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Experimental Investigation of Gas Phase Ions of the Form $[c\text{-}C_nH_{2n}S\therefore ICH_3]^+$ where $n = 2$, 3, 4, and 5. Metastable and Collision-Induced Dissociation Results

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We report an experimental study of the metastable and collision-induced dissociation spectra of association adducts with the suggested general formula $[c\text{-}C_nH_{2n}S\therefore ICH_3]^+$ where $n = 2$, 3, 4, and 5. These association adducts are examples of gas-phase cations which may contain 2c−3e sulfur−iodine bonding interactions. Metastable cleavage of the sulfur−iodine bonds result in predominately one reaction, $[c\text{-}C_nH_{2n}S\therefore ICH_3]^+ \rightarrow c\text{-}C_nH_{2n}S^{\bullet+} + CH_3I$; this reaction cleaves the proposed 2c−3e bond. The product ion for each adduct exhibits a small average kinetic energy release implying a fragmentation with a small or no reverse activation barrier. Fragmentation by collision-induced dissociation yields two intense product peaks and numerous weaker peaks. These metastable and collision-induced dissociation results support hypervalent $S\therefore I$ bonding within the ionic adducts. The spectra also suggest that the sulfur-containing moieties in the adducts are ring-closed.

Introduction

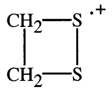
Two-center−three-electron (2c−3e) bonds were first proposed by Linus Pauling in 1931;[1] the bonds were described as covalent bonds with bond order of one-half. 2c−3e bonds have been observed and extensively described[2] in the gas phase, in solution, in the solid state, and as reactive intermediates. Here, we will only introduce a few studies which directly relate to the current research.

Several groups, including Nibbering's, Baer's, and our group, have studied gas-phase cations containing 2c−3e bonds. Nibbering et al.[3] have reported $S\therefore S$ and $Cl\therefore Cl$ connectivety, whereas Baer et al.[4] have reported $Cl\therefore Cl$ connectivety. In our work, $S\therefore S$, $S\therefore X$, $X\therefore X$, and $X\therefore Y$ atomic connectivity where X and Y represent I, Br, and Cl have been reported.[5−12] We have found evidence for these bonds in adducts containing both cyclic[7−9] and noncyclic[5,6,10−12] moieties. With noncyclic moieties, we have observed 2c−3e bonding between the heteroatoms: $S\therefore S$, $S\therefore I$, $S\therefore Br$, $I\therefore I$, $Br\therefore Br$, $Cl\therefore Cl$, and $I\therefore Br$.[5,6,10−12] Many of these same 2c−3e bonded interactions have also been reported in the condensed phase.[2] In the gas-phase work, the association products containing these interactions undergo metastable and collision-induced dissociation (CID) reactions that strongly support 2c−3e bonds and heteroatom-to-heteroatom connectivity.[3−12]

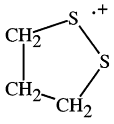
We are not aware of many solution-phase studies involving 2c−3e bonding with cyclic moieties. However, in our gas-phase research with cyclic moieties aiming to examine $[c\text{-}C_nH_{2n}S\therefore S\ c\text{-}C_nH_{2n}]^+$, ($n = 2$−5), [7,8,9] we found that $[c\text{-}C_2H_4S\therefore S\ c\text{-}C_2H_4]^+$ and $[c\text{-}C_3H_6S\therefore S\ c\text{-}C_3H_6]^+$ undergo ring-expansion reactions, reaction 1.[7,8]

$$c\text{-}C_nH_{2n}S^{\bullet+} + c\text{-}C_nH_{2n}S \rightarrow [c\text{-}C_nH_{2n}S\therefore c\text{-}SC_nH_{2n}]^+ \rightarrow c\text{-}C_nH_{2n}S_2^{\bullet+} + C_nH_{2n} \qquad n = 2 \text{ and } 3 \quad (1)$$

The reactions proceed with retention of both sulfur atoms in the newly formed ionic products. Computations suggested that these ring-expansion reactions involve 2c−3e bonded adducts in the first step. The ring expansion then proceeds resulting in a new ring containing two adjacent sulfur atoms; hence, there is a sulfur insertion into the ring. The product ion structures are shown as *a* and *b*. We also found that stabilization of the 2c−3e adduct was very difficult because of the competing reaction which resulted in ring-expanded products.



a



b

With five- and six-membered rings,[9] reaction 1 did not occur, rather the formation of adducts was facile and the reactions terminated with formation of adducts, reaction 2.

$$c\text{-}C_nH_{2n}S^{\bullet+} + c\text{-}C_nH_{2n}S \rightarrow [c\text{-}C_nH_{2n}S\therefore c\text{-}SC_nH_{2n}]^+ \qquad n = 4 \text{ and } 5 \quad (2)$$

In these cases, it was even possible to conduct thermodynamic ion−molecule equilibrium measurements to determine reaction enthalpies and entropies.

With this background, it seemed logical to investigate the adducts and reactions of sulfur ring-containing systems with neutral methyl halide moieties. A strong motivation for the study is the effect of sulfur-containing ring moieties on the formation of 2c−3e bonded adducts between sulfur and halogen atoms to determine if the halogen could be incorporated into the ring system in a reaction similar to (1). The present research describes the first such studies on mixed sulfur ring-containing moieties bonded with the methyl halides. The research also addresses the bonding within the adducts and the fragmentation reactions that they undergo.

Experimental Methods

Tandem mass spectrometric studies were carried out on a highly modified ZAB-1F (VG Analytical Ltd., Manchester, UK),

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which has been described in detail elsewhere.[6] Four modifications are relevant to this work. First, a 1 cm long collision cell was added before the β slit in the second field-free region. Second, the electron multiplier (an ETP Scientific AF130) was placed in-line to the ion beam. This geometry significantly reduces the energy discrimination in metastable peak shape analysis. Third, an ion source consisting of a coaxial electron entrance/ion exit geometry was built. The coaxial electron entrance/ion exit geometry allows for high ion source sensitivity at high ion source pressures. The ion source is heated and cooled by gaseous nitrogen which is temperature controlled by either Ohmic heating or by cooling with liquid nitrogen. The heat transfer takes place though a stainless steel tube silver-soldered to the source body and isolated from ground potential by glass to metal seals. Fourth, the ZAB was interfaced with a PC. The PC was used to control the MIKES scan and collect pulsed signals from a MTS 100 pulse preamplifier.

Adducts were formed by ion−molecule reactions within the ion source. In all cases, adduct formation required high source pressures. The actual ion source pressures are not known in this apparatus, but the background gas pressure in the ion source housing was very close to our trip point of 1×10^{-4} Torr. With comparisons to other ion sources in which we can measure the gas pressure, we estimate the ion source pressure to be on the order of 0.5 Torr. The high pressure in the source region induced CID background peaks during our metasable scans in the second field-free region. These induced peaks probably arose from a combination of activation in the first field-free region and from the slightly increased pressures in the second field-free region. Pressure-dependent experiments were conducted to determine the genuine metastable processes. In these qualitative experiments, the relative variation of peak intensities were examined to determine the true metastable reactions. Kinetic energy release distributions, KERD's, were obtained by standard methods from metastable peak shape analysis.[13] CID spectra were recorded using helium as the stationary gas at pressures needed to reduce the main beam intensity by 40%.

All chemicals used were commercially available. Sample preparation was accomplished by simple outgassing through several freeze−pump−thaw cycles with a Pyrex vacuum line with a base pressure of approximately 1×10^{-5} Torr.

Results and Discussion

Adduct Formation. With the history described in the Introduction, we decided to initiate the present investigation on the reactions of the sulfur-containing ring systems, $c\text{-}C_2H_4S^{\bullet+}$, $c\text{-}C_3H_6S^{\bullet+}$, $c\text{-}C_4H_8S^{\bullet+}$, and $c\text{-}C_5H_{10}S^{\bullet+}$ with the methyl halides, CH_3X where X = I, Br, and Cl. The first finding is that formation of adducts of the form $[c\text{-}C_nH_{2n}S\therefore XCH_3]^+$ through reaction 3 was successful in our hands only with methyl iodide.

$$c\text{-}C_nH_{2n}S^{\bullet+} + XCH_3 \rightarrow [c\text{-}C_nH_{2n}S\therefore XCH_3]^+ \qquad n = 2, 3, 4, \text{and } 5 \quad (3)$$

Reaction 3 was repeatedly attempted with X = Br and Cl; however, the parent adduct ion beams were very weak, and reliable metastable and CID experiments were not possible. This result differs from previous studies of dimethyl sulfide and the methyl halides. With dimethyl sulfide, adducts of the form $[(CH_3)_2S\therefore XCH_3]^+$ were formed for CH_3I, CH_3Br, and CH_3Cl, whereas with CH_3F, a hydrogen bonded adduct was observed.[10]

Another interesting finding is that, in this work, with X = I we were able to form adducts for all four-ring systems. This contrasts with the bicyclic studies discussed in the Introduction[7−9] where adduct formation was facile only for $[c\text{-}C_4H_8S\therefore c\text{-}SC_4H_8]^+$ and $[c\text{-}C_5H_{10}S\therefore c\text{-}SC_5H_{10}]^+$ [reaction 2] and where adducts for the $[c\text{-}C_2H_4S\therefore c\text{-}SC_2H_4]^+$ and $[c\text{-}C_3H_6S\therefore c\text{-}C_3H_6S]^+$ systems were very difficult to form because of the second step in reaction 1. In our previous studies on these last two adducts, we proposed that adducts were not observed because of rearrangement and fragmentation involving a ring-opened intermediate [reaction 1]. Apparently, for the $[c\text{-}C_nH_{2n}S\therefore ICH_3]^+$ adducts presented in this paper, such rearrangements do not dominate for the small rings, and it is possible to stabilize and study all of the adducts. This result suggests to us that the rings in the adducts may be intact. Hence, a rearrangement reaction, such as the example shown below, involving a ring-opened species does not predominate in the metastable time window as it does for the three- and four-membered bicyclic S∴S cases. It is possible that in the present examples the large size and polarizability of iodine stabilizes the sulfur containing rings.

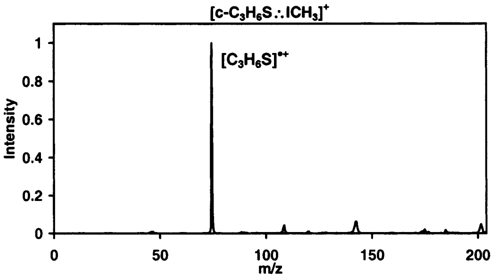
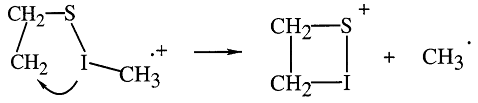


Figure 1. Metastable spectrum of $[c\text{-}C_3H_6S\therefore ICH_3]^+$ showing only one major fragmentation reaction resulting in $c\text{-}C_3H_6S^{\bullet+} + CH_3I$.



We note, however, that, for the gas mixture used in the $[c\text{-}C_2H_4S\therefore ICH_3]^+$ studies, a peak at $m/z = 187$ corresponding to $C_2H_4SI^+$ was observed in the normal mass spectrum. In addition, peaks at m/z = 201, 215, and 229 were also observed in the normal mass spectra of the mixtures used for the $[c\text{-}C_3H_6S\therefore ICH_3]^+$, $[c\text{-}C_4H_8S\therefore ICH_3]^+$, and $[c\text{-}C_6H_{10}S\therefore ICH_3]^+$, respectively. We did not further investigate these ions in the normal mass spectra.

Metastable Spectra of $[c\text{-}C_nH_{2n}S\therefore ICH_3]^+$. The metastable reactions for $[c\text{-}C_nH_{2n}S\therefore ICH_3]^+$ ($n = 2-5$) are all similar, implying all four ions have similar structural features. The metastable spectra and results for all four ions will thus be presented together. Figure 1 shows a representative metastable spectrum for $[c\text{-}C_3H_6S\therefore ICH_3]^+$. As shown in Figure 1, there is only one major metastable fragmentation path, that resulting from cleavage of the 2c−3e bond yielding $c\text{-}C_3H_6S^{\bullet+}$ m/z 74. In this fragmentation reaction, the positive charge is retained on the sulfur-containing moiety with loss of neutral CH_3I. The corresponding metastable reaction, yielding $CH_3I^{\bullet+}$ and $c\text{-}C_3H_6S$ is not observed (the small peak at m/z 142 in Figure 1 is due to residual CID; compare peak intensities in Figures 1−3b). The observed fragmentation reaction is in accord with what one would expect from the relative ionization energies of the two moieties. The three other association adducts have similar fragmentation paths, always resulting in loss of neutral CH_3I. The kinetic energy release distribution for the $c\text{-}C_3H_6S^{\bullet+}$ peak in Figure 1 is shown in Figure 2. The distribution has a sharp peak near zero KER and a small average kinetic energy release of 8 meV. These features suggest direct cleavage reactions with

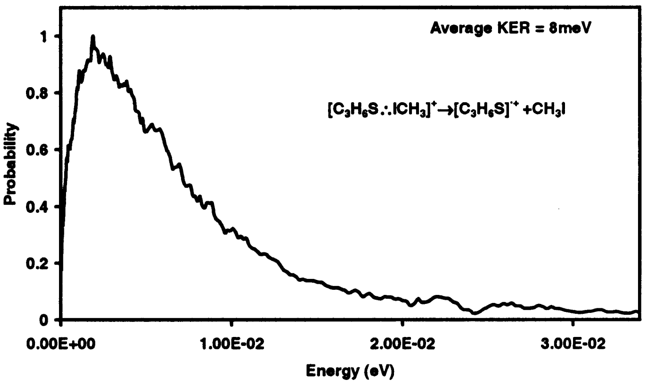


Figure 2. Kinetic energy release distribution for the fragmentation in Figure 1. The average kinetic energy release for this distribution is 8 meV.

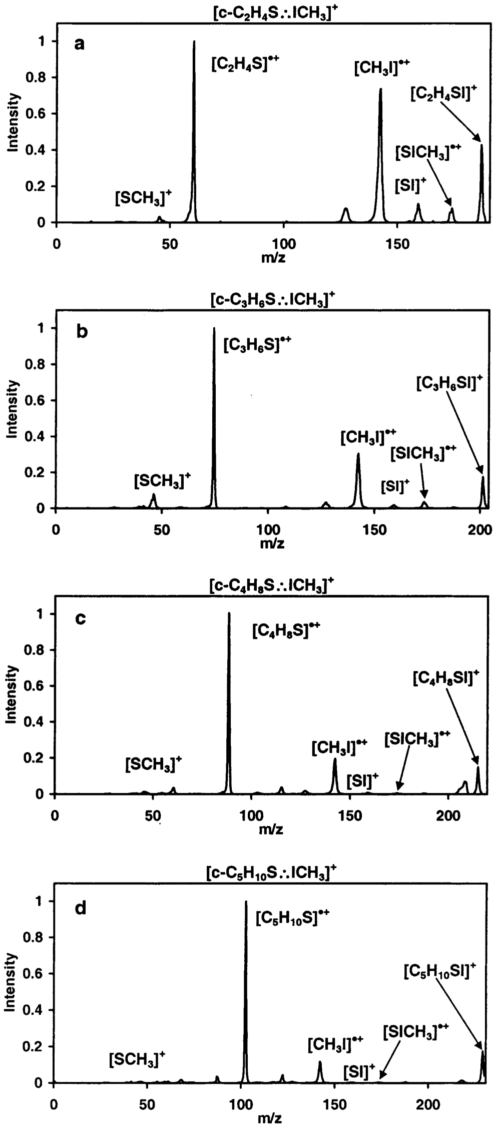


Figure 3. (a−d) Collision-induced dissociation spectra for $[c\text{-}C_2H_4S\therefore ICH_3]^+$, $[c\text{-}C_3H_6S\therefore ICH_3]^+$, $[c\text{-}C_4H_8S\therefore ICH_3]^+$, and $[c\text{-}C_5H_{10}S\therefore ICH_3]^+$ top to bottom, respectively. The spectra show how the $c\text{-}C_nH_{2n}S^{\bullet+}$ to $CH_3I^{\bullet+}$ ratio varies with increasing ring size. This variation correlates with the difference in ionization energies of the two moieties.

TABLE 1: Difference in the Ionization Energies (IE) between the Adduct Moieties[a]

adduct	ΔIE[b] (eV)
$[c\text{-}C_2H_4S\therefore ICH_3]^+$	0.49
$[c\text{-}C_3H_6S\therefore ICH_3]^+$	0.93
$[c\text{-}C_4H_8S\therefore ICH_3]^+$	1.16
$[c\text{-}C_5H_{10}S\therefore ICH_3]^+$	1.24

[a] IE of CH_3I minus the IE of the sulfur containing moiety. [b] The NIST Chemistry webbook, http://webbook.nist.gov/, and references therein. When available, the evaluated IE were used. The IE of the other species were evaluated by the authors.

small or no reverse activation barriers. The average kinetic energy releases for all four fragmentations are all relatively small (on the order of 5−9 meV). These data are in agreement with all our previous studies on direct metastable fragmentations of 2c−3e bonded ions.

We note the absence of metastable processes involving skeletal rearrangements with ejection of neutral iodine or sulfur atoms (Figure 1). These metastable spectra differ from some previous results of other 2c−3e bonded adducts between different heteroatoms observed by our group. Previous work on 2c−3e bonded adducts sometimes resulted in two competing metastable fragmentation paths, direct cleavage of the 2c−3e bond and a fragmentation path that required structural rearrangement of the skeletal atoms. For instance, with $[(CH_3)_2S\therefore ICH_3]^+$, two metastable ions were observed, $(CH_3)_2S^{\bullet+}$ at *m/z* 62 and $(CH_3)_2S{-}CH_3^+$ at *m/z* 77.[10] The ion at *m/z* 77 could only result from rearrangement of the adduct with loss of iodine. In that work, we proposed that the S−I bond in the adduct would lengthen as the methyl group migrates and inserts into the lengthened S−I bond. The kinetic energy releases for the rearrangement paths were always greater than those for the direct cleavage. This finding is consistent with large reverse activation barriers upon skeletal rearrangement followed by fragmentation. As stated, analogous peaks in the present experiments were not observed. We suggest that the absence of the rearrangement paths in the experiments reported here may be due to the presence of an intact ring on the sulfur moiety. We suggest that, if there were a S−I linkage but with a ring-opened R group on the sulfur atom, the spectra might have a competing intense peak for the loss of a R group or for loss of one of the heteroatoms. Such processes would parallel the metastable reactions observed in the spectra of some of the 2c−3e adducts with noncyclic moieties.

CID Spectra of $[c\text{-}C_nH_{2n}S\therefore ICH_3]^+$. The CID spectra of $[c\text{-}C_nH_{2n}S\therefore ICH_3]^+$ are shown in Figure 3a−d. The main features of these spectra are all similar; however, the intensities of the two major peaks vary in a systematic way. A general feature of the CID spectra are intense peaks for the direct cleavage of the S∴I bond with retention of charge on either of the two moieties. Comparison of the four spectra shows how the intensity of $CH_3I^{\bullet+}$ decreases as the ring size increases. This trend correlates with the ionization energy difference between the two competing moieties. The ionization energy (IE) differences are presented in Table 1. Clearly, the smaller the IE difference the larger the $CH_3I^{\bullet+}$ intensity relative to the intensity of the sulfur-containing moiety.

The spectra in Figure 3a−d also show peaks for cleavage of a methyl group. Such peaks result from simple cleavage of the methyl group on the iodine moiety. In contrast, the $SICH_3^{\bullet+}$ peaks corresponding to loss of the hydrocarbon portion of the rings attached to the sulfur atoms are weaker and varied in intensity with the ring size. The strongest $SICH_3^{\bullet+}$ peak was observed for the three-membered ring, the adduct with the greatest ring strain. If the rings were intact, loss of the hydrocarbon portion of the rings resulting in $SICH_3^{\bullet+}$ would require breaking two C−S bonds, whereas loss of $CH_3^{\bullet}$ requires breaking only one C−I bond. Hence, the more intense peaks from loss of $CH_3^•$ provide convincing evidence that the ring in the adducts are intact.

Strong evidence for SI connectivity comes from CID product peaks resulting in SI^+; this peak is particularly evident in Figure 3a. The intensity of the SI^+ peak varies dramatically with the ring size. SI^+ is a significant product in Figure 3a, and its intensity drops until it can barely be discerned in Figure 3d. This intensity variation correlates with the expected ring strain energy; presumably, the ring strain helps cleave the two S−C and the C−I bonds. All of the observed fragments in these CID spectra are consistent with the proposed structures containing 2c−3e bonded adducts.

Conclusions

These metastable and CID spectra all lend strength to the proposed structures with intact rings and S∴I bonds. The data presented here indicate that the four adduct ions $[c\text{-}C_2H_4S\therefore ICH_3]^+$, $[c\text{-}C_3H_6S\therefore ICH_3]^+$, $[c\text{-}C_4H_8S\therefore ICH_3]^+$, and $[c\text{-}C_5H_{10}S\therefore ICH_3]^+$ are all bonded by 2c−3e interactions between sulfur and iodine atoms. Unlike other 2c−3e bonded adducts, we did not observe fragmentation involving loss of a heavy atom in the metastable spectra. The data presented here strongly suggest that the reactant ring is intact in the stabilized adducts.

References and Notes

(1) Pauling, L. *J. Am. Chem. Soc.* **1931**, *53*, 3225.

(2) For leading references, see: (a) Braida, B.; Hazebroucq, S.; Hiberty, P. *J. Am. Chem. Soc.* **2002**, *124*, 2371−2378. (b) Asmus, K.-D. *Nukleonika* **2000**, *45*, 3. (c) Asmus, K.-D. In *Sulfur-Centered Reactive Intermediates in Chemistry and Biology*; Chatgilialoglu, C., Asmus K.-D., Eds.; Plenum Press: New York and London, 1990; p 155.

(3) (a) de Visser, S. P.; de Koning, L. J.; Nibbering, N. M. M. *Int. J. Mass Spectrom.* **1998**, *120*, 1517. (b) de Visser, S. P.; Matthias, B. F.; de Koning, L. J.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1998**, *179*, 9/180, 43.

(4) Booze, J. A.; Baer, T. *J. Chem. Phys.* **1992**, *96*, 5541.

(5) (a) Illies, A. J.; Livant, P.; McKee, M. L. *J. Am. Chem. Soc.* **1988**, *110*, 7980. (b) Deng, Y.; Illies, A. J.; James, M. A.; McKee, M. L.; Peschke, M. *J. Am. Chem. Soc.* **1995**, *117*, 420. (c) James, M. A.; McKee, M. L.; Illies, A. J. *J. Am. Chem. Soc.* **1996**, *118*, 7842.

(6) (a) Illies, A. J.; Nichols, L. S.; James, M. A. *J. Am. Soc. Mass Spectrosc.* **1997**, *8*, 605. (b) James, M. A.; Illies, A. J. *J. Phys. Chem.* **1996**, *100*, 15794.

(7) Ekern, S.; Illies, A.; McKee, M. L.; Peschke, M. *J. Am. Chem. Soc.* **1993**, *115*, 12510.

(8) Peschke, M.; McKee, M. L.; Illies, A. J. unpublished work on the ring expansion involving $[c\text{-}C_3H_6S\therefore S\ c\text{-}C_3H_6]^+$

(9) Illies, A. J. *J. Phys. Chem.* **1998**, *102*, 8774

(10) Nichols, L. S.; Illies, A. J. *J. Am. Chem. Soc.* **1999**, *121*, 9176.

(11) (a) Livant, P.; Illies, A. *J. Am. Chem. Soc.* **1991**, *113*, 1510. (b) Nichols, L. S.; McKee, M. L.; Illies, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 1538.

(12) Nichols, L. S.; Illies, A. J. *Int. J. Mass Spectrom.* **1999**, *185/186/187*, 413.

(13) Bowers, M. T.; Illies, A. J.; Jarrold, M. F. *Chem. Phys.* **1982**, *65*, *19*