J. Am. Chem. Soc. 1983, 105, 5719-5724

entation of Z_{efg} which is most consistent with the established bond angles and distances. When this is done we find that the values of e^2Qq/h smaller than -1.3 MHz fit the data for C9 only at values of B_{C9} which are considerably smaller than the tetrahedral angle. Similarly, values of e^2Qq/h larger than -1.7 MHz fit the data for B_{C16} at angles which are much larger than the tetrahedral angle. The best fit to the data is given by a value of e^2Qq/h of -1.5 MHz. the angles between Z_{efg} and the three internuclear vectors are then given by β_{C9} = 102°, β_{C17} = 104°, and β_{C16} = 112°. The limits are taken to be ±0.2 MHz for e^2Qq/h and ±2° for the angles orienting Z_{efg} in the molecular frame.

Discussion

The value of -1.5 MHz for the quadrupole coupling constant derived from the above analysis is slightly larger than that observed by Brown and co-workers[20] for the protonated form of the tertiary amine 1,2-dipiperdinoethane, and it is much less than the value of 3-5 MHz found for free tertiary amines,[21] therefore it seems to be a resonable value for morphine with the nitrogen protonated. The angles between Z_{efg} and the respective internuclear vectors are all consistent with tetrahedral geometry about nitrogen. Smaller values for β_{C9} and β_{C17} may reflect the fact that the three CNC angles in this compound are all slightly greater than 109.5°.[15] The sign of the quadrupole coupling constant is unambiguously seen to be negative as a positive quadrupole coupling constant for values of β near the tetrahedral angle would give a ^{13}C spectrum with the orientation of the asymmetric doublet reversed.

The most important source of error in the determination of e^2Qq/h from this experiment is the experimental resolution available. The assumption that the asymmetry parameter, η, is close to zero when calculating the theoretical lines in Figure 3 is expected to be quite good for the case where there is no marked deviation from tetrahedral geometry. Substituting a value for η of 0.1 in the calculations would increase the derived coupling constant by 0.1 MHz. The method used to obtain a range of quadrupole coupling constants which will fit the data obviously depends on the choice for reasonable bounds to the values for β. This in turn depends on the accuracy of the bond distances and angles used in making the analysis. The NMR data alone can at least limit the magnitude and sign of the quadrupole coupling constant to relatively narrow ranges.

The value of e^2Qq/h allows use of the modified Townes and Daily[22] analysis described by Brown and co-workers[20] to compute electron occupation numbers for the orbitals about nitrogen.[20,23] In this analysis the quadrupole coupling constant is given by $e^2Qq/h = e^2Qq_0/h\cdot(3/4)(\sigma - \delta)$, where σ is the occupancy number of the nitrogen lone pair orbital and δ is the occupancy number of the N–C orbitals. δ is assumed to increase by an inductive effect when the nitrogen lone pair orbital goes from the free to a protonated state and is given by $\delta = \delta_0 + 0.15(2 - \sigma)$ where δ_0 is the N–C orbital occupancy of the free base which is calculated to be 1.259, with the factor 0.15 an estimate of the proportionally constant of the inductive effect.[20] Using our value for both the sign and magnitude of the observed quadrupole constant, and a value of -9.0 MHz for e^2Qq_0/h,[21] we calculate a value of σ of 1.5 e. This finding unambiguously shows that σ is larger than δ, a result that would have been difficult to predict due to the similarity of the electronegativities of the hydrogen and alkyl groups.[21] For example, this contrasts with the result of a semiempirical quantum mechanical calculation where the bond polarity of the NH orbital in protonated morphine was approximately equal to those of the N–C bonds.[17]

The NMR experiment provides an unambiguous determination of the sign of the quadrupole coupling constant, as well as its magnitude and orientation in the molecular frame, the accuracy of which depends on the experimental resolution available and the accuracy of the bond distances and geometry used to calculate the curves for fitting the experimental data.

Glasel[24] in a high field solution ^{13}C and ^{1}H NMR study of morphine described the prsence of major and minor components for the C15, C16, and C17 carbons and protons in an acidified sample. He attributed these components to nitrogen invertomer equilibrium "frozen out" at low pH. The ^{1}H coupling constants were nearly identical for both components. Since the conformation difference at C15 in our spectrum is seen only at that site, with approximately equal populations of two conformations present, it is unlikely that this represents the same phenomenon. However, in combination with the solution study, the solid-state spectrum draws attention to the possibility of the presence of two conformations of morphine at the receptor.

Acknowledgment. This research is supported by grants from the National Institutes of Health (GM-24266 and GM-29754). J.G.H. is supported by the NIGMS graduate research training program (GM-07612) of the Department of Anesthesiology, University of Pennsylvania. M.H.F. is supported by a Cell and Molecular Biology Training Grant.

Registry No. Morphine sulfate, 64-31-3.

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Structure and Reactivity of Gas-Phase Ions: $C_4H_4^{+\cdot}$

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Abstract: The structure and reactivity of $C_4H_4^{+\cdot}$ ions in the gas phase have been investigated with use of collision-induced dissociation (CID) and tandem ion cyclotron resonance spectroscopy. Two stable isomers were identified, one linear $C_4H_4^{+\cdot}$ and one cyclic $C_4H_4^{+\cdot}$, in agreement with observations of Ausloos. It is shown that the m/z 26/27 ratio in the CID pattern of $C_4H_4^{+\cdot}$ is strongly dependent on the isomeric content of the $C_4H_4^{+\cdot}$ beam. This ratio was calibrated against isomeric composition, and the percent cyclic and linear $C_4H_4^{+\cdot}$ arising from a variety of sources was explored. The ion chemistry of $C_4H_4^{+\cdot}$ with C_2H_2 was examined in the tandem ICR. The linear form reacted with a rate constant of $\sim(3 \pm 1.5) \times 10^{-10}$ cm^3/s, while the cyclic form reacted extremely slowly if at all. It was shown that acetylene "catalyzes" isomerization of linear $C_4H_4^{+\cdot}$ to cyclic $C_4H_4^{+\cdot}$ with a rate constant of $\sim 1 \times 10^{-10}$ cm^3/s, presumably via a long-lived $C_6H_6^{+\cdot}$ intermediate.

It has been pointed out repeatedly in the past that structure elucidation of small and medium sized hydrocarbon ions is not an easy task.[1] Isomerization barriers are often small, and thus the decomposition of the ions may be slow compared to the isomerization rates. Experimental methods which sample excited ions, therefore, often show either one or a mixture of interconverting structures. For example, according to isotopic labeling experiments, metastable ion spectra, field ionization kinetics, and photoion–photoelectron coincidence (PIPECO) measurements, $C_4H_8^{+\cdot}$ and $C_4H_6^{+\cdot}$ ions with sufficient energy to decompose have

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completely equilibrated prior to decomposition.[2] Unfortunately, experimental methods that are known to sample nondecomposing ions also sometimes fail in the structure elucidation of hydrocarbon ions. Thus, for the isomerization of a *tert*- to a *sec*-butyl ion, a barrier of 134 kJ/mol has to be overcome.[3] Nevertheless, the collision-induced dissociation (CID) spectra of both ions are almost indistinguishable.[4]

Extreme care has to be taken in interpreting small differences in CID and charge stripping (CS) spectra in terms of structural differences. It has recently been shown that differences in internal energies can affect CID and CS spectra[5] and hence proof of structural differences in such cases is only possible if the ion internal energies can be kept negligibly small or if it can be shown that the internal energy has little or no effect on the spectra. Ion–molecule reactions may also be influenced by the internal energy of the ions.[6] Besides the general problem of finding suitable reactions (i.e., reactions whose rate and/or product distribution is structurally selective), the ions' internal energy complicates the interpretation of these experiments. For the reasons given above, often a combination of experimental methods has to be employed in order to unequivocally determine an ion structure.

Among small hydrocarbon ions, $C_4H_4^{+}\cdot$ has recently received considerable attention. Appearance potential (AP) and ionization potential (IP) measurements were first carried out by Rosenstock et al.[7] The authors concluded from their measurements that $C_4H_4^{+}\cdot$ fragments formed by threshold decomposition of ionized benzene and pyridine have a cyclic rather than a linear structure. Baer et al.[8] suggest ionized methylene cyclopropene as the probable structure of the fragment. By assuming this structure, they found excellent agreement between QET calculations and the experimentally determined average kinetic energy release (KER) in the unimolecular decomposition of ionized benzene to form $C_4H_4^{+}\cdot$ over an energy range from 14.8 to 18 eV. The same authors present evidence for a second, probably linear, isomer. A plot of the ratio of the $C_3H_3^{+}/C_4H_4^{+}\cdot$ fragment intensity obtained from ionized benzene over an energy range from 15 to 19 eV shows a sudden dedrease at 15.6 eV, suggesting the accessibility of a new channel leading to the formation of $C_4H_4^{+}\cdot$. Surprisingly, the second channel is not reflected in the kinetic energy release data.

Ion–molecule reactions of $C_4H_4^{+}\cdot$ have been studied by Lifshitz et al.[9,10] and by Ausloos.[11] Using ion trapping in the space charge of a pulsed electron impact source, Lifshitz and Weiss[9] report a curved decay for the semilogarithmic plot of the $C_4H_4^{+}\cdot$ intensity in pure benzene vs. time. This curvature was discussed by Lifshitz et al.[10] where it was concluded that perhaps two structures are present or that the $C_4H_4^{+}\cdot$ ions are initially formed with internal excitation and are collisionally deexcited to a low-energy state, which can no longer charge exchange with benzene.

The same reaction has been studied by Ausloos[11] using trapped ion cyclotron resonance spectrometry. According to these experiments, only a fraction of the $C_4H_4^{+}\cdot$ population reacts with benzene; the other fraction shows no reaction even after 300 ms. An interesting aspect of Ausloos' experiments is that the ratio of reactive to unreactive $C_4H_4^{+}\cdot$ fragment ions is a strong function of the internal energy of the $C_6H_6^{+}\cdot$ precursor. Using $Ar^{+}\cdot$ and $N_2^{+}\cdot$ as charge transfer reagents, the author finds >80% of the reactive species; while with $CO^{+}\cdot$, 95% of the unreactive ions are formed. From thermodynamic considerations, Ausloos concludes that the reactive ions have the vinylacetylene structure while the unreactive part consists of methylene cyclopropene ions.

Metastable and collision-induced decompositions of $C_4H_4^{+}\cdot$ ions have been studied by Lifshitz et al.[10] According to these authors, not only the kinetic energy release of the metastable ions but also the relative intensity of the collision-induced fragments are, within experimental error, independent of the method of formation of $C_4H_4^{+}\cdot$. The authors claim that this points to either a single stable structure of $C_4H_4^{+}\cdot$ in the gas phase or a mixture of structures in constant proportions.

In this paper we report new data on bimolecular reactions of $C_4H_4^{+}\cdot$ generated under a variety of conditions.

Experimental Section

Ion–molecule reactions were studied on the UCSB tandem ion cyclotron resonance (TICR) spectrometer described in detail elsewhere.[12,13] Ions are formed by either electron impact or chemical ionization in an ion cyclotron resonance (ICR) cell at nearly ground potential. The ions are extracted from the cell, accelerated to 3 kV, mass selected in a 180° Dempster magnetic sector, and decelerated to ground potential as they pass through the entrance slit into a second ICR cell (the reaction chamber). The entrance slit consists of a miniature Wien velocity filter which is used to remove any translationally hot ions. Once in the second cell, the ions react with the desired neutral species. The drift times through the cell are measured with use of the trapping plate ejection method.[14] The pressure is measured either directly with use of a capacitance manometer (MKS Baratron, Model 170M-26) or with use of an ionization gauge calibrated against the capacitance manometer. Since all parts of the spectrometer are positioned between the poles of a 12 in. electromagnet, the magnetic field must remain fixed and products are detected by scanning the frequency of a marginal oscillator. Peak heights are corrected for the sensitivity of the marginal oscillator with use of a Q-spoiler.[15] Pressure isolation between ICR I (source region) and ICR II (reaction region) is ca. 2×10^5. All data are the average of at least three measurements; the reproducibility was better than 10% unless stated otherwise.

The CID experiments were performed with use of a reverse geometry mass spectrometer (VG Analytical ZAB-2F) fitted with a combined EI/CI ion source constructed at UCSB.[16] Ion source pressures were measured directly with use of a capacitance manometer (MKS Baratron, Model 170M). Unless stated otherwise, the electron energy was 150 eV, the source temperature 50 °C, and the accelerating voltage 8 kV. Both analog and pulse-counting detection methods were employed. CID spectra were obtained by adding helium to the collision cell, located at the focal point between magnet and electrostatic analyzer, until the main beam intensity was reduced by 50%. The CID fragmentation pattern was obtained by scanning the ESA voltage. All spectra are the mean of at least three measurements; the reproducibility was better than ± 10%.

The CID spectrum of $C_4H_4^{+}\cdot$ formed from metastable benzene ions was measured by passing the metastable ions formed in the first field-free region through the magnet and focusing them into the collision cell. The ESA was then scanned in the usual way.[17] Comparison of the CID spectra of $C_4H_4^{+}\cdot$ ions at 8 and 5 keV kinetic energy showed that the relative abundance of the collision-induced fragments does not change within this energy range.

The average KER of $C_4H_4^{+}\cdot$ formed from the benzene parent ions was determined from the kinetic energy release distribution which, in turn, was determined from the peak shape of metastable ions decomposing in

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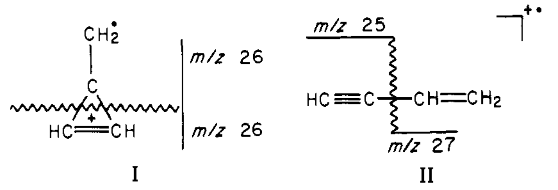
Table I. Partial CID Spectra of $C_4H_4^{+\cdot}$ Ions Generated under Varying Ion Source Conditions

neutral precursor (method of ion preparation)[a]	*m/z* 24	25	26	27	*m/z* 26/27	%[d] linear isomer
vinylacetylene (EI, 150 eV)	4	19	56	21	2.7	100[b]
vinylacetylene (EI, 10 eV)	4	19	55	22	2.4	
benzene (EI, 150 eV)	5	18	61	18	3.7	53
benzene (Cl, CI gas: benzene, 0.18 torr)	3	17	72	8	9.0	0[c]
benzene (CI, CI gas: Ar, 0.21 torr)	5	20	59	16	3.4	62
benzene (CI, CI gas: N_2, 0.2 torr)	6	22	58	15	3.9	48
methylene-2,3-dimethylcyclopropane (EI, 150 eV)	3	18	66	13	5.1	28
benzene (metastable $C_6H_6^{+\cdot *} \rightarrow C_4H_4^{+\cdot} + C_2H_2$)	3	18	66	13	6 ± 1	18 ± 10

[a] Under EI conditions the pressure in the ion source is low and there are no collisions of the ions formed with the background gas. Under CI conditions there are typically 10 to 100 s of collisions with background gas. [b] Assumed 100% linear vinylacetylene cation. [c] Assumed 100% cyclic methylene cyclopropene cation. [d] Estimated uncertainty is ±15%, i.e., 53 ± 8%.

Scheme I



the second field-free region. The methods employed have been described elsewhere.[18]

Vinylacetylene was synthesized from 1,3-dichloro-2-butene with use of a known procedure[19] and commerical reagents. All other reagents were commercially available and were used without further purification.

Results and Discussion

Two fundamentally different experiments are discussed here which shed light on $C_4H_4^{+\cdot}$ structures and mechanisms of formation: CID and ion–molecule reactions. In both cases, selective methods are used to generate the $C_4H_4^{+\cdot}$ precursor ion. The nature of this ion is then probed by using either CID or ion–molecule reactions. The two sets of data interrelate but will be discussed separately.

A. Collision-Induced Dissociation Studies. As discussed in the introduction, there appear to be two stable forms of $C_4H_4^{+\cdot}$, presumably the linear vinylacetylene cation and the cyclic methylene cyclopropene cation. The direct evidence for these different structures comes principally from the ion–molecule reaction work of Ausloos.[11] Lifshitz et al.[10] using CID were not able to distinguish the two structures. On the basis of the work of Ausloos[11] and our ion–molecule work to be described in the next section, we decided to reexamine the CID spectra of a number of $C_4H_4^{+\cdot}$ systems that should have different isomeric content.

There are many peaks in the CID spectrum of $C_4H_4^{+\cdot}$, and the relative intensities of most of them remain essentially constant as the method of generating $C_4H_4^{+\cdot}$ is varied. Further, our overall spectra are qualitatively very similar to those published by Lifshitz et al.[10] and will not be published in toto. However, the relative intensities of four peaks (*m/z* 24, 25, 26, and 27) were found to be diagnostic of the isomeric composition. We will concentrate the discussion on these peaks. Partial CID spectra for $C_4H_4^{+\cdot}$ ions prepared in several different ways are given in Table I.

The most apparent feature of the data in Table I is that the *m/z* 26/27 ratio is strongly dependent on the method of preparation of the $C_4H_4^{+\cdot}$ ion. This ratio can vary either because the internal energy in $C_4H_4^{+\cdot}$ is varying or because the isomeric composition of the ion beam is varying, or both. For reasons we will discuss shortly, we believe the variation in the *m/z* 26/27 ratio is due primarily to changes in the isomeric composition of the ion beam and not due to internal energy effects.

Ausloos[11] has shown that one isomer of $C_4H_4^{+\cdot}$ reacts with benzene and one does not. He convincingly argues on thermodynamic grounds that the reactive isomer is the linear vinylacetylene cation. In Table I the *m/z* 26/27 ratio for $C_4H_4^{+\cdot}$ ions from benzene increases from 3.7 to a limiting value of 9.0 as the benzene pressure is increased in the ion source. At the higher pressures the reactive $C_4H_4^{+\cdot}$ ions have been removed from the ion beam and only unreactive ions are left. In line with the conclusions of others,[7,8,11] we assume these unreactive ions have the cyclic methylene cyclopropene structure.

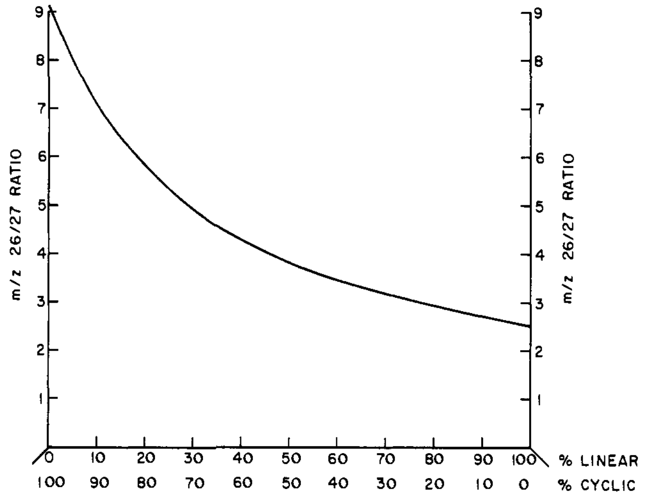


Figure 1. A plot of the *m/z* 26/27 ratio obtained by CID on $C_4H_4^{+\cdot}$ as a function of the isomeric content in the $C_4H_4^{+\cdot}$ ion beam.

When pure vinylacetylene is ionized in the ion source under EI conditions (zero collision conditions), an *m/z* 26/27 ratio of 2.4 (10-eV electrons) to 2.7 (150-eV electrons) is obtained.

A high value for the *m/z* 26/27 ratio for the methylene cyclopropene cation (I) and a low value for the vinylacetylene cation (II) can be rationalized. Direct fragmentation of I yields only *m/z* 26 products while direct fragmentation of II yields one product at *m/z* 25 and one at *m/z* 27. Some rearrangement will, of course, take place but the propensity for forming *m/z* 26 relative to *m/z* 27 should be greater in I than II, as is observed.

If the *m/z* 26/27 ratios for pure cyclic and pure linear $C_4H_4^{+\cdot}$ cations are known, then the calculated ratio for an arbitrary composition can be written as[20,21]

$$\frac{26}{27} = \frac{fI_c^{26} + (1-f)I_l^{26}}{fI_c^{27} + (1-f)I_l^{27}} \tag{1}$$

where f is the fraction of cyclic isomer and I_m^n is the intensity of fragment ion n arising from pure isomer m normalized to the main beam intensity (i.e., I_c^{26} is the intensity of the *m/z* = 26 fragment from the cyclic isomer normalized to the *m/z* = 52 main beam intensity). Assuming that the CID fragmentation pattern of 100%

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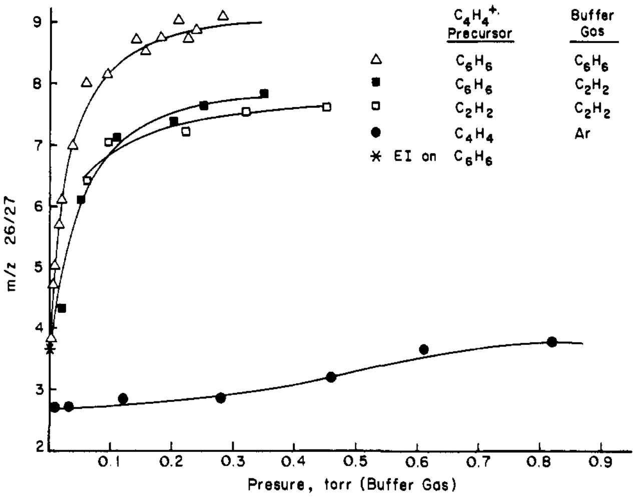
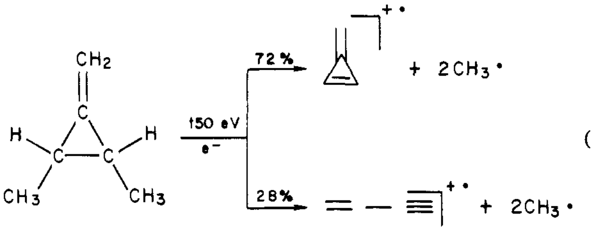


Figure 2. The m/z 26/27 ratio resulting from the collision-induced dissociation of $C_4H_4^{+}\cdot$ as a function of ion source pressure (see text for discussion).

l-$C_4H_4^{+}\cdot$ is given by electron impact of vinylacetylene, and that the CID fragmentation pattern of 100% c-$C_4H_4^{+}\cdot$ is given by the high-pressure benzene results, one can calculate the m/z 26/27 ratio as a function of composition by using eq 1. The resulting curve giving the fraction of cyclic or linear isomer as a function of m/z 26/27 ratio is given in Figure 1.

When the data in Table I and the fractional abundance curve of Figure 1 are used, ion beam isomeric compositions can be uniquely specified. These are given in the last column of Table I. The benzene EI result suggests 53% of the ion beam is the linear isomer and 47% the cyclic isomer. The estimated uncertainty in these numbers is ±8%. Ausloos[11] found that 60 ± 5% of the $C_4H_4^{+}\cdot$ ions from benzene reacted with benzene, i.e., had the linear structure. The two results agree within experimental error although radically different experimental techniques were utilized.

Also of interest is the fact that methylene-2,3-dimethylcyclopropane yields 72% cyclic ions under 150-eV EI conditions.



(2)

No effort was made to study this fragmentation at electron energies closer to threshold.

As pointed out by Lifshitz et al.,[10] the question of internal energy vs. isomer composition of the $C_4H_4^{+}\cdot$ ions is of central importance.[22] These two effects often cannot be clearly sorted out. In Figure 2 the m/z 26/27 ratio is plotted for several systems as a function of buffer gas pressure. The m/z 26/27 ratio for the pure benzene data (Δ) rapidly increases from its EI value of 3.7 to a value of ~9.0 as the benzene pressure increases. Above about 0.2 torr the ratio levels off. The ratio for the vinylacetylene data with argon buffer, however, increases only slightly from the EI value of 2.7 and levels off at about 3.3. Above 0.6 torr of argon the ratio remains constant. At the highest argon pressures the system has undergone about 700 stabilizing collisions. The small change in ratio from 2.7 to 3.3 with Ar pressure could be due either to removing internal energy or to a slow collision-induced isomerization process. It is not possible to distinguish between these two alternatives with the data in hand. In any case, internal energy effects appear to play only a minor role, if any, in the variation of the m/z 26/27 ratio compared with effects due to the method of preparation of the $C_4H_4^{+}\cdot$ ion.

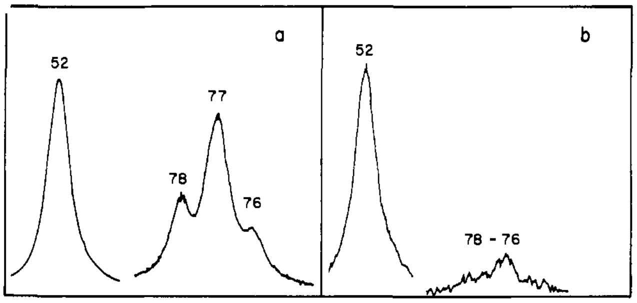
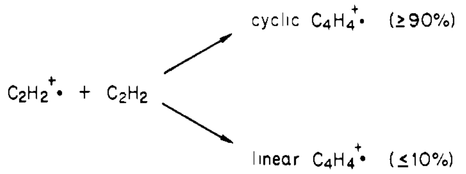


Figure 3. Products in the range m/z 76 to 78 for reaction of $C_4H_4^{+}\cdot$ with C_2H_2 in the TICR. (a) $C_4H_4^{+}\cdot$ precursor is vinylacetylene with an ion source pressure $<3 \times 10^{-5}$ torr. (b) $C_4H_4^{+}\cdot$ precursor is a mixture of vinylacetylene and benzene at an ion source pressure of vinylacetylene $<3 \times 10^{-5}$ torr and benzene 4×10^{-4} torr.

There are two additional curves of interest in Figure 2. First, the acetylene clustering reaction forms at least 90% cyclic product.



(3)

A van der Waals cluster ion $(C_2H_2)_2^{+}\cdot$ has been shown to exist,[23] but is ~50 kcal/mol higher in energy than the two more stable isomers. The barrier to rearrangement of this cluster to either of these isomers is smaller than the energy supplied by the $C_2H_2^{+}\cdot/C_2H_2$ reactions in (3).[23] Ono and Ng[23] discuss the reaction coordinate diagram for the $C_4H_4^{+}\cdot$ surface in more detail.

The second interesting piece of data in Figure 2 is the rapid increase in the m/z 26/27 ratio of benzene generated $C_4H_4^{+}\cdot$ when C_2H_2 is added to the source. By analogy to the pure benzene data,[11] the implication is that linear $C_4H_4^{+}\cdot$ ions react much more rapidly with C_2H_2 than cyclic $C_4H_4^{+}\cdot$ ions. This is an interesting possibility and will be explored more fully in the next section.

One final experiment was performed. In this case $C_4H_4^{+}\cdot$ ions were formed by metastable reaction of benzene parent ions in the first field-free region (1FFR) of the mass spectrometer followed by CID in the second field-free region (2FFR):

$$(C_6H_6^{+}\cdot)^* \rightarrow C_4H_4^{+}\cdot + C_2H_2 \qquad \text{1FFR}$$

$$C_4H_4^{+}\cdot + He \rightarrow \text{CID products} \qquad \text{2FFR}$$

The CID spectrum yielded an m/z 26/27 ratio of 6 ± 1. When the curve in Figure 1 is used, this ratio corresponds to 82 ± 10% cyclic $C_4H_4^{+}\cdot$ and 18 ± 10% linear $C_4H_4^{+}\cdot$. When the absolute unimolecular rate constant data of Baer et al,[8] are corrected for thermal energy in the benzene neutral,[24] it appears that the metastable benzene ions have internal energy in the range 15.2–15.6 eV if they dissociate in the first field-free region of our instrument. This energy is above the appearance potential of linear $C_4H_4^{+}\cdot$ and near the energy where Baer et al.[8] observe the onset of a second $C_4H_4^{+}\cdot$ channel in the fragmentation of benzene parent ions. Competition for formation of the two $C_4H_4^{+}\cdot$ structures in the metastable reaction is thus reasonable.

B. Ion–Molecule Reactions in the Tandem ICR. Ausloos[11] has shown that only linear $C_4H_4^{+}\cdot$ ions react with benzene. In the CID experiments discussed above it appears that linear $C_4H_4^{+}\cdot$ ions also react much faster with C_2H_2 than do cyclic ions. To test this suggestion, the following experiment was done. First, $C_4H_4^{+}\cdot$ from electron impact on vinylacetylene in the tandem source (ICR I) were injected into ICR II and reacted witth C_2H_2. The product ion distribution in the m/z 76–78 range is given in

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[22] This area of internal energy effects vs. isomeric content in CID studies is under active investigation. See ref 5; also: P. A. M. van Koppen, A. J. Illies, and M. T. Bowers, *Org. Mass Spectrom.*, **17**, 229 (1982); A. J. Illies, S. Liu, and M. T. Bowers, *J. Am. Chem. Soc.*, **103**, 5673 (1981); and C. Proctor and F. M. McLafferty, *Org. Mass Spectrom.*, in press. The earlier work is well referenced in the above listed papers.

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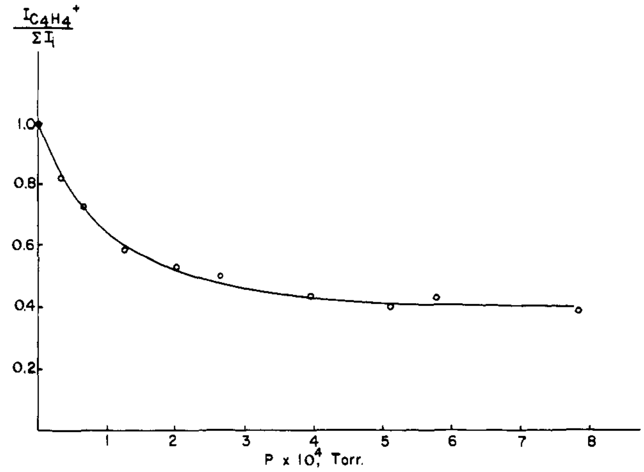

Figure 4. Relative intensity of $C_4H_4^{+}\cdot$ as a function of C_2H_2 pressure in the TICR reaction chamber. The relative intensity is given by $I_{C_4H_4^{+}\cdot}/\sum_i I_i$, where $\sum_i I_i$ is the sum of reactant and product ions.

Figure 3a.[25] It is apparent that substantial reaction occurs under these conditions. When the same experiment is repeated with a high pressure of benzene in ICR I and the same pressure of C_2H_2 in ICR II, then the spectrum in Figure 3b is obtained. Under these conditions most linear $C_4H_4^{+}\cdot$ ions would have reacted with benzene in ICR I and mainly cyclic $C_4H_4^{+}\cdot$ ions are injected into ICR II. The extent of reaction is very much reduced. From these data one can conclude linear $C_4H_4^{+}\cdot$ reacts very much faster than cyclic $C_4H_4^{+}\cdot$ with C_2H_2.

The next step was to measure the absolute rate constant for the reaction of linear $C_4H_4^{+}\cdot$ with C_2H_2. To do this, vinylacetylene was used as the $C_4H_4^{+}\cdot$ precursor in ICR I. The C_2H_2 pressure was then varied in ICR II and the extent of reaction measured. The results are plotted in Figure 4. In the previous section we had suggested that vinylacetylene yields essentially 100% $l\text{-}C_4H_4^{+}\cdot$. This suggestion was based on the similar CID fragmentation pattern near threshold (~10 eV) and at 150 eV. If this suggestion is correct, the extent of reaction should exponentially decrease to zero as the C_2H_2 pressure is raised. Clearly the data in Figure 4 indicate a fairly large portion (~40%) of the $C_4H_4^{+}\cdot$ signal remains at high pressure. One conclusion could be that the $C_4H_4^{+}\cdot$ beam from ICR I contained ~60% linear $C_4H_4^{+}\cdot$ and ~40% cyclic $C_4H_4^{+}\cdot$. This conclusion is inconsistent with the CID results, however, and we sought other explanations.

One reaction that cannot be observed when linear $C_4H_4^{+}\cdot$ reacts with C_2H_2 is the isomerization reaction

$$l\text{-}C_4H_4^{+}\cdot + C_2H_2 \rightarrow (C_6H_6^{+}\cdot)^* \rightarrow c\text{-}C_4H_4^{+}\cdot + C_2H_2 \quad (4)$$

which is estimated to be 0.5-eV exothermic.[7,8,11,24] If C_2D_2 is used in place of C_2H_2 in ICR II, then we obtain

$l\text{-}C_4H_4^{+} + C_2D_2 \longrightarrow$	$C_4H_2D_2^{+}\cdot + C_2H_2$	9%	(5a)
$\longrightarrow$	$C_4H_3D_2^{+}\cdot + C_2HD$	24%	(5b)
$\longrightarrow$	$C_4H_4^{+}\cdot + C_2D_2$	?	(5c)
$\longrightarrow$	all other products	67%	(5d)

A significant portion of the products is isotopically mixed $C_4(H,D)_4^{+}\cdot$ ions, presumably arising from reaction 4. The $C_4H_4^{+}\cdot$ product channel cannot be observed. However, if statistical H,D scrambling occurs, it is expected to be a minor channel, perhaps 5–10% of the total $C_4(H,D)_4^{+}\cdot$ intensity. As a consequence, the $C_4(H,D)_4^{+}\cdot$ channel probably accounts for 37 ± 5% of the products in reaction 5.

Using the product distribution obtained by reaction of $l\text{-}C_4H_4^{+}\cdot$ with C_2H_2, extrapolated to zero C_2H_2 pressure, and using the results discussed above to account for the cyclic $C_4H_4^{+}\cdot$ product channel, we obtain

		fraction	ΔH (eV)[26]	
$l\text{-}C_4H_4^{+}\cdot + C_2H_2$	$\rightarrow C_6H_6^{+}\cdot$	0.04	-4.84	(6a)
	$\rightarrow C_6H_5^{+} + H\cdot$	0.43	-1.15	(6b)
	$\rightarrow C_6H_4^{+}\cdot + H_2$	0.09	-1.43	(6c)
	$\rightarrow c\text{-}C_4H_4^{+}\cdot + C_2H_2$	0.37	-0.52	(6d)
	$\rightarrow C_3H_3^{+} + C_3H_3\cdot$	0.06	-0.49	(6e)

The small $C_6H_6^{+}\cdot$ product persists even when C_2H_2 pressures are extrapolated to zero and may signify a small amount of radiative stabilization. The H_2 loss channel, (6c), has a substantial reverse activation barrier[24] accounting for its low relative abundance. The relatively large abundance of the cyclic $C_4H_4^{+}\cdot$ product explains the apparent leveling off of the extent of reaction of $l\text{-}C_4H_4^{+}\cdot$ with C_2H_2 shown in Figure 4. As $l\text{-}C_4H_4^{+}\cdot$ reacts away, $c\text{-}C_4H_4^{+}\cdot$ is formed. Since $c\text{-}C_4H_4^{+}\cdot$ reacts very slowly, if at all, with C_2H_2, and since $c\text{-}C_4H_4^{+}\cdot$ cannot be distinguished from $l\text{-}C_4H_4^{+}\cdot$ due to their equal masses, the apparent extent of reaction of $l\text{-}C_4H_4^{+}\cdot$ will level off at high C_2H_2 concentrations. The fact that the extent of reaction in Figure 4 levels off at ~0.4 is consistent with the projected product distribution of $c\text{-}C_4H_4^{+}\cdot$ of 0.37 ± 0.05 given in reaction 6.

The absolute rate constant measurement for reaction 6 is complicated by the presence of $c\text{-}C_4H_4^{+}\cdot$ as a product. The interference is minimized when C_2D_2 is used in place of C_2H_2 (reaction 5). Even so, some product at m/z 52 is obtained. By working at very low extent of conversion, the problem is minimized. We obtain $l\text{-}C_4H_4^{+}\cdot + C_2D_2 \rightarrow$ products; $k = (3 \pm 1.5) \times 10^{-10}$ cm^3/s. The collision rate is $\sim 1 \times 10^{-9}$ cm^3/s. Hence, only one collision in three proceeds to products even though there are many exothermic product channels. This result suggests there may be a van der Waals type well in the entrance channel as observed for $C_2H_2^{+}\cdot/C_2H_2$[23] and $C_2H_4^{+}\cdot/C_2H_4$.[27] The presence of such a well has been proposed by Jarrold et al. in their theoretical modeling[24,28] of bimolecular and unimolecular reactions occurring on the $C_6H_6^{+}\cdot$ surface. The $l\text{-}C_4H_4^{+}\cdot/C_2H_2$ reacting system encounters a tight transition state between the van der Waals well and the more stable chemically bonded part of the $C_6H_6^{+}\cdot$ surface. As a consequence, it appears about two thirds of the encounters are reflected back through the orbiting transition state to the $l\text{-}C_4H_4^{+}\cdot/C_2H_2$ reactants. The temperature dependence of the rate constant would be an interesting check on this mechanism, but at present it is not possible to do this experiment accurately with our equipment.

Conclusions

1. The m/z 26/27 ratio in the CID spectrum of $C_4H_4^{+}\cdot$ is shown to be strongly dependent on the isomeric content of the ion beam. By using suitable "calibration" sources of $C_4H_4^{+}\cdot$, it was possible to quantitatively correlate the experimentally measured ratio with the isomeric content of the beam (eq 1 and Figure 1). With use of this curve, sources of $C_4H_4^{+}\cdot$ with unknown isomeric content can be analyzed. In this paper we showed that low-pressure EI on benzene yielded 53 ± 8% linear $C_4H_4^{+}\cdot$ and 47 ± 8% cyclic $C_4H_4^{+}\cdot$, a result in good agreement with the determination of Ausloos[11] on the basis of diagnostic ion–molecule

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[25] This spectrum was taken at a C_2H_2 pressure in ICR II of $\sim 3 \times 10^{-4}$ torr. If the product distribution is extrapolated to zero pressure, then the m/z 76 peak corresponding to clustering of $C_4H_4^{+}\cdot$ with C_2H_2 becomes very much smaller. Hence, this peak is due primarily to collisional stabilization of the excited $C_6H_6^{+}\cdot$ adduct. The fact that the m/z 76 ion does not extrapolate to zero, but rather to 6 ± 2%, indicates a radiative association may be occurring to a small extent.

[26] The heats of formation of the various reaction channels were obtained from a thorough literature search and a judicious selection among available values. A summary of the appropriate references is given in ref 24.

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reactions. We were also able to show the $C_4H_4^{+}\cdot$ cluster ion in acetylene is >90% cyclic isomer and the $C_4H_4^{+}\cdot$ ion from methylene-2,3-dimethylcyclopropane is 72 ± 10% cyclic isomer. Also, the $C_4H_4^{+}\cdot$ ion originating from the metastable reaction of benzene parent ion is 82 ± 10% cyclic $C_4H_4^{+}\cdot$. Finally, it was possible to infer that linear $C_4H_4^{+}\cdot$ reacts very much faster than cyclic $C_4H_4^{+}\cdot$ with acetylene.

2. The ion chemistry of l-$C_4H_4^{+}\cdot$ reacting with acetylene was explored by using the tandem ICR. The total rate constant for reaction of l-$C_4H_4^{+}\cdot$ was measured to be $(3 \pm 1.5) \times 10^{-10}$ cm^3/s. The rate constant for the cyclic isomer with acetylene was immeasurably slow ($<10^{-11}$ cm^3/s). With use of C_2D_2 it was possible to show acetylene "catalyzed" the isomeric conversion reaction

$$\text{l-}C_4H_4^{+}\cdot + C_2H_2 \rightarrow \text{c-}C_4H_4^{+}\cdot + C_2H_2$$

with a rate constant of $\sim 1 \times 10^{-10}$ cm^3/s. A complete product distribution for reaction of l-$C_4H_4^{+}\cdot$ is reported.

3. The techniques of collision-induced dissociation and tandem ion cyclotron resonance are complimentary and allow determination of the isomeric content in $C_4H_4^{+}\cdot$ beams and information on the mechanism of formation and reactivity of $C_4H_4^{+}\cdot$ ions.

Acknowledgment. The support of the National Science Foundation under Grant CHE80-20464 is gratefully acknowledged. One of us (W.W.R.) wants to thank the Deutsche Forschnungsgemeinschaft for a Fellowship.

Registry No. I, 79105-72-9; II, 59699-48-8; vinylacetylene, 689-97-4; benzene, 71-43-2; methylene-2,3-dimethylcyclopropane, 62338-02-7; acetylene, 74-86-2.

Electrocyclic Ring Opening of 1-Phenylcyclobutene and 3-Phenylcyclobutene Radical Cations

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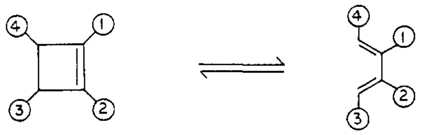
Abstract: The 1-phenyl- and 3-phenylcyclobutene radical cations have been studied by mass spectrometry/mass spectrometry (MS/MS) techniques to determine the effect of substitution on the electrocyclic ring opening of cyclobutene radical cation. Substitution at the double bond of cyclobutene stabilizes the cyclobutene radical cation compared to the unsubstituted moiety, whereas phenyl substitution at the 3-position enhances the rate of the electrocyclic reaction. The activation energy for the ring opening of the 1-phenylcyclobutene radical cation is estimated to be less than 14 kcal mol^{-1}, whereas that for the 3-phenylcyclobutene radical cation is close to the threshold for ionization. Raising the internal energy of the ions causes the two phenyl-substituted cyclobutenes and their ring-opened isomers to rearrange to a stable structure or a mixture of structures. The probable ultimate structure is assigned as that of the radical cation of 3-methylindene on the basis of the thermochemical measurements and the CAD spectra of other isomeric $[C_{10}H_{10}]^{+}\cdot$ radical cations.

The electrocyclic ring opening of thermally activated neutral cyclobutene and its derivatives to the corresponding 1,3-butadienes is a well-established phenomenon (eq 1). The transformation takes place in a stereospecific conrotatory manner for the thermally allowed process and in a disrotatory manner for the photochemical process.[1] The experimental activation energy is 32.9 kcal mol^{-1} for the thermal process[2] occurring for the parent compound.



(1)

The effects of substituents on the electrocyclic interconversion of the neutral cyclobutene and 1,3-butadiene pair have been the subject of many theoretical and experimental investigations.[3-8] By use of a theoretical model proposed by Carpenter,[3] it can be qualitatively predicted that any substituent at the double bond of cyclobutene should decrease the rate of conrotatory ring opening. On the other hand, substitution at the 3- and 4-positions should increase the rate of the reaction. These predictions have received considerable experimental support.[4,5,8] More recently, Wilcox and Carpenter[6] were able to predict quantitatively the relative activation enthalpies for the ring opening of various substituted cyclobutenes.

Although understanding of the electrocyclic ring opening of closed shell systems is quite well developed, relatively little is known of similar ring-opening processes of open shell systems. One approach has been to search for correlations between the chemistry of the gas-phase ions with the thermal and photochemical processes of neutrals.[9-16] Johnston and Ward[9] presented evidence that some mass spectral fragmentations take place through the electronically excited state (a photochemical analogy), whereas Bishop and Fleming[11] concluded that prediction of the stereochemical path for the ions is not straightforward, and both allowed and forbidden processes may be observed. Thus, the effect of removal of an electron on the course of most electrocyclic reactions is still not understood.

Recently, we have reported the ring opening of low internal energy cyclobutene radical cations.[17] Our conclusion was that the isomerization to the 1,3-butadiene radical cation is essentially complete at less than 0.6 eV above threshold. The corresponding activation energy was estimated to be less than 0.3 eV, which is much smaller than the activation energy needed for the similar ring opening of neutral cyclobutene.[2] Similar conclusions were drawn by Haselbach and co-workers[18] on the basis of theoretical studies. Thus, the effect of ionization is to reduce the energy

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