur-containing cations $[c\text{-}C_nH_{2n}S]^+$ react with small cyclic neutral molecules $[c\text{-}C_nH_{2n}S]$ where $n = 2$ and 3, ring expansion reactions have been observed.[1,2] The reactions involve opening of one of the rings, followed by attack of the opened R group on the sulfur atom in the intact ring. The mechanism results in incorporation of both sulfur atoms into a new ring followed by expulsion of an R group. In the experiments discussed above, ring expansion reactions were not observed with the five- and six-membered rings; rather the association reactions 1 to 3 resulting in the adducts containing intact rings were seen.

In this study, the reactions of $[c\text{-}C_5H_{10}S]^+$ and $[c\text{-}C_4H_8S]^+$ with c-C_2H_4S and c-C_3H_6S were also investigated. Small quantities of c-C_2H_4S or c-C_3H_6S were added to samples of c-$C_5H_{10}S$ and to samples of c-C_4H_8S in the DuPont ion source. Only one expansion step corresponding to reaction 10 was observed.

$$[c\text{-}C_4H_8S]^+ + c\text{-}C_2H_4S \rightarrow [c\text{-}C_4H_8S_2]^+ + C_2H_4 \quad (10)$$

The intensity of $[c\text{-}C_4H_8S_2]^+$ was weak; however, it correlated with the c-C_2H_4S neutral gas pressure. Ions corresponding to the products in reactions 11 through 13 were not observed:

$$[c\text{-}C_4H_8S]^+ + c\text{-}C_3H_6S \not\rightarrow \mathrm{X}\ [c\text{-}C_4H_8S_2]^+ + C_3H_6 \quad (11)$$

$$[c\text{-}C_5H_{10}S]^+ + c\text{-}C_2H_4S \not\rightarrow \mathrm{X}\ [c\text{-}C_5H_{10}S_2]^+ + C_2H_4 \quad (12)$$

$$[c\text{-}C_5H_{10}S]^+ + c\text{-}C_3H_6S \not\rightarrow \mathrm{X}\ [c\text{-}C_5H_{10}S_2]^+ + C_6H_6 \quad (13)$$

Thus, a ring expansion reaction of $[c\text{-}C_4H_8S]^+$ proceeds with c-C_2H_4S and not with c-C_3H_6S. These new results and the published results[1,2] suggest that ring strain plays an important role as a driving force in the ring expansion reactions. Also, the fact that the ring strain in the neutral moiety plays a direct role in the ring expansion is indicated by the fact that reaction 10 is observed but not reaction 11. In summary, the smaller ring systems react by a ring expansion mechanism which proceeds through an intermediate association adduct which is not observed while the larger rings react by an association step which is observed while the ring opening process does not take place.

IV. Conclusions

Both association and ring expansion reactions were observed in this study. Equilibrium, MS/MS metastable and CID results strongly support sulfur−sulfur 2c−3e interactions with intact cyclic groups for $[c\text{-}C_4H_8S\therefore c\text{-}SC_4H_8]^+$, $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_4H_8]^+$, and $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_5H_{10}]^+$. Metastable reactions of the parent ions cleave the S∴S 2c−3e bond by processes which require no reverse activation barriers. The product peaks resulting from cleavage of the S∴S 2c−3e bond yield the most intense peaks in both the metastable and CID spectra. Equilibrium experiments resulted in reliable S∴S 2c−3e bond enthalpies for the cyclic compounds and in reliable reaction entropies for reactions 1 through 3.

A ring expansion reaction was observed only for the reaction of $[c\text{-}C_4H_8S]^+$ with $c\text{-}C_2H_4S$. This and previous results suggest that ring strain provides a driving force for the ring expansion reactions this group has observed with cyclic sulfur-containing rings. We propose that the first step in the ring expansion mechanism is similar to the loss of an R group in the case of the dialkyl S∴S 2c−3e bond containing compounds.

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