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plays an important role in the degree of nonplanarity of ω_1. Interestingly, the ECEPP calculations do not show significant deviations from planarity in ω resulting from different low-energy backbone conformations[34] even though upon N-methylation large deviations are found.[35]

Comparison to Other ab Initio Calculations. A comparison of the results presented here with other ab initio calculations of Ala[3] shows one very obvious difference. That is, in the ϕ–ψ map prepared without geometry optimization on the STO-3G level,[3] the C_7^{ax} conformation does not appear as a region of low energy. We believe that this difference is an artifact of refinement related to the special nature of C_7^{ax} as a narrow cavity in the Ala potential energy surface.

As indicated in Figure 9, C_7^{ax} is a narrow potential energy minimum in the ECEPP calculation. Even though our torsional angles are somewhat uncertain for the reasons pointed out above and even though the space around this conformation has not been examined here on the 4-21G level, it is not impossible that this conformer was missed in the 20° grid used to obtain the ϕ–ψ map.[3] In addition, the rather large geometry change (see above) is required for this structure to be optimized. Thus, conformational problems inherent in the use of rigid geometry appear to be present whether empirical methods or the more rigorous ab initio calculations are used. The other conformational regions of low energy found in the STO-3G ϕ–ψ map[3] are relatively close to the characteristic areas considered here.

Conclusion

The geometry-optimized conformations described here clearly show the structural changes that must be considered in future conformational studies of peptides. Some geometry changes are very significant, such as that found for the C_7^{ax} conformer, while others are more subtle. We consider the perpendicular peptide interaction between the nitrogen N7 and second amide hydrogen H18 to be a most significant and important factor for the understanding of dipeptide conformation. The calculated details of local geometry make it very likely that this interaction is responsible for the observed correlation (see Figure 10) between the ϕ and ψ torsional angles in the α-helix conformational region and must play an important role in the formation and stability of protein structure. Its role in bend structures is being examined, and its incorporation into empirical calculations should lead to improved conformational predictions of larger polypeptides.

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Gas-Phase Derivatization for Determination of the Structures of $C_3H_5^+$ Ions

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Abstract: The structure of the $C_3H_5^+$ ions formed via halide atom loss from ionized allyl, cyclopropyl, and 1- and 2-propenyl halides was investigated by derivatizing the ions with neutral benzene and substituted benzenes to produce gas-phase adduct ions. The structures of pressure stabilized adduct ions were directly determined by obtaining their collision-induced decomposition spectra and comparing them with the CID spectra of model ions. Two $C_3H_5^+$ ion structures were found to be stable, the allyl cation from cyclopropyl and allyl halides and the 2-propenyl cation from 2-propenyl halides. The $C_3H_5^+$ ions from 1-propenyl halides exist as a 2:1 mixture of the two ion structures. The mechanism of reaction was shown to be electrophilic attack on the ring π system to produce a Wheland intermediate or other structure with the proton relocated. The reaction pathway was confirmed by Fourier transform mass spectrometry, and rate constants for the derivatization reaction were determined by using pulsed ICR.

Vinyl and allyl cations have been the subjects of considerable study both in solution[1] and in the gas phase. In solution, the ions are important as reactive intermediates in synthesis[2] and as models for rearrangement reactions.[3] However, direct observation has been limited to studies of appropriately substituted ions or those formed via loss of "super" leaving groups.[4] Moreover, their reactivity in solution may largely reflect the nature of the solvent system rather than the properties of the ions themselves.

The simplest vinyl–allyl system, namely, the $C_3H_5^+$ isomers and in particular the allyl cation, has been the subject of a number of recent studies in the gas phase. The vertical and adiabatic ionization potential (IP) of the allyl radical as well as the appearance potential (AP) of allyl cations were measured.[5] These measurements lead to a heat-of-formation of 226 kcal/mol, which has been independently verified.[6] The heats of formation of numerous $C_3H_5^+$ fragment ions from simple hydrocarbons were determined to be identical with the value for allyl cation.[7]

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(1) See for example: (a) Hanack, M. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 331. (b) Deno, N. C. In "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1970; Vol. II, 783.

(2) See for example: (a) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. "Vinyl Cations"; Academic Press: New York, 1979. (b) Hoffman, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 819. (c) Klein, H.; Mayr, H. *Ibid.* **1981**, *20*, 1027.

(3) See for example: Olah, G. A.; Mayr, H. *J. Am. Chem. Soc.* **1976**, *98*, 7333.

(4) (a) Grob, C. A., Cseh, G. *Helv. Chim. Acta* **1964**, *47*, 194. (b) Grob, C. A. *Chimia* **1971**, *25*, 87. (c) Rappoport, Z.; Gal, A. *J. Am. Chem. Soc.* **1969**, *91*, 5246. (d) Rappoport, Z. *Acc. Chem. Res.* **1976**, *9*, 265. (e) Hanack, M. *Ibid.* **1976**, *9*, 364; **1970**, *3*, 209. (f) Stang, P. J.; Summerville, R. H. *J. Am. Chem. Soc.* **1969**, *91*, 4600. (g) Stang, P. J. *Acc. Chem. Res.* **1978**, *11*, 107. (h) Pfeifer, W. D.; Bahn, C. A.; Schleyer, P. v. R.; Bocher, S.; Harding, C. E.; Hummel, K.; Hanack, M.; Stang, P. J. *J. Am. Chem. Soc.* **1971**, *93*, 1513.

(5) (a) Lossing, F. P. *Can. J. Chem.* **1971**, *49*, 357. (b) Beck, D.; Osberghaus, O. *Z. Phys.* **1960**, *160*, 406. (c) Beck, D. *Discuss. Faraday Soc.* **1963**, *36*, 56. (d) Lossing, F. P.; Ingold, K. U.; Henderson, I. H. S. *J. Chem. Phys.* **1954**, *22*, 621. (e) Omura, I. *Bull. Chem. Soc. Jpn.* **1961**, *34*, 1227; **1962**, *35*, 1845.

(6) (a) Golden, D. M.; Benson, S. W. *Chem. Rev.* **1969**, *69*, 125. (b) Golden, D. M.; Rodgers, A. S.; Benson, S. W. *J. Am. Chem. Soc.* **1966**, *88*, 3196. (c) Buff, R. D.; Parr, A. C.; Jason, A. J. *Int. J. Mass Spectrom.* **1981**, *40*, 31.

(7) (a) Lossing, F. P. *Can. J. Chem.* **1972**, *50*, 3973. (b) Meisels, G. G.; Park, J. Y.; Giessner, B. G. *J. Am. Chem. Soc.* **1969**, *91*, 1555, **1970**, *92*, 254.

0002-7863/83/1505-3445$01.50/0

Collision-induced dissociation (CID)[8] and charge stripping[9] spectra were interpreted to show that a single $C_3H_5^+$ isomer, presumably allyl cation, is the fragment commonly observed in the electron-impact mass spectra of many hydrocarbons.[10] Studies of unimolecular decompositions of $C_3H_5^+$ ions also indicated the existence of a single isomer.[11]

A second isomeric form, the 2-propenyl cation, was studied by ab initio molecular orbital calculations.[12] This ion was estimated to be 12–17 kcal/mol less stable than allyl cation, with a 17 kcal/mol isomerization barrier. CID measurements of $C_3H_5^+$ ions from ionized C_3H_5Br isomers provided experimental confirmation that two low-energy, nondecompsing cations, presumably allyl and 2-propenyl isomers, do not interconvert.[13] Similar CID experiments were interpreted to show that the $C_3H_5^+$ ions from 1-propenyl bromide were a mixture of the two isomers.[14] The ab initio calculations predicted the 2-propenyl isomer to be 14–18 kcal/mol more stable than the 1-propenyl cation with little or no activation barrier for interconversion via a 1,2 H shift.[12] Isomerization to the more stable 2-propenyl cation may then be followed by isomerization to the allyl isomer, because the internal energy of the newly formed 2-propenyl cations is approximately equal to the calculated height of the isomerization barrier.

The existence of a third, cyclic $C_3H_5^+$ isomer was suggested on the basis of data from studies of proton-transfer reactions.[15] Radiolysis experiments at atmospheric pressure have produced neutral products also suggestive of the transient existence of a cyclic structure.[16] Theoretical studies differ regarding the stability of this isomer.[12]

Despite the enormous efforts expended, the actual structures of gas-phase $C_3H_5^+$ ions are still not firmly established. Two serious difficulties exist. First, predictions regarding the stability of the cyclic and 1-propenyl isomers seem to be dependent on the theoretical models used, and furthermore, the measured heat of formation of the cyclic isomer is considerably lower than the value calculated by the *ab initio* methods.[15] Second, the interpretation of CID spectra in terms of structure is difficult because only the ratio of two signal intensities (masses 26 and 27) varies from one assigned structure to another. Under such circumstances, $C_3H_5^+$ ions which give a signal ratio for m/z 26 and 27 intermediate between the values assigned for allyl and 2-propenyl cations could either be a mixture of allyl and 2-propenyl isomers, or a third unique structure. Even more basic problems are that the assignment of the allyl or 2-propenyl structures to CID spectra is equivocal and also that the spectra may be of mixtures rather than pure structures.

The first purpose of this paper is to determine more directly the structures of various $C_3H_5^+$ ions by a different approach, that is by derivatizing them in the gas phase using reactions conducted in a high-pressure chemical ionization (CI) source and then obtaining their CID spectra. The general experimental approach was first suggested by Dymerski and McLafferty[17] but has been seldom applied. The derivatization procedure may be particularly fruitful for hydrocarbon ions because these ions frequently give very similar CID spectra.[17] Introduction of additional functional groups or structural features via ion derivatization may enhance the characteristic differences of the CID spectra or even provide new differences. Furthermore, the derivatization procedure, if conducted at high pressures, permits collisional stabilization which minimizes ion isomerization during the transit from ion source to collision chamber. Finally, since CID spectra are believed to be relatively insensitive to differences in internal energy, the exothermicity of the derivatization reaction should not affect the appearance of the CID spectrum.[18]

A similar approach involving the use of ion cyclotron resonance (ICR) spectrometry has been successful for a number of ion systems.[19] Distinctive ion–molecule reactions have been found at low pressure (10^{-6} torr) for various isomeric ion structures. However, under the single collision conditions of the ICR spectrometer, the adduct ion is often an activated intermediate which fragments rapidly to product ions, which may not be characteristic of reactant ion structure. The use of high ion-source pressures, as in the tandem mass spectrometer technique, allows us to conduct specific ion–molecule reactions under conditions where the actual intermediate can be observed. The disadvantage is that we are unable to conduct double-resonance experiments as in the ICR spectrometer.

The principal advantage of studying adduct ions is that ion structures may be determined directly by comparing adduct ion CID spectra with those of model ions of known structure. Without model compounds and their reference spectra, CID spectra are most often interpreted in terms of the nonequivalence of a set of isomers, while assignment of the actual ion structures may be equivocal. We will demonstrate this advantage for the study of various $C_3H_5^+$ ions.

In addition to elucidating $C_3H_5^+$ ion structures, we will also investigate the mechanism of the ion–molecule derivatization reaction. The derivatization of $C_3H_5^+$ ions was achieved by reactions with neutral benzene and other aromatic neutrals. These reactions may proceed via electrophilic attack on the aromatic ring. Electrophilic aromatic attack has been the subject of recent publications,[20] including some specifically relating to the adduct formed in the reaction of allyl cation and benzene.[21] We will show that knowledge of the *adduct* ion structure, obtained by comparing the CID spectra of the derivatized adducts with the CID spectra of model compounds, not only provides more *direct evidence* than previous studies for reactant ion structure but also yields substantial data relevant to the mechanism of adduct formation.

Results and Discussion

Our experimental work started with studies of the reactivity of $C_3H_5^+$ ions with substituted benzenes under single collision conditions (10^{-6} torr) using Fourier transform mass spectrometry (FTMS)[22] and pulsed ICR spectrometry.[23] Specifically, the FTMS experiments were used to establish the course of the ion–molecule reactions while rate constants were measured by using pulsed ICR spectrometry.

Following that, CID and charge-stripping spectra were taken of collisionally activated $C_3H_5^+$ ions from a variety of sources.

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(8) (a) Cooks, R. G. In "Collision Spectroscopy"; Cooks, R. G., Ed.; Plenum Press: New York, 1978. (b) Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, G. R. In "Metastable Ions"; Elsevier: Amsterdam, 1973. (c) Nibbering, N. M. M.; Nishishita, T.; Van de Sande, C. C.; McLafferty, F. W. *J. Am. Chem. Soc.* **1974**, *96*, 5668. (d) McLafferty, F. W. *ACS Symp. Ser.* **1978**, *No. 70*.

(9) Jennings, K. R. *Int. J. Mass Spectrom.* **1968**, *1*, 227.

(10) Maquestiau, A.; Haverbeke, Y. V.; Flammang, R.; Meyer, C. D.; Menu, A. *Org. Mass Spectrom.* **1977**, *12*, 706.

(11) (a) Holmes, J. L.; Osborne, A. D.; Weese, G. M. *Org. Mass Spectrom.* **1975**, *10*, 867. (b) Holmes, J. L.; Terlouw, J. K. *Ibid.* **1975**, *10*, 787.

(12) (a) Random, L.; Hariharan, P. C.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 6531. (b) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649. (c) Merlet, P.; Peyerimhoff, S. D.; Buenker, R. J.; Shih, S. *J. Am. Chem. Soc.* **1974**, *96*, 959. (d) Halgren, T. A.; Lipscomb, W. N. *Chem. Phys. Lett.* **1977**, *49*, 225.

(13) Bowen, R. D.; Williams, D. H.; Schwarz, H.; Wesdemiotis, C. *J. Am. Chem. Soc.* **1979**, *101*, 4681.

(14) Bowers, M. T.; Shuying, L.; Kemper, P.; Stradling, R.; Webb, H.; Aue, D. H.; Gilbert, J. R.; Jennings, K. R. *J. Am. Chem. Soc.* **1980**, *102*, 4830.

(15) Aue, D. H.; Davidson, W. R.; Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 6700.

(16) Colosimo, M.; Bucci, R. *J. Chem. Soc., Chem. Commun.* **1981**, 659.

(17) Dymerski, P. P.; McLafferty, F. W. *J. Am. Chem. Soc.* **1976**, *98*, 6070.

(18) McLafferty, F. W.; Bente, P. F., III; Kornfield, R.; Tsai, S.-C.; Howe, I. *J. Am. Chem. Soc.* **1973**, *95*, 2120.

(19) See for example: Gross, M. L.; Lin, P.-H. *Org. Mass Spectrom.* **1974**, *9*, 1194.

(20) (a) Morrison, J. D.; Stanney, K.; Tedder, J. M. *J. Chem. Soc., Perkin Trans. 2* **1981**, 838, 967. (b) Luijten, W. C. M. M.; Onkenhout, W.; Thuijl, J. van *Org. Mass Spectrom.* **1980**, *15*, 329. (c) Attina, M.; Cacace, F.; Ciranni, G.; Giacomello, P. *J. Am. Chem. Soc.* **1977**, *99*, 4101. (d) Cacece, F. *J. Chem. Soc., Perkin Trans 2* **1982**, 1129. (e) Miller, D. L.; Lay, J. O., Jr.; Gross, M. L. *J. Chem. Soc., Chem. Commun.* **1982**, 970.

(21) Houriet, R.; Elwood, T. A.; Futrell, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 2320.

(22) For a review, Wilkins, C. L.; Gross, M. L. *Anal. Chem.* **1981**, *53*, 1661A.

(23) McIver, R. T., Jr. *Rev. Sci. Instrum.* **1971**, *49*, 111.

Table I. Rate Constants for the Reaction of $C_3H_5^+$ Ions and Benzene or Anisole[a,b]

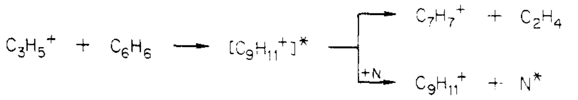
parent	neutral	rate[a]	RSD	*n*
allyl bromide	benzene	11.4	1.5	8
cyclopropyl bromide	benzene	11.3	1.0	4
2-propenyl bromide	benzene	8.8	1.0	7
1-propenyl bromide	benzene	7.1	1.6	7
allyl bromide	anisole	14.9	1.4	6

[a] $k \times 10^{-10}/\mathrm{cm}^3/\mathrm{mol}$. [b] n = number of measurements.

The CID spectra are compared with those literature spectra that are available.

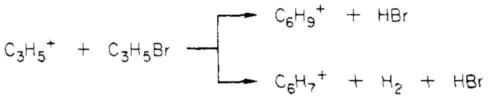
We then turned to derivatizing various $C_3H_5^+$ ions in a chemical ionization source (0.1–1.0 torr) using neutral benzene, benzene-d_6, and phenol as neutral reagents. The structures of the adduct ions were determined by comparing CID spectra of adduct ions with the CID spectra of model or reference compounds.

Low-Pressure Ion–Molecule Reactions. FTMS Results. The ion–molecule reactions of neutral benzene or substituted benzenes with $C_3H_5^+$ ions under single collision conditions lead to formation of a product ion corresponding to CH transfer to the neutral (eq 1a). This product, presumably a fragment of an unseen high-



$$C_3H_5^+ + C_6H_6 \longrightarrow [C_9H_{11}^+]^* \begin{cases} \longrightarrow C_7H_7^+ + C_2H_4 & \text{(1a)} \\ \xrightarrow{+N} C_9H_{11}^+ + N^* & \text{(1b)} \end{cases}$$

energy adduct ion, was observed for all $C_3H_5^+$ ions generated by radical halide loss from cyclopropyl, allyl, or 1- and 2-propenyl halide molecular ions. Double-resonance results showed that the precursor ion for $C_7H_6R^+$ is exclusively the $C_3H_5^+$ ion. Products at *m/z* 79 and 81 were also observed; they resulted from the reactions of $C_3H_5^+$ ions with their parent neutrals (eq 2). Additionally, $C_3H_5^+$ ions, particularly from 2-propenyl halides, transferred a proton to their parent neutral and to C_6H_5R (eq 3 and 4). Protonation of the aromatic species was particularly



$$C_3H_5^+ + C_3H_5Br \begin{cases} \longrightarrow C_6H_9^+ + HBr & \text{(2a)} \\ \longrightarrow C_6H_7^+ + H_2 + HBr & \text{(2b)} \end{cases}$$

$$C_3H_5^+ + C_3H_5Br \rightarrow C_3H_6Br^+ + C_3H_4 \qquad (3)$$

$$C_3H_5^+ + C_6H_5R \rightarrow C_6H_6R^+ + C_3H_4 \qquad (4)$$

difficult to monitor because the $(M + H)^+$ and the carbon-13 component of the molecular ion were unresolved in the FTMS experiments. Hence, we did not use data from the proton-transfer reactions to assign the $C_3H_5^+$ ion structures.

ICR Results. Rate constants for the reactions of $C_3H_5^+$ ions and aromatic neutrals were determined by using pulsed ICR. The rates of disappearance of isomeric $C_3H_5^+$ ions were measured in both the absence and presence of the aromatic neutral species C_6H_5R. This allowed us to extract the rate constants for reaction 1 for $C_3H_5^+$ ions generated from cyclopropyl, allyl, and 1- and 2-propenyl bromides (for results, see Table I). The value of the rate constant for the reaction of $C_3H_5^+$ from allyl bromide was identical with the value determined for that from cyclopropyl bromide but was significantly different than the values determined for $C_3H_5^+$ from 1- and 2-propenyl bromide.

The rate constants for the reactions involving $C_3H_5^+$ ions from 1- and 2-propenyl bromide cannot be distinguished which may be partially due to the relatively large random error associated with the measurement of the rate constant for the $C_3H_5^+$ ion from 1-propenyl bromide. In addition, the $C_3H_5^+$ ions from 1- and 2-propenyl bromide react extensively with their parent neutral via eq 2 and 3, introducing an additional source of error. Finally, it should be mentioned that ICR rate measurements are potentially subject to variations due to ion internal energy. Excess internal energy particularly pertains to any ions which undergo exothermic isomerization prior to reaction. However, the nearly identical rate constants for the $C_3H_5^+$ ions from allyl and cyclopropyl bromide are in agreement with the concept of facile isomerization for the cyclic isomer and rule out any significant internal energy effect for this isomer even though the exothermicity of ring opening is 39 kcal/mol.[12]

Table II. CID Spectra of $C_3H_5^+$ Ions[a]

	source of $C_3H_5^+$ ions			
m/z	cyclopropyl bromide	allyl bromide	1-propenyl bromide	2-propenyl bromide
40	5.4	6.1	5.0	7.5
39	48.5	48.9	48.6	48.9
38	17.7	17.2	17.7	17.8
37	12.6	12.5	12.9	13.4
36	2.8	2.7	2.8	3.1
27	2.6	2.7	2.5	1.7
26	4.0	4.0	4.1	4.2
25	2.1	1.9	2.0	2.2
24	0.8	0.7	0.7	0.8
15	1.4	1.3	1.5	1.5
14	1.1	1.0	1.0	1.0
13	0.6	0.6	0.6	0.6
12	0.5	0.4	0.5	0.5

[a] Expressed as $i/\Sigma i$, 10% RSD or ±0.1.

The rate constant for the reaction of $C_3H_5^+$ from allyl bromide and benzene is 11.4×10^{-10} cm^3/molecule which is almost identical with the value determined by Houriet et al.[21] This value is 76% of the Langevin or collision rate constant, 15×10^{-10} cm^3/molecule, indicating that the reaction occurs for three of every four collisions. The rate constant for the reaction of $C_3H_5^+$ from allyl bromide with anisole was also determined (14.9×10^{-10} cm^3/mol) to be in agreement with previous measurements.[21]

Collisional Activation of Underivatized Ions. CID Spectra. The $C_3H_5^+$ ions from allyl, cyclopropyl, and 1- and 2-propenyl bromides all gave very similar CID spectra (see Table II), as was observed by Bowen et al.[13] and Bowers et al.[14] The only differences are the intensities of *m/z* 27 relative to those of *m/z* 26 corresponding to losses of methylene and methyl groups, respectively. Specifically, the $C_3H_5^+$ ions from allyl, cyclopropyl, and 1-propenyl bromide show a larger CID fragment signal for CH_2 loss than the $C_3H_5^+$ ions from 2-propenyl bromide. These observations point to extensive, although *not* complete, interconversion of structures in the collisional activation process. Increased signal for CH_2 loss may be interpreted to mean that at least a fraction of the $C_3H_5^+$ ions from allyl, cyclopropyl, and 1-propenyl bromide have the allyl ion structure with two terminal CH_2 groups rather than the 2-propenyl ion structure, which has a CH_3 as well as a terminal CH_2 group. This interpretation could be extended as a prediction that the smallest signal for *m/z* 27 would be observed for the 1-propenyl structure (if it exists) because it lacks a terminal CH_2 group. This prediction does not hold for the $C_3H_5^+$ from 1-propenyl bromide, however.

The largest relative intensity difference in the CID spectra corresponds to only about 1% of the total CID signal. While this small difference coupled with evidence from proton transfer to C_3H_4 to give $C_3H_5^+$[14] and from proton transfer from $C_3H_5^+$[15] have been used to classify $C_3H_5^+$ ion structures, the actual structures have not been proven unequivocally.

To test for changes in the ion population as a function of internal energy, the CID spectra for $C_3H_5^+$ ions from allyl, cyclopropyl, and 1- and 2-propenyl bromides were acquired at various ionization energies from 50 to about 12 eV (nominal). The intensity ratio of *m/z* 27 to *m/z* 26 was monitored for changes in the ion population. This intensity ratio did not change appreciably before accurate measurements of CID spectra became impractical due to a low signal-to-noise ratio. These results indicate that the relative populations of ion structures do not change appreciably under the conditions of the experiment. Furthermore, if, as has been previously suggested, the $C_3H_5^+$ ions from 1-propenyl bromide contain a fraction of $C_3H_5^+$ ions with a second isomeric structure, the proportion of the less numerous isomer does not increase sufficiently to allow detection.

Charge-Stripping Spectra. The charge-stripping spectra (Table III) for each of the $C_3H_5^+$ ions are similar to those reported for

Table III. Charge-Stripping Spectra of $C_3H_5^+$ Ions[a]

	source of $C_3H_5^+$ ions			
m/z	cyclopropyl bromide	allyl bromide	1-propenyl bromide	2-propenyl bromide
20.5	1.35	1.55	1.24	1.39
20.0	1.00	1.00	1.00	1.00
19.5	0.52	0.51	0.53	0.53
19.0	0.86	0.80	0.84	0.80

[a] Expressed as $i/\Sigma i$, 6% RSD.

Table IV. Partial CID Spectra for $C_9H_{11}^+$ Ions from $C_3H_5^+$ Ions and Benzene[a]

	source of $C_3H_5^+$ ions				
m/z	cyclopropyl bromide	allyl bromide	allyl chloride	1-propenyl bromide	2-propenyl bromide
117	36.6	33.6	32.9	31.4	24.2
103	6.3	6.6	7.2	9.0	13.6
79	2.9	2.8	3.0	4.1	7.3
77	9.2	9.9	10.8	11.8	14.6

[a] Expressed as $i/\Sigma i$, 5% RSD.

Table V. Partial CID Spectra for $C_9H_{11}O^+$ Ions from $C_3H_5^+$ and Phenol[a]

	source of $C_3H_5^+$ ions			
m/z	cyclopropyl bromide	allyl bromide	1-propenyl bromide	2-propenyl bromide
133	19.5	20.4	16.3	10.1
119	6.6	6.4	7.1	8.5
95	3.6	2.7	7.5	17.7
77	10.2	10.3	11.7	12.9
	With 10× Excess of He Bath Gas			
133	20.0	20.6	17.5	11.0
119	6.5	6.5	6.9	7.1
95	3.7	3.0	6.7	16.8
77	10.3	10.2	11.4	13.4

[a] Expressed as $i/\Sigma i$, 17% RSD.

allyl cation.[10] The largest difference in the spectra is the signal for M^{2+}. This signal, however, is highly irreproducible and varies as much as 50% in intensity for otherwise identical experiments run on different days. Furthermore, the peak is flat-topped on occasions when its intensity is relatively less and Gaussian at other times. This could be an instrumental artifact and is the subject of continuing studies in our laboratory. The other signal intensities, for $(M - 1)^{2+}$, $(M - 2)^{2+}$, and $(M - 3)^{2+}$ are quite reproducible, as for M^{2+} for all experiments performed on a given day. Unfortunately, the charge-stripping spectra cannot be interpreted in terms of different structures for $C_3H_5^+$ ion, unlike the situation for the $C_3H_6^+$ isomers, for example.[24]

Collisional Activation of Derivatized Ions. Reactions with Benzene. Conducting the ion–molecule reactions in a high-pressure chemical ionization source allowed us to derivatize $C_3H_5^+$ ions with benzene and phenol. A high-pressure source was necessary so that adduct ions could be collisionally stabilized and the reaction observed in the 10^{-5}–10^{-6} second residence time of ions in the source. The reaction is the same as was observed in the ICR spectrometer under single collision conditions, except that at higher pressures the adduct ion is collisionally stabilized by nonreactive collisions with neutrals (N) and is detected (see eq 1b), whereas the $C_7H_7^+$ ion, corresponding to ethene loss, was the product ion observed at lower pressures (see eq 1a).

Derivatization of $C_3H_5^+$ ions with benzene leads to a set of $C_9H_{11}^+$ (*m/z* 119) adduct ions whose CID spectra are much more information rich than the spectra of the underivatized $C_3H_5^+$ ions (see Table IV). Specifically, CID fragments corresponding to loss of H_2 and CH_4, as well as proton transfer to and hydride transfer from benzene, are most indicative of adduct (and reactant) ion structures.

Allyl bromide and allyl chloride ions should lose a halide atom to give identical $C_3H_5^+$ ions. This is reflected in the correspondence of their CID spectra upon derivatization with benzene. The $C_3H_5^+$ ion from cyclopropyl bromide also gives a derivatization product whose CID spectrum is identical with the CID spectrum observed with the allyl halides. This suggests that the predicted disrotatory ring opening has occurred before collision with neutral benzene (ca. 10^{-8} s).[12,25]

The derivatized $C_3H_5^+$ ions from 2-propenyl bromide gave different CID spectra, consistent with a unique structure for these $C_3H_5^+$ ions.

The $C_3H_5^+$ ions from 1-propenyl bromide react to form an adduct with benzene whose CID spectrum is intermediate between the CID spectra obtained for the $C_3H_5^+$ ions from allyl and 2-propenyl halides. In fact, a linear combination of the CID spectra of the adducts from the latter two $C_3H_5^+$ isomers and benzene leads to the CID spectrum observed when the $C_3H_5^+$ ions from 1-propenyl bromide react with benzene. This observation is consistent with a mixture of ion structures, two-thirds of which have the same structure as the $C_3H_5^+$ ions from allyl or cyclopropyl halides. The existence of a third isomeric $C_3H_5^+$ structure cannot be ruled out. Observation of CID spectra that are a constant linear combination using a variety of neutral derivatizing reagents would provide more convincing evidence that the $C_3H_5^+$ ions from 1-propenyl bromide do not have a third isomeric structure. Such evidence would be considerably more convincing than conclusions based on small differences in the nearly identical CID spectra of the underivatized $C_3H_5^+$ ions.

Reactions with Phenol. The $C_3H_5^+$ ions were also derivatized at high pressure with phenol (eq 5). The CID spectra of the

$$C_3H_5^+ + C_6H_6O \rightarrow C_9H_{11}O^+ \qquad (5)$$

derivatized ions were similar to those observed with benzene. Fragments corresponding to H_2 and CH_4 loss from the adduct and proton transfer to and hydroxide transfer from phenol are useful in distinguishing ion structures (Table V). Nearly identical CID spectra for the adducts were observed when reagents were introduced with a 10-fold excess of a helium bath gas, which indicates that the CID spectra of the $C_9H_{11}O^+$ adduct ions do not change appreciably with pressure from about 0.1–1.0 torr.

Allyl and cyclopropyl bromides gave $C_3H_5^+$ ions which reacted with phenol to give adducts whose CID spectra were identical. With 2-propenyl bromide, the adduct ion CID spectrum was significantly different. The adduct for $C_3H_5^+$ from 1-propenyl bromide gave a CID spectrum that is a linear combination of the spectra for adducts from derivatization of $C_3H_5^+$ ions from allyl bromide and 2-propenyl bromide in a 2.1:1.0 ratio, respectively. This result agrees very well with the ratio calculated from the benzene data.

Reactions with Benzene-d_6. The structural information available in CID spectra may be further enhanced by derivatization with isotopically labeled reagents. Derivatization of $C_3H_5^+$ ions with benzene gave adducts whose CID spectra show signals at *m/z* 41 ($C_3H_5^+$) and *m/z* 39 ($C_3H_3^+$) corresponding to reversion to reactants and additional loss of H_2. Use of benzene-d_6 results in an adduct whose CID spectrum is a measure of the ability of the adduct ion to undergo H/D interchange between the exocyclic and ring carbons before collision-induced fragmentation. We might expect that the H/D exchange would be a further test of ion structure.

On the basis of the CID spectra, the $C_9H_5D_6^+$ adducts from reaction of the $C_3H_5^+$ from allyl or cyclopropyl bromide show the least H/D exchange prior to collision induced reversion to reactants (see Table VI). The $C_3H_5^+$ ions from 2-propenyl bromide, on the other hand, show the most exchange. The results for the $C_3H_5^+$ from 1-propenyl bromide are again intermediate, suggesting a linear combination of the other CID spectra. On the basis of the data in Table VI, the $C_3H_5^+$ ions from 1-propenyl bromide are a mixture of approximately 1.6:1.0 of the $C_3H_5^+$ ions from allyl

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[24] (a) Bowen, R. D.; Barbalas, M. P.; Pagano, F. P.; Todd, P. J.; McLafferty, F. W. *Org. Mass Spectrom.* **1980**, *15*, 51. (b) Holmes, J. L.; Terlouw, J. K.; Burgers, P. C.; Rye, R. T. B. *Ibid.* **1980**, *15*, 149.

[25] Thiel, W. *J. Am. Chem. Soc.* **1981**, *103*, 1420.

Table VI. Partial CID Spectra for $C_9H_5D_6^+$ Ions from $C_3H_5^+$ and Benzene-d_6[a]

	source of $C_3H_5^+$ ions			
m/z	cyclopropyl bromide	allyl bromide	1-propenyl bromide	2-propenyl bromide
45	1.3	1.3	1.3	1.0
44	2.7	2.9	2.9	2.7
43	5.7	5.5	7.2	8.6
42	17.5	16.8	22.2	30.6
41	51.2	50.8	42.7	30.6
40	10.8	11.0	12.3	14.4
39	10.8	11.6	11.3	12.3

[a] Expressed as $i/\Sigma i_{41}$, 10% RSD.

Table VII. Partial CID Spectra of Model $C_9H_{11}^+$ Ions from Isobutane CI of C_9H_{10}[a]

	m/z					
	117	103	79	77	41	39
β-methylstyrene	40.0	6.9	<3	9.5	4.3	4.6
cyclopropylbenzene	40.6	5.1	<3	8.0	10.8	5.0
allylbenzene	37.1	6.2	<3	8.4	11.3	4.4
α-methylstyrene	27.2	12.9	9.9	14.2	7.5	4.2
o-methylstyrene	39.7	12.2	<3	9.2	1.5	3.0
m-methylstyrene	37.7	11.9	<3	10.0	1.7	3.4
p-methylstyrene	38.8	11.9	<3	9.7	1.6	3.2
indan	47.7	4.7	<3	6.1	3.0	3.7

[a] Expressed as $i/\Sigma i$, 12% RSD.

and 2-propenyl bromide, respectively, a ratio which agrees well with the ratios computed from results obtained for the adducts with unlabeled benzene and phenol.

CID of Model Compounds. Protonation of various C_9H_{10} isomers with $C_4H_9^+$ (isobutane chemical ionization) gave reference $C_9H_{11}^+$ ions whose CID spectra could be compared with the spectra of adduct ions. These structural types can be identified clearly by their CID spectra (Table VII). For example, H_2 loss is unusually large for protonated indane and quite small for protonated α-methylstyrene. Methane loss is large for $[M + H]^+$ from α-, *o*-, *m*-, and *p*-methylstyrene. Loss of C_3H_4 is only observed for protonated α-methylstyrene. The $C_9H_{11}^+$ ions from α-methylstyrene and indane give the largest and smallest loss of C_3H_6, respectively. Also, the intensity of the $C_3H_5^+$ fragment exceeds the signal for $C_3H_3^+$ only for protonated cyclopropyl- and allylbenzene, as well as α-methylstyrene.

While the signal for $C_3H_5^+$ in the CID spectra of the protonated C_9H_{10} species was used to characterize these model $C_9H_{11}^+$ isomers, it was not used for elucidation of the structure of the corresponding adducts from $C_3H_5^+$ and benzene. This CID signal, corresponding to simple reversion to products, may contain a sizeable contribution from weakly bonded adducts (such as π complexes) which would more readily revert to reactants. For this reason, CID fragments from ion–molecule reactions corresponding to simple reversion processes should be used for structural interpretation only with care.

Weakly bonded adducts may also be responsible for the slightly larger day-to-day variation of the signal for reversion to products, particularly for the $C_9H_{11}^+$ formed via the reaction of $C_3H_5^+$ ions from cyclopropyl bromide. An alternative explanation is that the exothermicity of the cyclopropyl-to-allyl ring-opening process produces excited allyl cations which are not completely collisionally stabilized. The excess internal energy, together with energy from the exothermicity of the derivatization reaction (about 60 kcal/mol),[26] could lead to a preference for reversion to reactants. In any event, the intensity of the CID fragment corresponding to a reversion reaction would be expected to vary with pressure, and this was observed.

Table VIII. Partial CID Spectra of Model $C_9H_{11}O^+$ Ions from Methane CI of $C_9H_{10}O$ and Phenol Derivatized $C_3H_5^+$ Ions[a]

	m/z				
	117	115	95	77	41
allyl phenyl ether	1.8	2.0	4.9	17.3	29.6
o-allylphenol	3.8	10.4	<3	13.3	19.4
allyl chloride + phenol	5.6	10.6	3.7	14.1	16.3

[a] Expressed as $i/\Sigma i$ (for narrow scans *m/z* 20–120), 10% RSD.

Finally, the protonated model compounds might be expected to show a slightly greater tendency for $C_3H_5^+$ formation upon collisional activation than adduct ions, due to some direct protonation of the π bond external to the ring.

Comparison of CID Spectra of $C_9H_{11}^+$ Ions. The CID spectrum of the $C_9H_{11}^+$ adduct ion from the reaction of the suspected allyl ion isomer (from allyl bromide) with neutral benzene shows the same characteristic features as the spectra of protonated allylbenzene and β-methylstyrene, the two reference compounds having a linear three carbon group attached to benzene. This is consistent with the allyl ion structure for $C_3H_5^+$ and with electrophilic attack to form a adduct which is either a Wheland intermediate (eq 6)

(6)

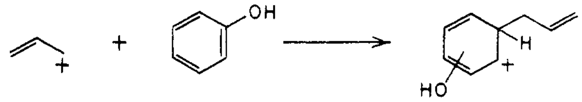
or similar structure with the proton in another position. The small differences in CID spectra are expected because the precise location of the "added" proton in the derivatized adduct ions and in the reference ions is uncertain.

The CID spectrum for $C_9H_{11}^+$ from the reaction of the presumed 2-propenyl cation (from 2-propenyl bromide) with benzene is nearly identical with the CID spectrum of pronated α-methylstyrene. The large signals for CH_4 and C_3H_4 loss are particularly characteristic of these $C_9H_{11}^+$ ions. The correspondence of CID spectra is the first *direct evidence* that the structure of the $C_3H_5^+$ ion from 2-propenyl halides is indeed that of the 2-propenyl cation and is consistent with electrophilic attack of its center-charge carbon on benzene (eq 7).

(7)

The CID spectrum of $C_9H_{11}^+$ generated in the reaction of $C_3H_5^+$ from 1-propenyl bromide and benzene is intermediate between those observed for protonated allylbenzene and protonated α-methylstyrene. The consistent intermediate behavior of $C_3H_5^+$ ions from 1-propenyl bromide is good evidence that these $C_3H_5^+$ ions are a mixture of allyl and 2-propenyl isomers.

Model $C_9H_{11}O^+$ Ions: Two model $C_9H_{11}O^+$ ions were obtained by protonating *o*-allylphenol and allyl phenyl ether with CH_5^+ (methane CI). The CID spectrum of the ion–molecule adduct of allyl cation (from allyl bromide) and phenol was more similar to the CID spectrum obtained of protonated *o*-allylphenol than that of protonated allyl phenyl ether (see Table VIII); compare for example the *m/z* 115 ions corresponding to loss of H_2O and H_2. We would expect a CID fragment involving loss of water to be structurally significant considering the proposed structures of the product ions for reaction of $C_3H_5^+$ ions and phenol. Furthermore, the results are in accord with a mechanism involving electrophilic attack on the ring rather than attack on the oxygen atom (eq 8). Such a mechanism is in complete agreement with



(8)

the well-known preference for phenol to undergo electrophilic attack on the ring rather than at the oxygen atom in gas-phase proton-transfer reactions.[27]

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(26) Calculated on the basis of data from: (a) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. "Journal of Physical and Chemical Data"; American Institute of Physics: New York, 1977; Vol. 6, suppl 1. (b) Hartman, K. N.; Lias, S.; Ausloss, P.; Rosenstock, H. M., Schroyer, S. S.; Schmidt, C.; Martinsen, D.; Milne, G. W. A. "A Compendium of Gas Phase Basicity and Proton Affinity Measurements"; National Bureau of Standards: Washington, D.C., 1979; No. NBSIR 79-1777.

Conclusion

These experiments demonstrate the advantages of high-pressure ion derivatization coupled with CID analysis for determination of the structures of gas-phase $C_3H_5^+$ ions. This technique allowed: (1) addition of phenyl and phenoxy functional groups to $C_3H_5^+$, to give collisionally stabilized adduct ions with more characteristic CID spectra than the $C_3H_5^+$ ions themselves, (2) use of d_6-labeled benzene, which further enhanced the structural significance of the CID spectra, and (3) use of model compounds to provide direct evidence for determination of the $C_3H_5^+$ ion structures.

Two isomeric $C_3H_5^+$ ion structures were determined: allyl cation from allyl halides and 2-propenyl cation from 2-propenyl halides. The structures of these isomeric ions were assigned on the basis of the first *direct* evidence obtained for these gas-phase ions; that is, the correspondence of the CID spectra of the derivatized adduct ions and the corresponding model ions.

Ionized 1-propenyl bromide gave $C_3H_5^+$ ions which are approximately a 2:1 mixture of allyl and 2-propenyl isomers. While previous experiments were also interpreted in terms of a mixture of isomers, we believe that this conclusion is now more firmly established because it is now arrived at on the basis of linear combinations of more characteristic CID spectra of three derivatives.

The $C_3H_5^+$ ion from cyclopropyl halide was determined to be identical with the $C_3H_5^+$ ion from allyl bromide; that is, it also appears to have the allyl ion structure.

The mechanism of reaction of allyl cation and benzene was shown to be electrophilic attack on the benzene to produce a Wheland intermediate, in accord with the results of Colosimo and Bucci[28] (also at high pressure), and not the protonated indane structure previously advocated in studies at low pressure.[21] However, we cannot distinguish the Wheland structure from closely related forms in which the proton is substituted elsewhere on the ring. The difference between the high- and low-pressure results may be explained by collisional stabilization at higher pressures to freeze the adduct ions in the "Wheland" form which, in the absence of stabilization, isomerizes to an indanyl structure before fragmenting. The 2-propenyl cation also reacted by electrophilic substitution on the aromatic ring.

Additional evidence for electrophillic attack was provided by low-pressure ICR experiments. The reaction pathway, ethene loss from the "activated" adduct, was independent of substitution on benzene. The rate constant for the reaction of allyl cation with benzene is 30% greater than for the 2-propenyl cation. The rate constant for the reaction of the $C_3H_5^+$ ion from 1-propenyl bromide is 60% of the value for allyl cation, reflecting the contribution from 2-propenyl cations, the effects of additional internal energy liberated in the isomerization of the 1-propenyl ions, and somewhat higher experimental errors.

Experimental Section

The FTMS instrument has been described previously.[29] The instrument was operated in the mixer mode with a start frequency of 100 KHz and a bandwidth of approximately 400 KHz allowing operation in the mass range 37–180 amu with a 1.2-T magnetic field strength. The trapping voltage was 1 V. Filament bias was typically 30 eV with a beam duration of 5 ms. Double-resonance pulses were set at the minimum level necessary to eject the ion of interest with continuous ejection throughout the reaction period. Typical operating pressures were $(2–8) \times 10^{-7}$ torr with typically 1:1 mixture of reactant neutrals.

The pulsed ICR results were obtained with a modified Varian ICR-9. The magnetic field was adjusted to bring the $C_3H_5^+$ ions into resonance with a radio frequency of 153 KHz. The electron beam current was typically 400 nA for 5 ms. Ion image currents were detected via a bridge circuit[30] after the 150-mV, 5-ms RF pulse (at the end of the variable reaction period). The filament was biased at 15 eV with a 1.9-eV trap voltage. Typical pressures were about $0.1–1.0 \times 10^{-5}$ torr. The pulse sequence was controlled by an Intel 8039 microprocessor and interface of our own design.

Rate constants were calculated on the basis of the rate of disappearance of the $C_3H_5^+$ ion corrected for loss of reactant ions due to the reaction of $C_3H_5^+$ ions with their parent neutrals (eq 2 and 3) and for trapping losses. The method of correcting the rate constants is based on the scheme

$$A^+ + A \xrightarrow{k_1} \text{products}$$

$$A^+ + B \xrightarrow{k_2} \text{products}$$

where $C_3H_5^+ = A^+$, $C_3H_5Br = A$, and $C_6H_6 = B$. The concentration of A^+ is governed by the equation

$$[A^+] = [A^+]_0 e^{-\{k_1[A] + k_2[B]\}t}$$

Initial experiments were carried out without the neutral derivatizing reaction so that the equation simplifies to

$$[A^+] = [A^+]_0 e^{-k_1[A]t}$$

and gives the familar form

$$k_1 = -\ln \{[A^+]/[A^+]_0\}/[A]t$$

The value of k_1 was then used to calculate the desired rate constant k_2 for the derivatization reaction from

$$-d/dt \ln \{[A^+]/[A^+]_0\} = k_1[A] + k_2[B]$$

CID and charge-stripping spectra of $C_3H_5^+$ ions were obtained via 70-eV electron-impact ionization of C_3H_5Br isomers in a Kratos MS-50 TA (triple analyzer), described elsewhere.[31] The $C_3H_5^+$ fragment ions were mass selected by using the double focusing MS-I (R = 3000) and subjected to 4–8 keV collisions with helium target gas to produce CID and charge-stripping spectra. Helium was introduced to a pressure to give 50% suppression of the ion beam. Charge-stripping measurements were made with narrow scans of the final electrostatic sector from 45 to 50% of the "main-beam" voltage. Typically nine scans were averaged to obtain the spectra, and typically three or more spectra were averaged to obtain the data in the tables.

The effects of ionizing energy were obtained by lowering the nominal electron voltage to a value of about 12 eV without adjustment of the ion repellers. Acquisition of CID spectra below 12 eV was prohibited because of the poor signal-to-noise ratio.

Derivatization reactions were carried out in the chemical ionization source of the MS50-TA. Product ions were mass analyzed and subjected to CID analysis as described above. The electron ionization energy was increased to 280 eV. Typical operating pressures were 0.1–1.0 torr for a 2:1 mixture of C_6H_5R and C_3H_5X (X = Br or Cl). C_3H_5 halides and benzene were introduced through a molecular leak via a heated volatile liquids inlet. Phenol was introduced via direct probe and desorbed from basic alumina in some experiments and via the volatile liquids inlet with a 10-fold excess of He carrier to aid carry through in others. Benzene-d_6 was introduced via the volatile liquids inlet with a controlled flow of a 10-fold excess of He to assure maximum collisional stabilization and also to better control the total pressure and hence internal energy of product ions undergoing H/D exchange.

Reference ions were prepared by isobutane chemical ionization of various C_9H_{10} compounds and methane chemical ionization of $C_9H_{10}O$ compounds at a source pressure of 0.1–1.0 torr. Ionization was by 280-eV electrons.

The partial CID spectra for adducts were normalized to the sum of all CID fragment signals except for the fragments corresponding to H and ethene loss. These signals were omitted because the intensity for H loss showed excessive (>25%) run-to-run variability, and the signal corresponding to ethene loss contained a large metastable component whose intensity was dependent on pressure (internal energy).

All chemicals were the highest quality (>98%) commercially available materials. They were outgassed extensively before use. Their mass spectra were consistent with literature reports.

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(27) DeFrees, J. D.; McIver, R. T.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 3853 and references therein.

(28) Colosimo, M.; Bucci, R. *J. Chem. Soc., Perkin Trans. 2* **1982**, 461.

(29) Ghaderi, S.; Kulkarni, P. S.; Ledford, E. B., Jr.; Wilkins, C. L.; Gross, M. L. *Anal. Chem.* **1981**, *53*, 428.

(30) See: (a) McIver, R. T., Jr. In "Ion Cyclotron Resonance Spectrometry"; Hartmann, H., Wanczek, K. P., Eds.; Springer-Verlng: Berlin, 1978. (b) McIver, R. T., Jr.; Ledford, E. B., Jr.; Hunter, R. L. *J. Chem. Phys.* **1980**, *72*, 2535.

(31) Gross, M. L.; Chess, E. K.; Lyon, P. A.; Crow, F. W.; Evans, S.; Tudge, H. *Int. J. Mass Spectrom.* **1982**, *42*, 243.

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Registry No. Allyl bromide, 106-95-6; cyclopropyl bromide, 4333-56-6; 2-propenyl bromide, 557-93-7; 1-propenyl bromide, 590-14-7; benzene, 71-43-2; anisole, 100-66-3; phenol, 108-95-2; benzene-d_6, 1076-43-3; β-methylstyrene, 637-50-3; cyclopropylbenzene, 873-49-4; allylbenzene, 300-57-2; α-methylstyrene, 98-83-9; *o*-methylstyrene, 611-15-4; *m*-methylstyrene, 100-80-1; *p*-methylstyrene, 622-97-9; indan, 496-11-7; allyl phenyl ether, 1746-13-0; *o*-allylphenol, 1745-81-9; allyl chloride, 107-005-1.

Energetics and Structures of Organosulfur Ions: $CH_3SSCH_3^+$, CH_3SS^+, $C_2H_5S^+$, and CH_2SH^+

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Abstract: The photoionization of dimethyl disulfide (CH_3SSCH_3) yields seven fragment ions between 10.0 and 10.7 eV. Among these are CH_3SS^+ and $C_2H_5S^+$ whose respective measured heats of formation, $\Delta H_f{}^\circ{}_{298}$, of 891 and 803 kJ/mol are significantly lower than previously reported. The rate of parent ion dissociation between 10.6 and 10.9 eV forming $C_2H_5S^+$ and H_2CS^+ was measured by photoelectron photoion coincidence. Comparison of the experimental rates with statistically expected rates leads to the conclusion that the dimethyl disulfide ion, which is initially produced with a CSSC dihedral angle of 90°, rearranges to the more stable 180° dihedral angle geometry prior to dissociation. The statistical theory rates fit the measured rates when a 298 K heat of formation of 690 kJ/mol is assumed for the energy of the dimethyl disulfide ion in its lowest energy state. This is 87 kJ/mol lower than previously assumed on the basis of the adiabatic ionization energy. The dimethyl disulfide ion is, therefore, 154 kJ/mol more stable with a CSSC dihedral angle of 180° than with an angle of 90°.

I. Introduction

One of the most striking differences between neutral molecules and the corresponding ions is the geometry of the most stable structure. Classic examples are found in the studies of keto–enol tautomers.[1-3] As a neutral molecule, for instance, the keto form of 2-propanone (acetone) is more stable than its enol tautomer, $CH_2{=}COHCH_3$. However, this relative stability reverses in gas-phase ions where the enol of acetone is 58 kJ/mol more stable than its keto counterpart.[2] Another example of a structural change in the most stable isomer is found in methyl cyanide. As a neutral molecule, the most stable structure is CH_3CN. However, in the ionic form, the structure $CH_2{=}CNH^+$ is 268 kJ/mol more stable than the CH_3CN^+ isomer.[4] Further differences between the most stable structures of neutrals and ions are the radical CH_3O and the ion CH_2OH^+,[5] and HCN and CNH^+.[6] Many of these ionic structures have been verified by ab initio and semiempirical calculations. A very common type of structural transformation is a simple bond-angle change encountered in the ionization of NO_2 to NO_2^+, and NH_3 to NH_3^+, in which the neutral molecule is bent or nonplanar and the ion is linear or planar. Dimethyl disulfide (CH_3SSCH_3) belongs to the latter category in that it has a CSSC dihedral bond angle of 90°, as determined by microwave spectroscopy,[7] while the lowest energy ion, $CH_3SSCH_3^+$, has a dihedral angle of 180° as deduced from both Walsh's rule and CNDO/2 calculations.[8-10] This bond-angle change is evident in the first band of the He I photoelectron spectrum (PES) which is broad, structureless, and rises very slowly.[11] Although an adiabatic ionization energy (IE) of 8.3 eV has been reported, it most likely does not correspond to the 0–0 transition.

Experimental and theoretical studies on the energetics of both diaryl and dialkyl disulfide ions (e.g., $RSSR^+$) are of immense importance because results from these studies should provide a sound basis for understanding the complexities of sulfur–sulfur bonding interactions.[12a] Disulfide bonds also play important roles in maintaining protein structure[12b,c] as well as possessing strong bonding interactions in coal and petroleum extracts.[12d] It is evident that, because of the ease with which disulfides are oxidized to cations, an understanding of the energetics surrounding simple disulfide ions (e.g., $CH_3SSCH_3^+$) will lead to an improved recognition of those factors influencing and ultimately controlling conformational mobility and reactivity of macromolecules containing disulfide bonds.

Numerous mass spectrometric[13-16] and photoelectron[17-19] investigations have been reported on dimethyl disulfide; however, no mass-analyzed photoionization study has been performed. We have undertaken this photoionization study of dimethyl disulfide as part of a continuing program to determine accurate gas-phase heats of formation and structures of organosulfur ions and neutral molecules. This is the first in a series of studies on the structure and energetics of the disulfide linkage in ions.

[†] Present address: National Bureau of Standards, Washington, DC 21228.

(1) (a) Holmes, J. L.; Terlow, J. K.; Lossing, F. P. *J. Phys. Chem.* **1976**, *80*, 2860. (b) Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1980**, *102*, 3732.

(2) (a) Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1980**, *102*, 1591. (b) Lifshitz, C.; Tzidony, E. *Int. J. Mass Spectrom. Ino Phys.* **1981**, *39*, 181.

(3) Splitter, J. S.; Calvin, M. *J. Am. Chem. Soc.* **1979**, *101*, 7329.

(4) Willett, G. D.; Baer, T. *J. Am. Chem. Soc.* **1980**, *102*, 6774.

(5) Berkowitz, J. *J. Chem. Phys.* **1978**, *69*, 3044.

(6) Bieri, G.; Jonsson, B. O. *Chem. Phys. Lett.* **1978**, *56*, 446.

(7) Sutter, D.; Dreizler, H.; Rudolph, H. D. *Z. Naturforsch. A* **1965**, *20*, 1676.

(8) Kimura, K.; Osafune, K. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2421.

(9) Van Wart, H. E.; Shipman, L. L.; Scheraga, H. A. *Acc. Chem. Res.* **1974**, *78*, 1848.

(10) Gillbro, T. *Phosphorus Sulfur* **1978**, *4*, 133.

(11) Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, Y.; Iwata, S. "Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules"; Japan Scientific Society Press: Tokyo, 1980.

(12) (a) Bass, S. W.; Evans, Jr., S. A. *J. Org. Chem.* **1980**, *45*, 710. (b) Boyd, D. B. *J. Am. Chem. Soc.* **1972**, *94*, 8799. (c) Boyd, D. B. *Theor. Chim. Acta* **1973**, *30*, 137. (d) Ahar, A. "Analytical Methods for Coal and Coal Products"; Karr, C., Jr., Ed.; Academic Press: New York, 1979; Vol. 3, Chapter 56, pp 585–624.

(13) Bowie, J. H.; Lawesson, S. O.; Madsen, J. O.; Nolde, C.; Schroll, G.; Williams, D. H. *J. Chem. Soc. B* **1966**, 946.

(14) Cullen, W. R.; Frost, D. C.; Pun, M. T. *Inorg. Chem.* **1970**, *9*, 1976.

(15) Mockel, H. J. *Fresenius Z. Anal. Chem.* **1979**, *295*, 241.

(16) Watanabe, K.; Nakayama, T.; Mottl, J. *J. Quant. Spectrosc. Radiat. Transfer* **1962**, *2*, 369.

(17) Cullen, W. R.; Frost, D. C.; Vroom, D. A. *Inorg. Chem.* **1969**, *8*, 1803.

(18) Coulton, R. J.; Rabalais, J. W. *J. Electron Spectrosc.* **1974**, *3*, 345.

(19) Wagner, G.; Bock, H. *Chem. Ber.* **1974**, *107*, 68.

0002-7863/83/1505-3451$01.50/0