Ion–Molecule Reaction Chemistry of Various Gas-Phase C₆H₆ Radical Cations

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Abstract: Various gas-phase C_6H_6 radical cations can be grouped in three general reaction categories depending on their origin. Ionized benzene reacts with 2-propyl iodide to displace an iodine atom and produce $C_9H_{13}^+$. The rate constant for this reaction is 1.4×10^{-9} cm³ molecule⁻¹ s⁻¹ at 11 eV of ionizing energy. The major fraction of fragment C_6H_6 ions from styrene, cyclooctatetraene, anisole, benzaldehyde, phenylhydrazine, and chroman participate in the same reaction. A small proportion of the fragment $[C_6H_6]^+\cdot$ from benzaldehyde, chroman, and phenylhydrazine react with 2-propyl iodide by a second channel to give charge exchange. Ionic decarbonylation of tropone produces $[C_6H_6]^+\cdot$ which reacts with 2-propyl iodide exclusively by the charge exchange channel. These ions constitute a second category for gas-phase C_6H_6 ions. A third general class of $[C_6H_6]^+\cdot$ is produced by direct ionization of various acyclic isomers of benzene (1,5-hexadiyne, 1,4-hexadiyne, 2,4-hexadiyne, and 1,3-hexadien-5-yne). The ions undergo charge exchange with 2-propyl iodide and give no detectable $C_9H_{13}^+$. Moreover, these acyclic ions react with their neutral counterparts to produce a rich array of gas-phase products and with 1,3-butadiene to give $C_8H_7^+$, $C_9H_9^+$, and $[C_{10}H_{10}]^+\cdot$. This chemistry is not found with ionized benzene or the second category of $[C_6H_6]^+\cdot$. The differences in bimolecular chemistry are attributed to structural and energetic variations for the various C_6H_6 cations.

This paper is a report of some highly specific ion–molecule reactions of various C_6H_6 radical cations produced by direct ionization of benzene and four of its acyclic isomers and by fragmentation of several more complex molecules. Because the structure and chemical properties of $[C_6H_6]^+\cdot$ have been of interest to many investigators, this study was undertaken to provide complementary information which would serve as a basis for reasonable deductions concerning the structure of this important gas-phase ion. Previous studies may be conveniently divided into two groups: (1) investigations of decomposing or "unstable" C_6H_6 ions, and (2) ion–molecule reactions and thermochemical measurements which reflect the stable, nonfragmenting C_6H_6 cations.

The results for fragmenting ions have been employed either to determine the structure of ionized benzene or to understand the mode of carbon and hydrogen atom rearrangements which take place prior to fragmentation. Ever since the early study of Momigny et al.[1] who reported the similarity in the mass spectra of benzene and various acyclic isomers (especially 1,3-hexadien-5-yne), it has been tempting to assume the intermediacy of an open chain isomer in the decompositions of $[C_6H_6]^+\cdot$. The similar kinetic energy released by $[C_6H_6]^+\cdot$ formed in direct ionization of benzene and by acyclic[2] $[C_6H_6]^+\cdot$ from charge exchange of $[C_6H_6]^{2+}$ provides convincing support for this idea.[3] Other $C_6H_6^+\cdot$ ions, generated by decomposition of more complex species, are nearly identical with ionized benzene, using the kinetic energy release criterion,[4] and presumably are also acyclic. Possible exceptions are the tropone-produced C_6H_6 ion, which releases twice the kinetic energy in the loss of acetylene,[4b] and $[C_6H_6]^+\cdot$ from benzenechromium tricarbonyl, which yields distinctively different metastable intensities from ionized benzene.[5]

However, there is a question whether C_6H_6 ions from benzene decompose from a single state or structure. The results of Andlauer and Ottinger,[6] which have recently been confirmed by Smith and Futrell,[7] and those of Jonsson and Lindholm[8] have been interpreted in terms of isolated states, which give rise to noncompeting channels for loss of H and H_2 vis-á-vis loss of C_2H_2 and C_3H_3. Quasi-equilibrium theory (QET) calculations[9] point to dissociation from the cyclic ground state ion to give $C_6H_5^+$ and $[C_6H_4]^+\cdot$ whereas formation of $[C_4H_4]^+\cdot$ and $C_3H_3^+$ involves either an electronically excited benzene ion or a ring-opened form. Recent photoelectron–photoion coincidence spectroscopy studies[10] confirm the interpretations of Andlauer and Ottinger[6] but may

rule out the intervention of an electronically excited state. The early QET calculation of Vestal[11] shows that it is possible to account semiquantitatively for the fragmentation of ionized benzene by employing only the ground state of the molecular ion.

Although the isolated states argument seems to be in contradiction with interpretations drawn from kinetic energy release measurements[3,4] and comparative mass spectrometry studies,[1] both sets of data may be accommodated by a rate-determining isomerization of $[C_6H_6]^+\cdot$ from benzene followed by rapid fragmentation.[4b] Moreover, the supporting QET calculations are not sufficiently sensitive to the choice of a cyclic ground state benzene ion rather than a ring-opened form.

The other focus of studies of decomposing C_6H_6 ions has been the carbon and hydrogen scrambling which occurs prior to fragmentation.[12,13] Contrary to the earlier suggestion that hydrogen scrambling proceeded via valence isomerization,[12] the more recent and thorough ^{13}C and ^{2}H labeling shows independent C and H rearrangements.[12] Although there are few experimental data to shed light on the mechanism of scrambling, we have reported a molecular orbital calculation which indicates that a single 1,2 exchange of hydrogen atoms on the intact ring can account for hydrogen atom reorganization.[14]

Like all simple aromatics, the molecular ion of benzene is stable, requiring between 4.7[9] and 5.0[15] eV of internal excitation before fragmenting. This means that electronic excitation, ring-opening, and carbon/hydrogen scrambling may preempt fragmentation. One purpose of this study is to determine if the existence of these processes can be verified by intercepting the "stable" ions in ion–molecule reactions. Before turning to a discussion of our results, a brief account of the available information on the stable C_6H_6 ions will be set forth.

Thermochemical measurements show that the ground-state heat of formation of benzene is 233 kcal/mol[16] which is too low for threshold formation of an acyclic ion.[16,17] Except for cubane and 1,3,5-hexatriene, other sources of $[C_6H_6]^+\cdot$ such as styrene, cyclooctatetraene, etc., give an excited benzene ion, not the acyclic form, at the threshold.[17] These results do not agree with the conclusions drawn from perturbation molecular orbital theory that ionization of benzene yields an acyclic ion as the low-energy structure.[18] A compilation of the thermochemical data is presented in Table I.

High kinetic energy ion–molecule reactions also have been

Source of $[C_6H_6]^+$	Ionization or appearance potential, eV	$\Delta H_f(C_6H_6^+)$, kcal/mol	Ref
Benzene	9.25	233	a
	11.5 (E_{2g})	285	a
1,3-Hexadien-5-yne	9.5	307	a
1,5-Hexadiyne	10.0	330	b
1,4-Hexadiyne	9.75	319	a
1,3-Hexadiyne	9.25	307	a
1,2-Hexadien-5-yne	9.4	316	b
1,2,4,5-Hexatetraene	8.53	296	b
Dewar benzene	9.0	300	c
Fulvene	8.36	240	d
3,4-Dimethylenecyclo-butene	8.80	280	d
Styrene	12.3	262	e
Cyclooctatetraene	9.7	239	e
Anisole	11.3	268	f
Tropone	10.0	261	g

^{a} Reference 16. ^{b} Estimated adiabatic ionization potential: P. Bischof, R. Gleifer, H. Hopf, and F. T. Lenich, *J. Am. Chem. Soc.*, **97**, 5467 (1975). ^{c} Estimated adiabatic ionization potential: G. Bieri, E. Heilbronner, M. J. Goldstein, R. S. Leight, and M. S. Lipton, *Tetrahedron Lett.*, 581 (1975). ^{d} E. Heilbronner, R. Gleiter, H. Hopf, V. Hornung, and A. de Meijere, *Helv. Chim. Acta*, **54**, 783 (1971). ^{e} Reference 17a. ^{f} Reference 28. ^{g} This work. Corrected for release of 0.45 eV of translational energy.

utilized to determine the structure for "stable" C_6H_6 ions generated from both benzene and numerous other sources including two acyclic isomers, 2,4-hexadiyne and 1,5-hexadiyne.[19,20] The results of collision-induced dissociation (CID), which is generally assumed to sample "stable" ions, show little difference for a variety of C_6H_6 ions. However, high energy charge stripping reactions yield more distinctive data which have been interpreted to indicate at least two different forms of $[C_6H_6]^+$, one generated from benzene and the other from the acyclic isomers.[20] The sensitivity of collision-induced dissociation to detect structural isomers may be reduced because of prior rate-determining isomerizations.[20] Overlooking the CID measurements because of this limitation, we see the first evidence for existence of different structures for nondecomposing C_6H_6 ions produced from different precursors.

The only low-energy ion–molecule reaction of $[C_6H_6]^+$ that has been reported is that in ionized benzene.[21] Although extensively studied, the reaction order for "dimerization" has been a controversial subject for over 10 years. The major "dimerization" is now well-established to be fourth order (first order in $[C_6H_6]^+$ and third order in benzene) for internally excited reactant ions[21i] and third order for ground state ions from benzene.[21l-o] However, the existence of a second-order reaction to give $[C_{12}H_{12}]^+$ is fraught with conflicting observations. Many authors detect no $[C_2H_{12}]^+$.[21a,b,d,h] whereas others report low-yield ($k \sim 1 \times 10^{-11}$ cm^3 molecule^1 s^{-1}) bimolecular dimerization.[21c,f,k,o] The most definitive study of the bimolecular reaction by Jones, Bhattacharya, and Tiernan[21o] indicates participation of either an electronically excited or an acyclic $[C_6H_6]^+$ whereas the ground state ion (presumably still cyclic) is the reactant in the higher order reactions. Only two electronically excited states are thermodynamically stable to fragmentation, i.e., the $^2E_{2g}$ and $^2A_{2u}$. Freiser and Beauchamp[22] have reported that the $^2A_{2u}$ state, formed by photoexcitation of ionized benzene in an ICR cell, does not exhibit any different reactivity toward neutral benzene, which rules out this state to be sufficiently reactive or long-lived to form $[C_{12}H_{12}]^+$ in the bimolecular reaction.[21o]

From the extensive literature on the ionic chemistry of C_6H_6, two general conclusions can be gleaned. (1) The fragmenting C_6H_6 ions from benzene comprise a mixture of states or structures, a fraction of which appears to be acyclic. (2) The stable molecular ions of benzene are cyclic at the threshold. However, the large energy difference between the ionization potential and the lowest appearance potential, makes thermodynamically possible the phenomena of electronic excitation, isomerization to acyclic or valence forms, and carbon and hydrogen scrambling prior to fragmentation. In fact, there is some evidence that two stable states may show different chemical reactivities with neutral benzene.[21o] Our major purpose is to investigate the bimolecular reactivity of C_6H_6 ions using ion cyclotron resonance spectrometry. By employing the strategy of generating this ion by direct ionization of isomeric C_6H_6 molecules and by fragmentation, we hope to develop correlations which will lead to a better understanding of this important hydrocarbon radical cation in the gas phase.

Results and Discussion

Reaction with Neutral Benzene. In view of the conflicting evidence for the bimolecular reaction of ionized benzene with its neutral precursor, we began our study with an investigation of this reaction at the low pressure (up to 10^{-4} Torr), moderate residence times (~ 10 ms) available in the drift mode of ICR operation. We were unable to find any bimolecular reaction to form $C_{12}H_{12}^+$. Our *upper* estimate for the rate constant for second-order "dimerization" is $\sim 1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} which is more than an order of magnitude smaller than the bimolecular rate constant reported by Field, Hamlet, and Libby[21c] and by Stockdale.[21k] The latter author observed a small increase in the rate constant from 7×10^{-12} to 1.3×10^{-11} cm^3 molecule^{-1} s^{-1} as the ionizing energy was increased from 20 to 50 eV. We employed ionizing voltages to 25 eV but were unable to observe $[C_{12}H_{12}]^+$ even at the highest energies. Replacing benzene with the perdeuterio form allowed us to extend the pressure range by a factor of 3 because of the lower resolution necessary to separate $C_{12}D_{11}^+$ from $C_{12}D_{12}^+$, but no "dimer" could be observed. Pulsed double resonance showed that $C_{12}D_{11}^+$, $[C_{12}D_{10}]^+$, and $C_{12}D_9^+$ were produced by reactions of $C_6D_5^+$.

We then turned to a variety of other sources of $[C_6H_6]^+$ including 1,5-hexadiyne, 1,4-hexadiyne, 2,4-hexadiyne, 1,3-hexadien-5-yne, styrene, cyclooctatetraene, anisole, benzaldehyde, and tropone. In all cases, no $[C_{12}D_6H_6]^+$ could be found as the above precursors were diluted with high partial pressures of benzene-d_6. However, the intensity of m/e 78 decreased with increases in the pressure of C_6D_6. Pulsed double resonance showed that this was due to charge exchange to give $[C_6D_6]^+$. Thus, it is clear that bimolecular formation of $[C_{12}H_{12}]^+$ by reaction of C_6H_6 ions from cyclic and acyclic sources is not an important chemical reaction. These observations are not in accord with one interpretation of Jones et al. that the reactive form of $[C_6H_6]^+$ from benzene is an acyclic isomer. These authors could not rule out an electronically excited state of the benzene ion as the reacting species. Of course, the difference between the ICR experiments reported here and by others[21l,m,22] and the higher pressure mass spectrometric investigations in which bimolecular dimer is observed[21c,f,k,o] is the longer time between collisions in the ICR cell. The additional time may allow depopulation of an excited state by radiative processes to form an inert ground state ion.[21f]

Reaction of Ionized Benzene with 2-Propyl Iodide. Failing in the search for the elusive bimolecular reaction of ionized benzene with its neutral counterpart, we began an investigation of mixed systems to find a distinctive bimolecular reaction of $[C_6H_6]^+$. No condensations were found for ionized benzene with simple olefins (ethene, propene, and vinyl chloride), with

Table II. Comparison of the Experimental and Theoretical Rate Constants for Reaction of Ionized Benzene and 2-Propyl Iodide

k(disappearance $C_6H_6^+$)[a]	k(appearance $C_9H_{13}^+$)[a]	Origin of k	Ionizing[b] energy
1.4×10^{-9}	1.4×10^{-9}	Exptl	11.0
1.35×10^{-9}	1.34×10^{-9}	Exptl	13.0
1.23×10^{-9}	1.23×10^{-9}	Exptl	15.0
1.05×10^{-9}	1.08×10^{-9}	Exptl	17.0
1.09×10^{-9}	1.09×10^{-9}	Langevin	
3.65×10^{-9}	3.65×10^{-9}	LDO[c]	
1.54×10^{-9}	1.54×10^{-9}	ADO[c]	

[a] cm^3 molecule^{-1} s^{-1}. [b] Nominal values in eV. [c] See text for reference.

acetylene, 1,3-butadiene, ethanol, nitric oxide, methyl iodide, ethyl iodide, and 1-propyl iodide. The corresponding chlorides and bromides also proved to be inert. However, a facile bimolecular reaction was observed with 2-propyl iodide (eq 1) to yield a product ion at m/e 121 ($C_9H_{13}^+$) corresponding to displacement of an iodine atom.

$$[C_6H_6]^{+\cdot} + 2\text{-}C_3H_7I \rightarrow C_9H_{13}^+ + I \qquad (1)$$
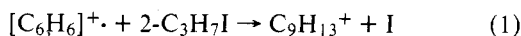
Pulsed double resonance experiments confirmed that $[C_6H_6]^{+\cdot}$ is the sole origin of the product ion. The reaction is observed at ionizing energies as low as 10 eV which demonstrates that the reactive species is not electronically excited.

To evaluate the efficiency of the reaction, the rate constant was measured (see Experimental Section) and compared with the theoretical collision rate constants calculated using Langevin,[23] locked dipole orientation (LDO),[24] and the average dipole orientation (ADO)[25] theories. Experimental rate constants for disappearance of $[C_6H_6]^{+\cdot}$ and for appearance of $C_9H_{13}^+$ were determined to be the same, i.e., 1.4×10^{-9} cm^3 molecule^{-1} s^{-1} at 11 eV of ionizing energy (see Figure 1 for typical data). This identity is strong evidence that $C_9H_{13}^+$ is the only reaction product. Comparison of the experimental rate constants at various ionizing energies with the theoretical values is presented in Table I.

As expected, Langevin theory underestimates the rate constant because no account is taken of the permanent dipole in 2-propyl iodide, and the locked dipole theory gives an overestimate. The average dipole orientation theoretical calculation agrees quite well with the experimental value. If we accept the ADO calculation as the best estimate for the collision rate constant,[25] we conclude that the reaction is quite facile and occurs for ~90% of the collisions.

A small, smooth decrease in the rate constants is found as the ionizing energy is increased. We attribute this to an internal energy effect.[26] An alternative explanation is that increasing the ionizing energy depletes the reactive population of $[C_6H_6]^{+\cdot}$ by either electronic excitation or isomerization to a ring-opened form. However, no bimolecular formation of $[C_{12}H_{12}]^{+\cdot}$ with neutral benzene could be observed at high ionizing energy (25 eV) which rules out formation or persistence of the reactive form of ionized benzene observed by Jones et al.[21o] As will be discussed later, the typical reactions of $[C_6H_6]^{+\cdot}$ from acyclic sources are not found with benzene ionized at these higher energies. Moreover, the rate of disappearance of $[C_6H_6]^{+\cdot}$ could be followed to ~90% reaction at 13 eV which excludes formation of greater than 10% of an inert state or isomeric ion. Isomerization to unreactive valence isomers or to the fulvene radical cation at a concentration of less than 10% of the total $[C_6H_6]^{+\cdot}$ cannot be excluded as possibilities. Nevertheless, the decrease in rate constant with increasing electron energy is a documented phenomenon for low translational energy ion-molecule reactions.[26] This explanation is favored pending other experimental evidence.
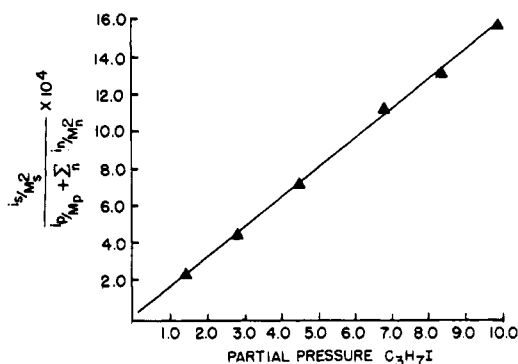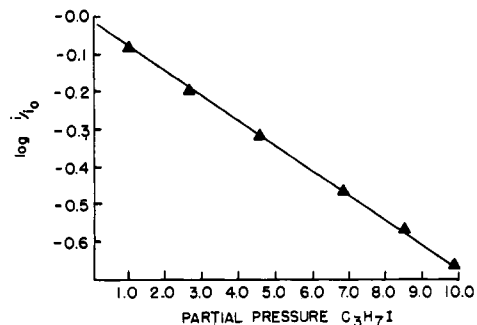
Figure 1. Variation of ion abundances for the reaction of ionized benzene with 2-propyl iodide as a function of the partial pressure of 2-propyl iodide. Ionizing energy = 11 eV. Pressure expressed in arbitrary units.

Reaction of 2-Propyl Iodide and C_6H_6 Ions from Other Sources. Generating $[C_6H_6]^{+\cdot}$ by ionization of acyclic isomers of benzene or by fragmentation of other molecules will allow us to test whether reactive forms are generated from these $[C_6H_6]^{+\cdot}$ sources. Further stimulus is provided by the fact that the structures of $C_6H_6^+$ formed as fragment ions with excess excitation are not well-established. A comparison of the relative rates of disappearance of m/e 78 and of appearance of m/e 121 ($C_9H_{13}^+$) in the reaction with 2-propyl iodide is contained in Table II.

As can be seen, the C_6H_6 fragment ions formed by loss of C_2H_2 from styrene and cyclooctatetraene and by loss of CH_2O from anisole react with nearly the same rate as does ionized benzene. The somewhat enhanced rates for $[C_6H_6]^{+\cdot}$ from benzaldehyde, chroman, and phenylhydrazine may originate because the C_6H_6 fragment is formed with a distribution of internal energies which is shifted to lower values. Lower internal energy causes a larger rate for ion-molecule reactions.[26] Metastable studies and exact mass measurements show that $C_6H_6^+$ from chroman is produced in a two-step process (eq 2).

$$\text{chroman}^{+\cdot} \xrightarrow{-C_2H_4} [C_7H_6O]^{+\cdot} \xrightarrow{-CO} [C_6H_6]^{+\cdot} \qquad (2)$$
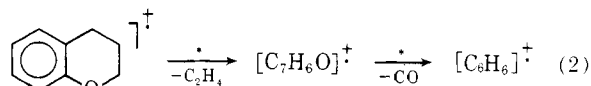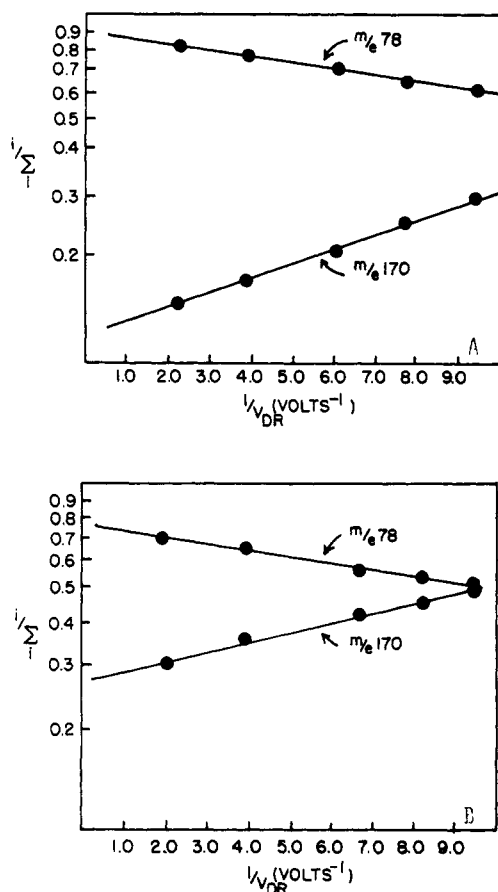
In all cases, the rate constants were measured by following the ion intensities as a function of the partial pressure of 2-propyl iodide.

The acyclic isomers of benzene upon direct ionization react by charge exchange with 2-propyl iodide (eq 3) but give no detectable $C_9H_{13}^+$ according to eq 1.

$$[C_6H_6]^{+\cdot} + C_3H_7I \rightarrow [C_3H_7I]^{+\cdot} + C_6H_6 \qquad (3)$$

In fact, all the discrepancies between the rate constants for appearance of $C_9H_{13}^+$ and for disappearance of $[C_6H_6]^{+\cdot}$ (Table III) are attributed to a parallel reaction to give charge exchange. For example, $[C_6H_6]^{+\cdot}$ from benzaldehyde reacts

Figure 2. Temporal variation of the ion intensities for $[C_6H_6]^+\cdot$ and $[C_3H_7I]^+\cdot$ in a 1:1 mixture of 1,3-hexadien-5-yne and 2-propyl iodide (top) and 2,4-hexadiyne and 2-propyl iodide (bottom) at 12 eV of ionizing energy. Variations in residence time were made by changing the source and analyzer drift fields.

Table III. Comparison of the Relative Rate Constants for Disappearance of m/e 78 and for Appearance of $C_9H_{13}^+$ at 13.0 eV[a]

Source of $[C_6H_6]^+\cdot$	k^D	$k^A(C_9H_{13}^+)$
Benzene	1.0	1.0
Anisole	1.0	0.97
Styrene	1.0	1.0
Cyclooctatetraene	1.0	0.82
Benzaldehyde	1.5	1.2
Chroman	1.5[c]	1.2
Phenylhydrazine	1.6	1.1
Tropone	0.8[c]	b
1,3-Hexadien-5-yne	1.0	
1,5-Hexadiyne	1.0	
2,4-Hexadiyne	1.0	
1,4-Hexadiyne	1.0	

[a] The relative precision of these measurements is ±7% for at least three determinations on different days. [b] No m/e 121 ($C_9H_{13}^+$) could be detected. An upper estimate for the relative rate constant is 0.05. [c] Measured and referenced to benzene at 15 eV of ionizing energy.

cations from benzene (by 11–13 eV electrons), anisole, styrene, and cyclooctatetraene are inert to charge exchange but reactive in displacing an iodine atom to give $C_9H_{13}^+$. At ionizing energies greater than 15 eV, $[C_6H_6]^+\cdot$ is produced by charge exchange of $[2\text{-}C_3H_7I]^+\cdot$ with neutral benzene. All acyclic isomers of benzene and the fragment $[C_6H_6]^+\cdot$ from tropone are reactive in charge exchange but inert to displacement. The fragment C_6H_6 ions from benzaldehyde, chroman, and phenylhydrazine exhibit both types of reaction chemistry. It is tempting to assign an acyclic structure to a fraction of the m/e 78 ions from chroman, tropone, and benzaldehyde. However, caution must be exercised because a positive result with charge exchange may not be structurally distinctive. It is interesting that decomposition of the tropone molecule ion (eq 4) produces a less reactive C_6H_6 ion which does participate in charge exchange but not in iodine atom displacement.

$$\text{(4)}$$
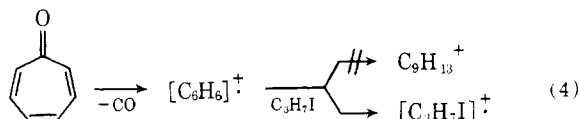
Internal Ion Chemistry of Acyclic Isomers of Benzene. As discussed previously, ionized benzene does not exhibit any bimolecular reactivity with its neutral precursor under the low-pressure ICR conditions. By way of contrast, low voltage ionization of all the acyclic C_6H_6 isomers leads to a rich and productive set of bimolecular reactions. We will begin with 1,3-hexadien-5-yne because its structure closely resembles that of a ring-opened benzene ion. In addition to observing a small abundance of "dimer" at m/e 156, eight other bimolecular reaction products were found (eq 5–12).

by two competitive channels: one to produce $C_9H_{13}^+$ and the other to give $[C_3H_7I]^+\cdot$ by charge exchange. The C_6H_6 ions from the acyclic isomers (1,3-hexadien-5-yne and the isomeric hexadiynes) react by charge exchange exclusively, and, therefore, constitute one extreme in the behavior of gas-phase $[C_6H_6]^+\cdot$. The other extreme, of course, is ionized benzene which reacts entirely by iodine atom displacement to give $C_9H_{13}^+$. The charge exchange reaction (eq 3) is approximately thermoneutral for benzene (ionization potential of 2-propyl iodide is 9.17[16]), endothermic for Dewar benzene, fulvene, and 3,4-dimethylenecyclobutene, but highly exothermic for nearly all the acyclic isomers (compare Table I).

We cite two experiments to support these conclusions. Pulsed double-resonance studies[27] showed that the intensity of $C_9H_{13}^+$ decreased with increasing kinetic energy of m/e 78 for the first six entries in Table II. The intensity of $C_9H_{13}^+$ is unaffected by increases in the kinetic energy of $C_3H_7^+$ or $[C_3H_7I]^+\cdot$, which is further evidence that $[C_6H_6]^+\cdot$ is the sole precursor for the $C_9H_{13}^+$ product ion. Charge exchange to give $[C_3H_7I]^+\cdot$ was verified by double resonance for $[C_6H_6]^+\cdot$ from benzaldehyde, chroman, phenylhydrazine, tropone, and the acyclic isomers of benzene. Second, the relative intensities of m/e 78 and 170 (C_3H_7I) in approximately equimolar gaseous mixtures of 2-propyl iodide and the $[C_6H_6]^+\cdot$ source were monitored as a function of ion residence time (see Figure 2 for typical data). Changes in residence time were made by tandem variations in the source and analyzer drift fields. The C_6H_6 ions which reacted by charge exchange exhibited a decrease in their intensity along with a corresponding increase for $[C_3H_7I]^+\cdot$.
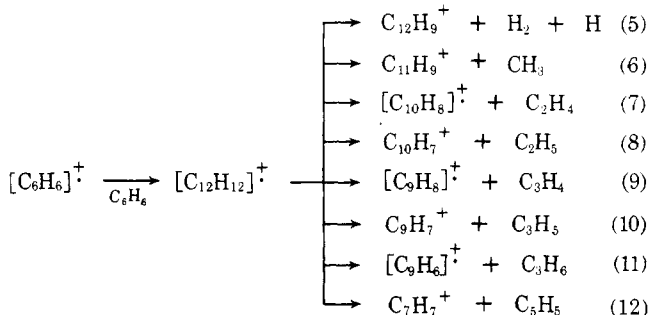
The results of the two experiments confirm that the C_6H_6

$$[C_6H_6]^+\cdot \xrightarrow{\ C_6H_6\ } [C_{12}H_{12}]^+\cdot$$

$$\longrightarrow\ C_{12}H_9^+\ +\ H_2\ +\ H \quad (5)$$
$$\longrightarrow\ C_{11}H_9^+\ +\ CH_3 \quad (6)$$
$$\longrightarrow\ [C_{10}H_8]^+\cdot\ +\ C_2H_4 \quad (7)$$
$$\longrightarrow\ C_{10}H_7^+\ +\ C_2H_5 \quad (8)$$
$$\longrightarrow\ [C_9H_8]^+\cdot\ +\ C_3H_4 \quad (9)$$
$$\longrightarrow\ C_9H_7^+\ +\ C_3H_5 \quad (10)$$
$$\longrightarrow\ [C_9H_6]^+\cdot\ +\ C_3H_6 \quad (11)$$
$$\longrightarrow\ C_7H_7^+\ +\ C_5H_5 \quad (12)$$

These results are structurally inconclusive because it is not possible to ascertain whether the C_6H_6 ion or neutral is responsible for the prolific bimolecular chemistry compared to
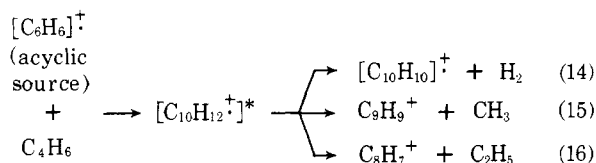
inertness of benzene. Therefore, relative product ion intensities were measured at a variety of partial pressures of the 1,3-hexadien-5-yne with and without added benzene-d_6 (SEE Figure 3). No new ion–molecule products were found, and the intensities of the product ions were not affected by addition of C_6D_6; i.e., the C_6D_6 acts merely as an inert diluent. We conclude that ionized benzene does not react with neutral 1,3-hexadien-5-yne and that the 1,3-hexadien-5-yne molecular ion is unreactive with neutral benzene to form any condensation products.

Assuming that ionized 1,3-hexadien-5-yne retains its acyclic structure, we are now able to comment on that fraction of ionized benzene which gives $[C_{12}H_{12}]^{+}\cdot$ via a bimolecular process.[21o] Certainly a ring-opened form resembling the 1,3-hexadien-5-yne structure cannot be involved. In fact, none of the acyclic sources of $[C_6H_6]^{+}\cdot$ react with neutral benzene-d_6 to produce $[C_{12}H_6D_6]^{+}\cdot$ or any other product ion except $[C_6D_6]^{+}\cdot$, which is formed by charge exchange (eq 13). This reaction was confirmed by pulsed double resonance as discussed previously.

$$[C_6H_6]^{+}\cdot \ + \ C_6D_6 \ \rightarrow \ [C_6D_6]^{+}\cdot + C_6H_6 \quad (13)$$
(acyclic source)   (benzene)
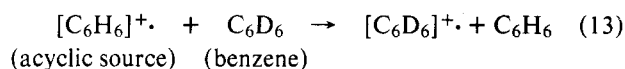
Similar reaction sequences are observed for the other acyclic C_6H_6 systems. For example, in both 1,5-hexadiyne and 1,4-hexadiyne, $[C_{10}H_8]^{+}\cdot$, $C_{10}H_7^{+}$, $C_9H_7^{+}$, and $C_7H_7^{+}$ are found as the dominant products. In these cases, the C_6H_6 ion intensity is attenuated by excessive fragmentation,[13] and this limits the dynamic range for bimolecular product observation. For 2,4-hexadiyne, $[C_{12}H_{12}]^{+}\cdot$, $C_{12}H_9^{+}$, $C_{11}H_9^{+}$, $[C_{10}H_8]^{+}\cdot$, $C_{10}H_7^{+}$, $[C_9H_6]^{+}\cdot$, and $[C_8H_6]^{+}\cdot$ comprise the list of bimolecular products arising from the reaction of the molecular ion with its neutral precursor. As in the 1,3-hexadien-5-yne case, no additional reactions were observed with added benzene-d_6.

Reaction of $[C_6H_6]^{+}\cdot$ with 1,3-Butadiene. The above results clearly show that direct ionization of various acyclic C_6H_6 isomers produces radical cations exhibiting totally different chemistry than ionized benzene and the fragment C_6H_6 ions studied here. Nevertheless, it is desirable to develop a bimolecular reaction using a common reagent neutral. In this way, one variable in the internal reaction chemistry can be removed, i.e., the variation in neutral C_6H_6 structure. We began our search with simple olefins (ethene, propene), allene, and propyne. Although considerable reaction chemistry was found, double resonance showed the reactant ion was not $[C_6H_6]^{+}\cdot$ but rather the molecular ion of the olefin. However, with 1,3-butadiene, the following reaction sequence was observed (eq 14–16).

$$[C_6H_6]^{+}_{\cdot}$$
(acyclic source)
$$+ \longrightarrow [C_{10}H_{12}^{+}\cdot]^* \left\langle \begin{array}{l} [C_{10}H_{10}]^{+}_{\cdot} \ + \ H_2 \quad (14) \\ C_9H_9^{+} \ + \ CH_3 \quad (15) \\ C_8H_7^{+} \ + \ C_2H_5 \quad (16) \end{array} \right.$$
$$C_4H_6$$

Pulsed double resonance[27] showed that the molecular ion of 1,3-butadiene also reacts with the neutral acyclic C_6H_6 to contribute to formation of the three products. To correct for the contribution of the $[C_4H_6]^{+}\cdot$, ion ejection studies[27] were initiated to obtain corrected relative rate constants for product ions formed via eq 14–16. The relative rate constants for disappearance of $[C_6H_6]^{+}\cdot$ were also measured. These data are presented in Table IV.

Although small differences exist for the relative rates of reaction of $[C_6H_6]^{+}\cdot$ from acyclic sources, these compounds are considered to constitute a single class of reactivity. In all cases, the molecular ion reacts with butadiene to give three ionic products. We cannot separate structural and energetic
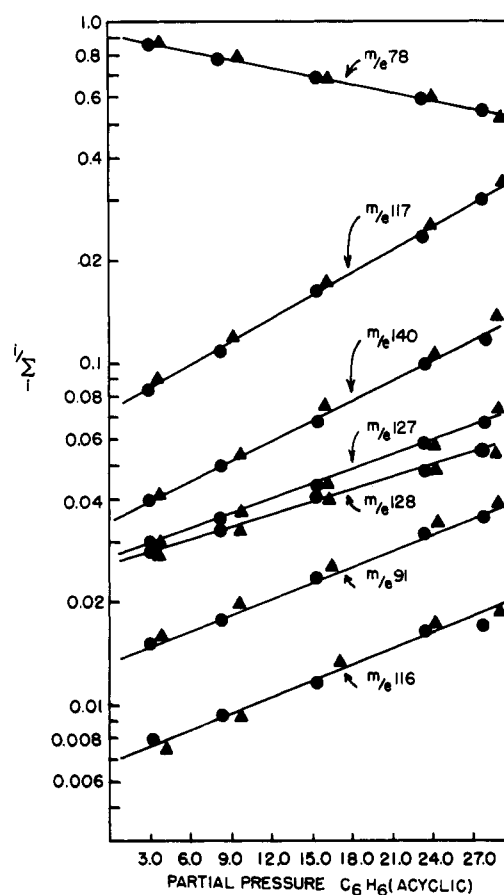

Figure 3. Variation of ion abundances in 1,3-hexadien-5-yne at 12 eV as a function of the pressure: (●) without added C_6D_6; (▲) with added C_6D_6.

Table IV. Relative Rate Constants for the Reaction of $[C_6H_6]^{+}\cdot$ from Various Sources with Neutral 1,3-Butadiene[a]

Source of $[C_6H_6]^{+}\cdot$	k^D	k^A $[C_{10}H_{10}]^{+}\cdot$	k^A $[C_9H_9]^{+}$	k^A $[C_8H_7]^{+}$
1,3-Hexadien-5-yne	1.6	0.30	1.0[b]	0.27
1,4-Hexadiyne	1.0[b]	0.13	0.74	0.11
1,5-Hexadiyne	1.1	0.20	0.75	0.12
2,4-Hexadiyne	1.4	0.14	0.84	0.40
Benzene	c			
Tropone	c			

[a] Ionizing energy = 13 eV. [b] Arbitrarily assigned a rate constant of unity. [c] No reaction detectable.

effects to explain the small variations observed within the series. Nevertheless, ionized benzene exhibits none of this chemistry and is clearly in a separate class. The third class of reactivity is shown by the C_6H_6 radical cation from tropone. Unlike the C_6H_6 ions generated by direct ionization of the acyclics, this ion does not react with 1,3-butadiene or with neutral benzene. And unlike ionized benzene and the various C_6H_6 fragment ions, the tropone $[C_6H_6]^{+}\cdot$ does not react with 2-propyl iodide to give $C_9H_{13}^{+}$. However, it does react by charge exchange with neutral 2-propyl iodide. The other C_6H_6 fragment ions (from benzaldehyde, chroman, etc.) which show some charge exchange with the 2-propyl iodide also do not give any detectable reaction with 1,3-butadiene.

Conclusion

Gas-phase C_6H_6 radical cations show significant variations in ion–molecule reaction chemistry which is a function of their

Table V. Summary of Bimolecular Ion Chemistry of Various C_6H_6 Cations

Source of $[C_6H_6]^+\cdot$	I displacement with 2-C_3H_7I	Charge exchange with 2-C_2H_7I	Reaction with neutral acyclic C_6H_6	Reaction with 1,3-butadiene	Reaction with benzene-d_6
Benzene	Yes	No	No	No	No
Anisole	Yes	No	No	No	No
Styrene	Yes	No	No	No	No
COT	Yes	No	No	No	No
Benzaldehyde	Yes	Yes	No	No	No
Phenylhydrazine	Yes	Yes	No	No	No
Chroman	Yes	Yes	No	No	No
Tropone	No	Yes	No	No	No
1,3-Hexadien-5-yne	No	Yes	Yes	Yes	No
1,5-Hexadiyne	No	Yes	Yes	Yes	No
2,4-Hexadiyne	No	Yes	Yes	Yes	No
1,4-Hexadiyne	No	Yes	Yes	Yes	No

origin and mode of formation (for summary of results, see Table V). We have been able to find only one bimolecular reaction of ionized benzene and that is with 2-propyl iodide to give $C_9H_{13}^+$ (m/e 121). The rate constant for the reaction shows a small dependence on ionizing energy which can be accounted for by an internal energy effect. The reaction is observed to go nearly to completion which rules out any significant concentration (<10%) of unreactive structural isomers or long-lived excited states. The existence of other states would serve to reduce the fraction of nondecomposing C_6H_6 ions which react in the iodine atom displacement and lead to a smaller rate constant for appearance of $C_9H_{13}^+$ relative to the rate constant for disappearance of $[C_6H_6]^+\cdot$. This is not observed even at 25 eV of ionizing energy. The absence of any other bimolecular reaction chemistry leads us to conclude that after 1 ms stable $[C_6H_6]^+\cdot$ from benzene is a nearly homogeneous population of cyclic ions in the electronic ground state. At this time, we can only speculate on the mechanism of the reaction with 2-propyl iodide. Structure I for C_9H_{13} may re-

I
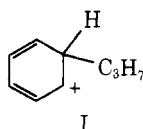
semble the intermediate formed in the solution Friedel–Crafts reaction alkylation of benzene. Of course, in the gas phase, $C_9H_{13}^+$ is formed by a radical cation mechanism, and the analogous solution reaction of $C_3H_7^+$ with neutral benzene cannot be detected under the single collision conditions which exist in the ICR cell.

Direct ionization of acyclic isomers of benzene (1,5-, 1,4-, 2,4-hexadiynes and 1,3-hexadien-5-yne) produces different C_6H_6 radical cations. No iodine atom displacement reaction can be observed, but only charge exchange with 2-propyl iodide is found. Moreover, these ions rapidly react with the various neutral acyclic C_6H_6 precursors and with neutral 1,3-butadiene. Ionized benzene shows none of this chemistry which supports the assertion that ring opening is not important for stable ions. We observe small variations in the relative rates of the three reactions with 1,3-butadiene, and these differences are probably due to a combination of internal energy effects and structural differences. Nevertheless, we conclude that these C_6H_6 ionic species exist as a separate class of chemical entities totally distinct from ionized benzene. The evidence does not allow us to postulate a single structural form. Based on the general propensity of olefins to undergo double bond migrations by hydrogen shifts and the specific evidence for hydrogen atom scrambling in 1,5-hexadiyne molecular ion,[13] a mixture of equilibrating acyclic structures would be the best representation for these ions.

A third class of stable C_6H_6 radical cations is produced in

small proportions in the fragmentation of benzaldehyde, chroman, and phenylhydrazine and as the major ion in the decarbonylation of tropone. The lack of reactivity with 1,3-butadiene and with 2-propyl iodide to yield $C_9H_{13}^+$ establishes its separate character. The only bimolecular reaction we were able to observe with this ion is the charge exchange with 2-propyl iodide.

Two interpretations are possible for the unique chemistry of this third class. First, the ion may possess the benzene structure but exist in a vibrationally or electronically excited state. Because no iodine displacement is observed, the excess energy must be sufficient to "turn off" this reaction. To check this idea, the heat-of-formation of the C_6H_6 ion from tropone was estimated by measuring the appearance potential of $[C_6H_6]^+$. The calculated ΔH_f is 261 kcal/mol which clearly rules out threshold formation of an acyclic ion or an electronically excited benzene ion ($^2E_{2g}$ state, see Table I). Moreover, there is a significant reverse activation energy in the ionic decarbonylation of tropone because 0.45 eV of translational energy is released for the metastable transition. The "heat-of-formation" is corrected for the kinetic energy release. Consequently, the excess excitation is likely to reside as vibrational energy in the tropone C_6H_6 ion. This explanation appears attractive until one notes that other cyclic C_6H_6 fragments are formed with comparable amounts of internal excitation (e.g., from styrene and anisole, see Table I). These ions do participate in the iodine displacement reaction in a manner similar to ionized benzene (see Table III).

A second interpretation ascribes these chemical differences to structural variations. If the reaction chemistry is understood to rule out both the benzene and acyclic structures, then no characterized structures remain as possibilities. Dewar benzene is not accessible in view of the energetics whereas fulvene and dimethylenecyclobutene cannot undergo an exothermic charge exchange with 2-propyl iodide. Therefore, the explanation based on internal energy is preferred, but it is not possible to specify the nature of the excitation at this time. Attempts to satisfactorily resolve these possibilities are the goals of studies in progress in our laboratory.

Experimental Section

The apparatus used was a Varian ICR-9 spectrometer equipped with a dual inlet and a three-section standard flat cell. Single resonance spectra were obtained in the field modulation mode normally at 153 kHz. For measurements at m/e values greater than 140, a frequency of 123 kHz was used. Typical values for source and analyzer drift fields were 0.16 V/cm with a trapping voltage of ~0.4 V. All ionizing energies were nominal values with emission currents of ~0.1 μA. Double resonance measurements were made in the pulsed mode. All studies were conducted at ambient temperature (~25 °C) except for tropone, which was admitted from a heated inlet at 80 °C.

Relative rate measurements were made by introducing a degassed sample of the source of m/e 78 to a pressure of ~4 × 10⁻⁶ Torr and

allowing the cell to equilibrate. Samples of the reagent neutrals were then admitted via the second inlet and the partial pressure changed with the variable leak valve using the total ion current monitor as a reference for relative pressure changes. The relative rate constants for product appearance were calculated from the least-squares slopes of the plots of $[(i_s/M_s^2)/(i_p/M_p + \Sigma_i i_{si}/M_{si}^2)]$ vs. partial pressure of the reagent neutral.[21] Comparisons of the relative rate constants for disappearance of m/e 78 were made from plots of log (i/i_0) vs. partial pressure of the reactant neutral where i_0 is the intensity of the m/e 78 signal without added neutral and i is the corresponding intensity with the reactant neutral present. Comparisons were derived from back-to-back runs of the unknown and reference compound (typically benzene). The values reported in the text were averages of at least three measurements done on different days. The relative precision was ca. ±5%.

The absolute rate constant for the reaction of ionized benzene and 2-propyl iodide was obtained using the rate constant for production of $C_3H_5^+$ in ethene as a reference. This strategy was employed because of the uncertainty in the calculation of residence times of ions in the cell. To circumvent this uncertainty, plots of the rates of appearance of m/e 121 in the benzene/2-propyl iodide mixture and of m/e 41 in ethene were made from 12 back-to-back experiments. For each case, the absolute pressures were measured using a Datametrics Barocel Electronic Manometer Model 1173. The ion pump was calibrated at pressures in the range of 5×10^{-5} to 20×10^{-5} Torr. Pressures in the low 10^{-5} Torr region were obtained by extrapolation of the linear calibration plots. The absolute rate constant was calculated from the ratio of slopes of the product appearance curves using a rate constant of 1.2×10^{-9} cm^3 molecule^{-1} s^{-1} for the production of CH_5^+ in methane.[29] The relative precision for this determination was ±10% for five determinations on different days.

Most samples were obtained from standard commercial sources and their purity was checked by mass spectrometry. Anisole, styrene, benzaldehyde, cyclooctatetraene, and tropone were vacuum distilled prior to use. Chroman was prepared by a lithium aluminum hydride reduction of 4-chromanone in dry ether.[30] The sample of 1,3-hexadien-5-yne was prepared by isomerization of 1,5-hexadiyne using potassium *tert*-butoxide in butanol according to the method of Sondheimer et al.[31] The material was purified by preparative GLC using a 5 ft × 14 in. column with 20% SE-30 on Chromosorb W at 60 °C, and its purity was checked by analysis with a Cary Model 14 UV–vis spectrophotometer. We obtained a molar absorptivity of 2550 at 252 nm with cyclohexane as solvent.

The 1,4-hexadiyne was prepared by coupling the Grignard reagent of propyne with propargyl bromide based on the literature general procedure.[32] A small sample was purified by preparative GLC at 50 °C as discussed above.

Conventional mass spectra were obtained on an AEI MS-5076 high-resolution mass spectrometer which is interfaced to an INCOS Data System. The appearance potential of $[C_6H_6]^+\cdot$ from tropone was determined by the semilog method using furan as a standard.

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