Conclusions

An attempt is made to explain the anomalous behavior of recently published polarized spectra of crystalline DA solids by considering the consequences of symmetry in DA complexes and the selection rules for electronic transitions which follow. Discussion is restricted to systems of the benzidine–chloranil types, where the component molecules (D and A separately) possess high symmetry (*e.g.*, D_{2h}). The DA complex is stabilized in a "sandwich" configuration of relatively large intermolecular π–π overlap. CT transitions of the DA complex are thus predicted to exhibit unique polarization effects. The first and second CT bands for benzidine–chloranil have, as the reported spectra indicate, axes of polarization perpendicular to one another under specific configurations (*i.e.*, C_{2v}, C_2, or $C_s(x)$). The crystal structures of this and related complexes have not been reported so that no direct comparisons are possible at present.

Symmetry-based wave functions provide a means to predict stable configurations of a large family of DA complexes once the respective molecular orbital representations of D^+ and A^- ion radicals are known. Tables VI–IX list the relative symmetry(s) under which the first CT state $|D^+A^-\rangle$ has the correct representation to allow CT stabilization of the ground state. Both must be of the totally symmetric representation (A_1, A, or A′). From reported crystal structure data of DA solids, this A_1 symmetry criterion is always found to hold. As a consequence, the benzidine–chloranil complex is predicted *not* to have symmetries C_{2v}^{90}, $C_s^{90}(y)$, or $C_s^{90}(x)$. From the incomplete list of molecules surveyed, one can make many other interesting predictions worth experimental verifications.

Finally if the DA structure *and* spectra are known as it is for the perylene–fluoranil complex, molecular orbital information on the D^- and A^- components can be extracted. Under the approximate $C_s(x)$ symmetry of the complex the important orbitals involved with the first and second CT bands are assigned as follows: perylene, a_u (first) and b_{2g} (second) donor orbitals; fluoranil, b_{2g} acceptor orbital. Accidental degeneracies of the second donor orbital of perylene made the origin of that state in doubt.

Acknowledgments. I am pleased to acknowledge the two laboratories (above) at which this work was carried out and from which the author received full support and cooperation.

Ion–Molecule Reactions of Hydrogen Sulfide with Ethylene and Acetylene

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Abstract: Ion cyclotron resonance spectroscopy has been used to study the ion–molecule reactions in mixtures of hydrogen sulfide with ethylene and acetylene. In ethylene the major products at 12.5 eV are CH_2S^+ and CH_2SH^+. Small amounts of HCS^+ are observed at higher electron energies. Deuterium labeling of ethylene shows that two of the hydrogens in CH_2SH^+ and the two hydrogens in CH_2S^+ come from the same ethylene carbon atom. The third hydrogen in CH_2SH^+ originates from the hydrogen sulfide. The hydrogen sulfide–ethylene reaction complex has an ethanethiol molecular ion structure and hydrogen rearrangement within the complex is slow compared to fragmentation to the reaction products. The products of the reaction of hydrogen sulfide ion with acetylene are HCS^+ and $C_2H_3S^+$. The acetylene ion does not react with hydrogen sulfide except by charge transfer. The reactions of hydrogen sulfide ion with acetylene-d_2 indicate that the reaction complex is best represented as the enol form of the sulfur analog of acetaldehyde molecular ion. Charge localization on sulfur in the reaction complex inhibits the extensive hydrogen rearrangement usually found in unsaturated hydrocarbon ion–molecule reactions.

Ion cyclotron resonance (icr) spectrometry has been used to study the ion–molecule reactions occurring in a variety of compounds.[2–9] There are two characteristics of the icr spectrometer which make it particularly well suited to this type of study: (1) spectra may be taken at high enough pressures (10^{-6}–10^{-4} Torr) that ion–molecule reactions are readily observed, and (2) the pulsed-double-resonance technique[10] makes possible the verification of ion–molecule reaction sequences.

Previous work with deuterium-labeled ethylene using icr,[5] tandem,[11] and high-pressure[12] mass spectros-

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[1] National Science Foundation Graduate Fellow 1966–1969. Address correspondence to: 139 Chemistry Building, University of Minnesota, Minneapolis, Minn. 55455.

[2] J. L. Beauchamp, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1967.

[3] J. D. Baldeschwieler, *Science*, **159**, 263 (1968).

[4] R. C. Dunbar, *J. Amer. Chem. Soc.*, 90, 5676 (1968).

[5] M. T. Bowers, D. D. Elleman, and J. L. Beauchamp, *J. Phys. Chem.*, 72, 3599 (1968).

[6] J. M. S. Henis, *J. Amer. Chem. Soc.*, **90**, 844 (1968).

[7] J. L. Beauchamp, L. R. Anders, and J. D. Baldeschwieler, *ibid.*, **89**, 4569 (1967).

[8] G. Gray, *ibid.*, 90, 2177, 6002 (1968).

[9] J. I. Brauman and L. K. Blair, *ibid.*, 90, 5636 6561 (1968).

[10] L. R. Anders, J. L. Beauchamp, R. C. Dunbar, and J. D. Baldeschwieler, *J. Chem. Phys.*, **45**, 1062 (1966); J. L. Beauchamp and S. E. Buttrill, Jr., *ibid.*, 48, 1783 (1968).

[11] T. O. Tiernan and J. H. Futrell, *J. Phys. Chem.*, **72**, 3080 (1968).

[12] J. J. Myher and A. G. Harrison, *Can. J. Chem.*, **46**, 101 (1968); "Ion-Molecule Reactions in the Gas Phase," Advances in Chemistry Series, No. 58, American Chemical Society, Washington, D. C., 1966, Chapter 14.

copy has shown that the ion–molecule reactions in ethylene proceed with extensive hydrogen scrambling. The product distributions obtained are similar to those that would result if all hydrogens in the reaction complex were completely randomized by intramolecular rearrangements. This extensive hydrogen rearrangement makes it impossible to use deuterium labeling to elucidate the structure of the ion–molecule reaction complex in ethylene. The same is true in the case of acetylene[13] and it has been suggested that all condensation reactions in unsaturated hydrocarbons result from the decomposition of an "intimate" reaction complex in which extensive hydrogen rearrangement occurs.[14]

There are however many examples of condensation reactions which occur without hydrogen rearrangement; most of them involve oxygen-containing species.[2] Gray has used isotopic labeling to determine the structures of the reaction complexes in some of the ion–molecule condensation reactions in acetonitrile.[8] A recent study of the structure of ions formed in the well-known McLafferty rearrangement mass spectral fragmentation of ketones reported a number of reactions of the enol and keto forms of acetone ions. None of these reactions involved any hydrogen scrambling[15] and subsequent work showed that there was no exchange of the oxygen and carbon bound hydrogens in the enol ion.[16]

This paper reports deuterium labeling studies of the ion–molecule reactions in mixtures of hydrogen sulfide with ethylene and acetylene. Hydrogen rearrangement is found to be slow compared to fragmentation in these ion–molecule reaction complexes and it is suggested that hydrogen rearrangement is only important in cases where there is extensive charge delocalization in the reaction complex.

Experimental Section

The Varian 5900 icr spectrometer and the details of the single- and double-resonance experiments have been described previously.[2,3,6,7] The ethylene-d_4 was obtained from Isomet and contained 5% ethylene-d_3. The 1,1-dideuterioethylene was obtained from Volk and contained no impurities detectable in the low-pressure icr spectrum. Acetylene-d_2 was prepared on a vacuum line treated with D_2O to remove exchangeable hydrogen. About 0.5 ml of degassed D_2O was distilled onto approximately 1 g of freshly broken calcium carbide at liquid nitrogen temperature. The mixture was allowed to warm slowly until about 300 Torr of acetylene-d_2 filled the vacuum manifold. The resulting acetylene-d_2 contained less than 1% acetylene-d_1.

All electron energies given in this paper are nominal, but our experience has been that the absolute electron energies differ from the nominal value by no more than ±0.3 eV.

Results

An icr single-resonance spectrum taken at 15.5 eV of an approximately 1:2 mixture of ethylene and hydrogen sulfide is shown in Figure 1. Prominent peaks in the spectrum in addition to the molecular ions of ethylene (*m/e* 28) and hydrogen sulfide (*m/e* 34) include protonated hydrogen sulfide (*m/e* 35) and $C_3H_5^+$ (*m/e* 41), both products of the principal reactions occurring in pure hydrogen sulfide[17] and ethylene,[5,11,12] respectively.

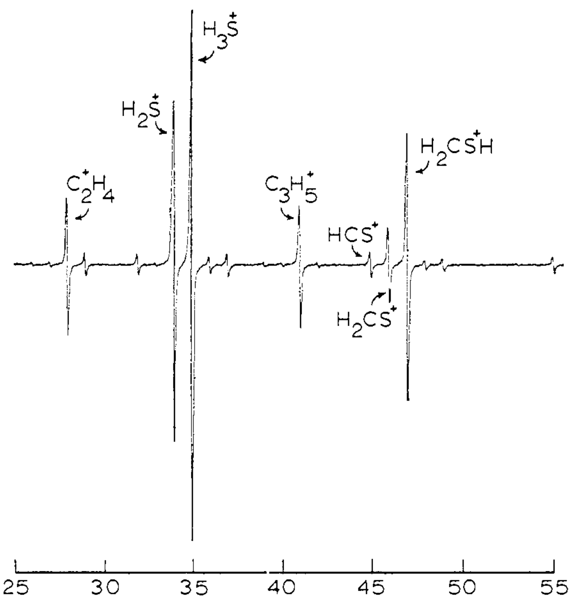

Figure 1. Single-resonance spectrum of an approximately 1:2 mixture of ethylene and hydrogen sulfide. The derivative-shaped peaks are produced by the 16-G magnetic field modulation. Experimental parameters: observing oscillator frequency, 307 kHz; trapping voltage, 0.50 V; source drift field, 0.80 V/cm; analyzer drift field, 0.31 V/cm; electron energy, 15.5 eV.

The peak at *m/e* 47 is the principal product of reactions between ethylene and H_2S and is formed by the reactions

$$H_2S^+ + C_2H_4 \longrightarrow CH_2\overset{+}{S}H + CH_3 \qquad (1)$$

and

$$C_2H_4^+ + H_2S \longrightarrow CH_2\overset{+}{S}H + CH_3 \qquad (2)$$

both of which have been verified by pulsed-double-resonance experiments. Double-resonance experiments also show that the smaller peak at *m/e* 46 is produced by the reactions

$$H_2S^+ + C_2H_4 \longrightarrow CH_2S^+ + CH_4 \qquad (3)$$

$$C_2H_4^+ + H_2S \longrightarrow CH_2S^+ + CH_4 \qquad (4)$$

A small peak at *m/e* 45 accounts for approximately 6% of the total cross-product ion intensity and is presumably due to the reactions

$$H_2S^+ + C_2H_4 \longrightarrow HCS^+ + CH_3 + H_2 \qquad (5)$$

and

$$C_2H_4^+ + H_2S \longrightarrow HCS^+ + CH_3 + H_2 \qquad (6)$$

Although no reproducible double-resonance results could be obtained for this small peak because of insufficient signal to noise, the pressure dependence of the HCS^+ ion signal is consistent with reactions 5 and 6. At an electron energy of 12.5 eV, the HCS^+ peak was no longer detectable, while at 40 eV its relative intensity increased to 23% of the total product intensity. The ratio of the CH_2S^+ and CH_2S^+H products was the same at all three electron energies. These results indicate that the HCS^+ ion is probably produced by the reaction of excited $C_2H_4^+$ or H_2S^+.

Figure 2 shows a 15.5-eV spectrum of an approximately 1:2 mixture of ethylene-d_4 and hydrogen sulfide taken under exactly the same conditions as that of

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[13] J. H. Futrell and T. O. Tiernan, *J. Phys. Chem.*, 72, 158 (1968).

[14] J. J. Myher and A. G. Harrison, *ibid.*, 72, 1905 (1968).

[15] J. Diekman, J. K. MacLeod, C. Djerassi, and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **91**, 2069 (1969).

[16] G. Eadon, J. Diekman, and C. Djerassi, *ibid.*, **91**, 3986 (1969).

[17] A. G. Harrison and J. C. Thynne, *Can. J. Chem.*, **44**, 3345 (1966).

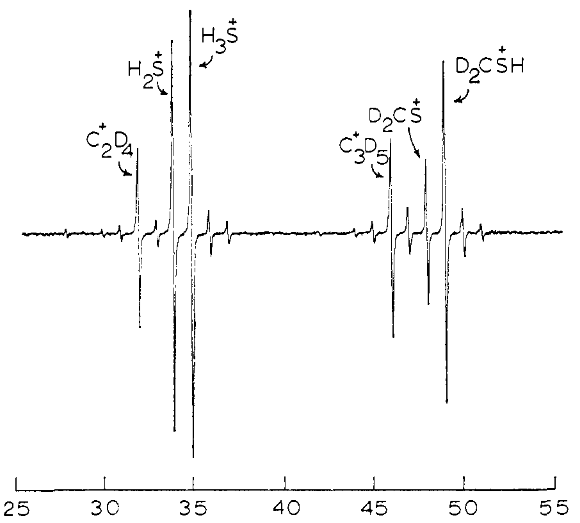

Figure 2. Single-resonance spectrum of an approximately 1:2 mixture of ethylene-d_4 and hydrogen sulfide taken under the same conditions as those of Figure 1.

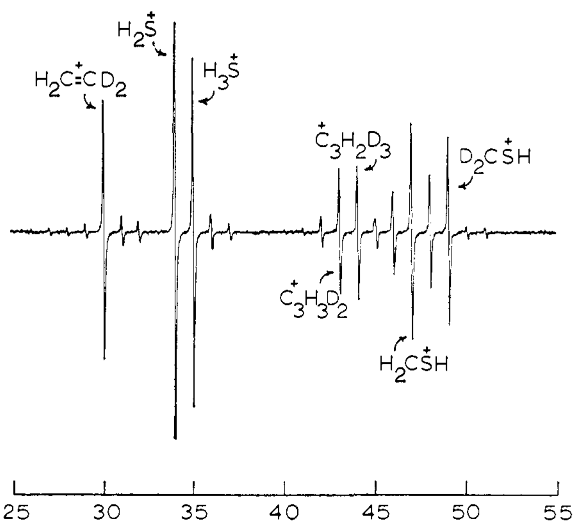

Figure 3. Single-resonance spectrum of an approximately 1:2 mixture of 1,1-dideuterioethylene and hydrogen sulfide taken under the same conditions as those of Figure 1.

Figure 1 (0.50-V trapping, source drift field of 0.80 V/cm, and analyzer drift field of 0.31 V/cm). The CH_2S^+H peak is shifted to *m*/*e* 49, indicating that just two of the four ethylene deuterium atoms are incorporated into the product of reactions 1 and 2. The remaining hydrogen must therefore come from the hydrogen sulfide. The CH_2S^+ peak is shifted to *m*/*e* 48, showing that the product of reactions 3 and 4 must contain two hydrogens from the ethylene molecule and none from hydrogen sulfide. Unfortunately, the $C_3D_5^+$ product from the C_2D_4 masks the CDS^+ peak at *m*/*e* 46.

The results given above show that the products of reactions 1–4 contain two hydrogens originating in the ethylene reactant. A further experiment is required to determine whether or not these hydrogens were originally attached to the same ethylene carbon atom. An approximately 1:2 mixture of 1,1-dideuterioethylene and hydrogen sulfide was examined under exactly the same conditions as above and the resulting spectrum is shown in Figure 3. There are now two major product peaks at *m*/*e* 47 and 49, indicating that both ethylene hydrogens in the product ion were attached to the same ethylene carbon.

Table I. Relative Product Ion Intensities in Hydrogen Sulfide–Ethylene Mixtures with 15.5-eV Ionizing Electron Energy

		Mixture of H_2S with				
		Exptl			Calcd[e]	
m/*e*	Species	C_2H_4	C_2D_4[a]	CD_2-CH_2	C_2D_4	CD_2-CH_2
50	CD_2SD^+		0.07		0.146	0.000
49	CD_2SH^+		0.59	0.31	0.438	0.146
48	CD_2S^+, $CDHSH^+$		0.26	0.19	0.230	0.452
47	CH_2SH^+, $CDHS^+$	0.73	0.07	0.36	0.112	0.258
46	CH_2S^+, DCS^+	0.21	*b*	0.14	0.054	0.104
45	HCS^+	0.06	0.01[c]	*d*	0.020	0.040

[a] Not corrected for the effects of the 5% ethylene-d_3 impurity. [b] Obscured by the $C_3D_5^+$ product from ethylene-d_4. [c] Corrected for the $C_3D_4H^+$ product from the 5% ethylene-d_3 impurity in the ethylene-d_4. [d] Obscured by the $C_3D_4H^+$ product from the reaction of 1,1-ethylene-d_2. [e] Assuming complete scrambling with the distributions for the three product ions weighted by the C_2H_4 mixture relative intensities.

The hydrogen sulfide and ethylene mixture results for 15.5-eV ionizing electrons are summarized in Table I. The product ion intensities at *m*/*e* 50 (CD_2S^+D) and 47 ($CHDS^+$) in the mixture with ethylene-d_4 are of particular interest since these ions must be formed entirely from reaction complexes in which hydrogen rearrangement occurs prior to fragmentation. Table I also includes the relative product ion intensities which would be expected if all six hydrogens in the reaction complex became equivalent through rapid rearrangement or intramolecular exchanges (see Discussion).

Aside from the reactions known to occur in pure hydrogen sulfide and acetylene,[18] the only condensation reactions observed in a mixture of hydrogen sulfide and acetylene at an electron energy of 12 eV are

$$H_2S^+ + C_2H_2 \longrightarrow HCS^+ + CH_3 \qquad (7)$$

and

$$H_2S^+ + C_2H_2 \longrightarrow C_2H_3S^+ + H \qquad (8$$

both of which were confirmed by pulsed double resonance. The ratio of the rates[19] of reactions 7 and 8 is 0.84. The reactions

$$C_2H_2^+ + H_2S \not\longrightarrow HCS^+ + CH_3 \qquad (9)$$

and

$$C_2H_2^+ + H_2S \not\longrightarrow C_2H_3S^+ + H \qquad (10)$$

are slower at low electron energy than reactions 7 and 8 by a factor of at least 20. This result is established by the complete absence of any pulsed-double-resonance signal from $C_2H_2^+$, even when irradiating fields are used which are sufficiently strong to eject the $C_2H_2^+$ ions from the icr cell.[6]

A small positive double resonance contribution from $C_2H_2^+$ to H_2S^+ and the pressure dependence of the single resonance spectra both indicate that charge transfer occurs from acetylene to hydrogen sulfide. This charge-transfer process apparently competes for H_2S^+ to the exclusion of reactions 9 and 10.

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(18) M. S. B. Munson, *J. Phys. Chem.*, **69**, 572 (1965); J. H. Futrell and T. O. Tiernan, *ibid.*, **72**, 158 (1968).

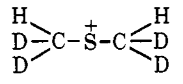
(19) S. E. Buttrill, Jr., *J. Chem. Phys.*, **50**, 4125 (1969).

When acetylene is replaced with acetylene-d_2, the product of reaction 7 shifts from *m/e* 45 to *m/e* 46, but a small amount of *m/e* 45 (HCS^+) remains (Figure 4). The ratio of *m/e* 45 to *m/e* 46 varies with electron energy; it is equal to 0.15 at 11.9 eV, 0.20 at 14 eV, and 0.23 at 14.5 eV. Since $C_2H_2^+$ and H_2S^+ are the only primary ions present even at 14.5 eV, this result indicates that some of the H_2S^+ ions are probably formed in a vibrationally excited state and that this excitation results in increased hydrogen rearrangement in the reaction complex. At 11.9 eV the $C_2H_3S^+$ product (*m/e* 59) becomes a doublet at *m/e* 60 and 61, both peaks having equal intensity. The relative intensities of these two peaks do not change with increasing electron energy. This is the expected behavior, since complete scrambling of the two deuteriums and two hydrogens in the reaction complex would also give an equal probability of loosing either hydrogen or deuterium. The ratio of the rate constant of reaction 8 to that of reaction 7, k_8/k_7, is 0.53 for acetylene-d_2 compared with 0.84 for normal acetylene.

Discussion

The deuterium-labeling results provide enough information to determine the structure of the ion-molecule reaction complexes involved in reactions 1-4 and 7 and 8. The fact that complete hydrogen scrambling is not observed indicates that these reactions proceed along a definite mechanistic pathway. Yet some hydrogen rearrangement did occur and the extent of rearrangement increased with increasing electron energy. The reaction complex must therefore have a lifetime significantly greater than a vibrational period and so is best considered as an excited molecular ion.

Considering first the ethylene mixture, there are two likely structures for the reaction complex (or intermediate), 2-thiapropane molecular ion and ethanethiol molecular ion. The formation of either of these ions from the reactants is exothermic[20] and their mass spectra[22] both show large peaks at *m/e* 47 together with smaller peaks at *m/e* 46. To be consistent with the deuterium-labeling finding that two ethylene hydrogens from the same ethylene carbon are incorporated into the *m/e* 47 ion, a 2-thiapropane ion reaction complex would have to be formed in such a way that one hydrogen sulfide hydrogen was bound to each of the two carbons. For example, the reaction complex formed by H_2S^+ and C_2D_4 would be 1,1,3,3-tetradeuterio-2-thiapropane (I). Cleavage of the carbon-sulfur bond would produce a product ion with the required CHD_2S^+ formula. However there is no way in which a 2-thiapropane reaction complex can account for the fact that the *m/e* 46 product also contains two hydrogens from ethylene.



I

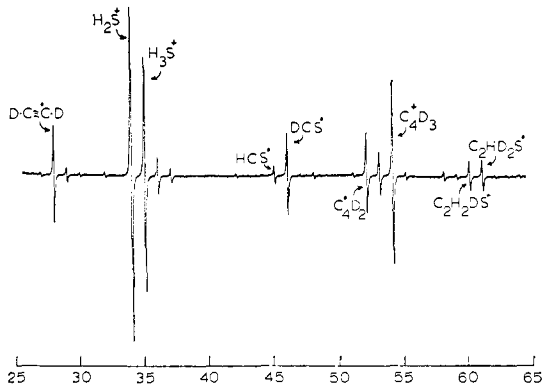
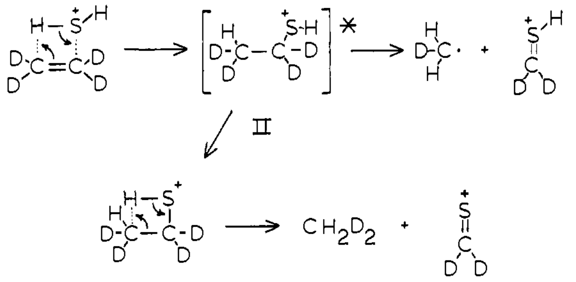


Figure 4. Single-resonance spectrum of an approximately 1:2 mixture of acetylene-d_2 and hydrogen sulfide taken with an ionizing electron energy of 14.5 eV.

All of the ethylene deuterium-labeling results are consistent with an ethanethiol structure for the reaction complex. The fact that exactly two of the ethylene hydrogens are retained in both the CH_2S^+H and CH_2S^+ products requires that the ethanethiol ion be formed by addition of hydrogen sulfide ion[23] to the ethylene double bond. Using the reaction with ethylene-d_4 as an example, the mechanism for reactions 1-4 can be written (Scheme I) as the fragmentation of an excited ethanethiol molecular ion II by either α cleavage or a four-centered rearrangement with loss of methane. The four-centered rearrangement is necessary to explain the fact that both deuteriums in the CD_2S^+ product come from the same ethylene carbon.

Scheme I



The experimental product ion intensities (Table I) in the ethylene-d_4 mixture are reasonably close to those calculated assuming complete hydrogen scrambling, and one might interpret these results alone as indicating extensive hydrogen rearrangement or near-total scrambling. However it is clear from the great difference between the calculated and experimental intensities for the 1,1-dideuterioethylene mixture that hydrogen rearrangement is not extensive and it appears to proceed somewhat more slowly than the fragmentation of the reaction complex into product ions.

In the ethylene-d_4 mixture, the *m/e* 50 (CD_2SD^+) product can be formed only from the fragmentation of a reaction complex in which the hydrogen on sulfur has exchanged with one of the deuteriums on carbon. From the relative intensities of the CD_2SD^+ and

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[20] $\Delta H_f(CH_3S^+CH_3)$ 191, $\Delta H_f(CH_3CH_2S^+H)$ 203, $\Delta H_f(C_2H_4^+) + \Delta H_f(H_2S)$ 248, $\Delta H_f(H_2S^+) + \Delta H_f(C_2H_4)$ 248 kcal/mol, from ref 21.

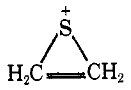
[21] J. L. Franklin, *et al.*, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, June 1969.

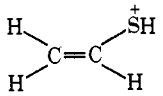
[22] "Mass Spectral Data," American Petroleum Institute Research Project No. 44, National Bureau of Standards, Washington, D. C., Spectra 546 and 909.

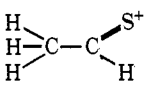
[23] Hydrogen sulfide has an ionization potential of 10.46 eV *vs.* 10.51 eV for ethylene, so that charge exchange to hydrogen sulfide should occur during the formation of the ethanethiol reaction complex if ethylene is the reactant ion. Ionization potentials are from R. W. Kiser, "Introduction to Mass Spectrometry and Its Applications," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, Appendix IV.

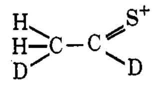
CD_2SH^+ peaks (0.07 and 0.59) and the fact that four of the five possible exchanges will place a deuterium on sulfur, one can calculate that α cleavage is faster than this particular hydrogen exchange by a factor of nearly 7. Similarly one can estimate from the $CDHS^+$ intensity that hydrogen exchange between carbons occurs at a rate nearly equal to the rate of fragmentation into CD_2S^+ (*m/e* 48). These estimates of relative rates for hydrogen exchange and fragmentation must be considered as only very approximate. The relative intensities from which they are obtained are assumed to result from the rearrangement and fragmentation of identical reaction complexes; in particular, it is assumed that they all have the same internal energy. However the relative intensities observed might also be the sum of those produced by two (or more) different complexes; one formed from excited reactant ions and rearranging rapidly, the other formed from ground-state ions and rearranging slowly or not at all.

There are three likely structures for the hydrogen sulfide–acetylene reaction complex, the cyclic ethylene sulfide (III) and the enol (IV) and keto (V) forms of the sulfur analog of acetaldehyde. The highly symmetrical ethylene sulfide ion can be ruled out immediately since it cannot possibly lead to the complete retention in the HCS^+ product of an acetylene hydrogen. If the reaction of H_2S^+ with acetylene-d_2 somehow led to a keto ion (V) with both hydrogens on the methyl carbon (V′), then α cleavage would give the required DCS^+ ion. However, it would be necessary to invoke rapid hydrogen rearrangement to explain the equal intensities of the *m/e* 60 and 61 ($C_2H_2DS^+$ and $C_2HD_2S^+$) products and this would be inconsistent with the formation of only DCS^+ by the α-cleavage fragmentation.


III

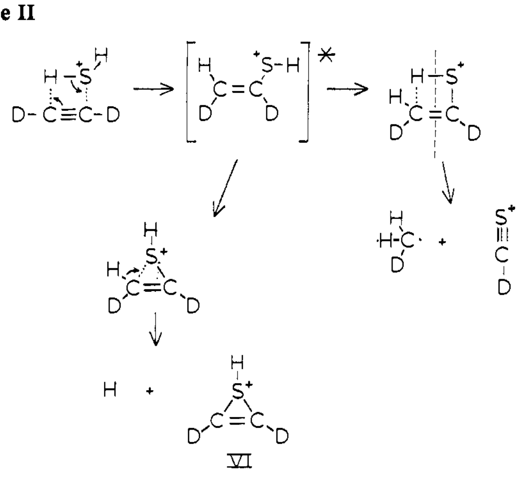

IV


V


V′

A reaction complex with structure IV is consistent with the labeling results. The proposed reaction mechanism is given in Scheme II using the reaction of H_2S^+ with acetylene-d_2 as an example. The hydrogen sulfide ion adds across the unsaturated carbon–carbon bond to give an enolic reaction complex. A four-centered rearrangement produces the keto form of the ion (V′) which immediately undergoes α cleavage to give DCS^+. It is not possible to determine from this data whether this rearrangement and fragmentation are concerted or consecutive processes for unexcited H_2S^+ reactant ions (see above). If the reaction complex exists as V′ for a finite time, then fragmentation occurs faster than hydrogen rearrangement by a factor of at least 6. The $C_2(H,D)_3S^+$ products are formed in a three-centered internal displacement reaction. The cyclic structure VI is suggested by the fact that loss of either hydrogen or deuterium is equally probable, but other structures are possible although they require extensive hydrogen rearrangement following the formation of the product ion.

Scheme II



It is well established that ion–molecule condensation reactions in small unsaturated hydrocarbons involve extensive hydrogen rearrangement.[5,11–14] In contrast, the reactions of molecules containing heteroatoms do not involve hydrogen scrambling.[2,8,15,16] The present results show that hydrogen rearrangement is slow when only one of the reactants contains a heteroatom. In mass spectroscopy the concept of charge localization in the molecular ion has proven to be extremely useful in the interpretation of fragmentation patterns, and hydrogen scrambling is unusual except in hydrocarbons.[24] Recent studies of the ion–molecule reactions of labeled propylene and higher olefins by tandem mass spectrometry[25] and icr[26] have shown that complete hydrogen scrambling does not occur. It has been suggested that ion–molecule reaction complexes of well-defined structure are formed in these reactions and that hydrogen rearrangement is limited to the part of the complex adjacent to the positive charge and remaining double bond.[25,26] Taken together this evidence suggests that it is the presence of delocalized positive charge that promotes hydrogen rearrangement within an ion and that the presence of a heteroatom on which the positive charge is localized therefore prevents hydrogen rearrangement.

Conclusions

An ion cyclotron resonance study of the ion–molecule reactions occurring between hydrogen sulfide and ethylene and acetylene shows that condensation with subsequent carbon–carbon bond cleavage is the major mode of reaction. Deuterium labeling of the ethylene and acetylene indicates that these reactions proceed by way of reaction complexes which can be characterized as excited molecular ions. The fragmentation of these reaction complexes into product ions is at least several times faster than internal hydrogen rearrangement, suggesting that charge localization on a heteroatom inhibits the extensive hydrogen rearrangement normally found in small unsaturated systems.

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(24) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, pp 1–28.

(25) F. P. Abramson and J. H. Futtrell, *J. Phys. Chem.*, **72**, 1994 (1968).

(26) J. M. S. Henis, *J. Chem. Phys.*, **52**, 292 (1970).