Ion–Molecule Reactions in Gaseous Benzene and Toluene[1]

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Abstract: The ion–molecule reactions of positively charged species in pure benzene and toluene were studied mass spectrometrically in the range of source pressures from 0.005 to 0.32 torr. Although more than 200 ionic species were observed for each gas, most were of low relative abundance, and the mass spectra consisted of only a few important species. By far the most prominent reactions in benzene were the condensation of $C_6H_6^+$ with a benzene molecule to form $C_{12}H_{12}^+$ and the formation of $C_6H_6^+$ by charge transfer from fragment ions. In gaseous toluene the dominant product ions were the $C_{14}H_{15}^+$ and $C_{14}H_{16}^+$ dimers formed by condensation of $C_7H_7^+$ and $C_7H_8^+$ with a toluene molecule, respectively. Again, charge exchange from fragment ions to give $C_7H_8^+$ was an important reaction. The dimeric species appeared to be unreactive or only slightly reactive with the respective gas. Correlations with observations on the radiolysis of these compounds are drawn, and ionic mechanisms for the formation of polymeric species by radiation are proposed.

During the past several years, a voluminous literature has grown concerned with observations on ion–molecule reactions in gases by means of "high-pressure" mass spectrometry. There have been studies of such diverse molecules as the lower hydrocarbons,[3–7] small oxygen-containing hydrocarbons,[8] ammonia,[9,10] water,[8,11] rare gases,[12] diatomic species,[13,14] and mixtures of a great variety of organic compounds with CH_4[15] and with H_2.[16] But aromatic compounds have been neglected, and, as a consequence, surprisingly little is known about them. Until quite recently, only a few studies on pure compounds at low source pressures have been reported, and these gave only fragmentary information on the many secondary product ions in the mass range from 89 to 155 resulting from reactions of primaries with benzene and toluene,[17] and on "sticky" collisions in benzene and halobenzenes.[18] While this work was being written up for publication, however, a paper by Field, Hamlet, and Libby[19] appeared, describing their high-pressure mass spectrometric results on benzene and benzene–rare gas mixtures. Ionic reactions involving charge or mass transfer to these molecules have also been observed. Rudolph and Melton[20] found evidence for charge transfer from $C_2H_2^+$ to C_6H_6 in mixtures of acetylene and benzene, while Field[21] obtained the mass spectrum of benzene, formed by chemiionization initiated by the CH_5^+ and $C_2H_5^+$ ions from methane, in mixtures of CH_4 with benzene or toluene in small fraction.

Since knowledge about ionic processes may give an insight into the possible mechanisms of the chemical reactions, particularly the predominant effect of polymerization, occurring in radiolysis of benzene and toluene, we have investigated the ion–molecule reactions that take place in these aromatic gases when they are introduced into our "high-pressure" mass spectrometer at pressures in the range from 5×10^{-3} to 0.32 torr. Positively charged species with masses up to 360 atomic units were searched for. The results are compared with the findings of Barker,[17] Henglein,[18] and Field, *et al.*,[19] and are correlated with reported observations in conventional radiation chemical studies of these compounds.

Experimental Section

Details of the design of the mass spectrometer and of the experimental procedure have been described in a previous publication.[5c] As before, the field strength in the source chamber was set at 12.6 V/cm, and the ion path length was estimated to be 3.2 mm. The temperature of the source was 122 ± 2°. The only change prior to these experiments was the installation of a grease-free, stainless-steel, gas-handling system and a calibrated capacitance manometer (Granville-Phillips Co., Boulder, Colo.) for accurate measurement of the pressure in the source chamber. The energy of the ionizing electrons was 80, 400, or 1000 eV in the investigations on benzene and 400 eV for the toluene measurements. Zone-refined benzene of 99.999% purity (James Hinton Co., Valparaiso, Fla.) and "research grade" toluene of 99.96 mole % purity (Phillips Petroleum Co., Bartlesville, Okla.) were used after thorough outgassing but without further purification.

Results

1. Benzene. Attenuation of the energy and scattering of the electrons in the ionizing beam by numerous

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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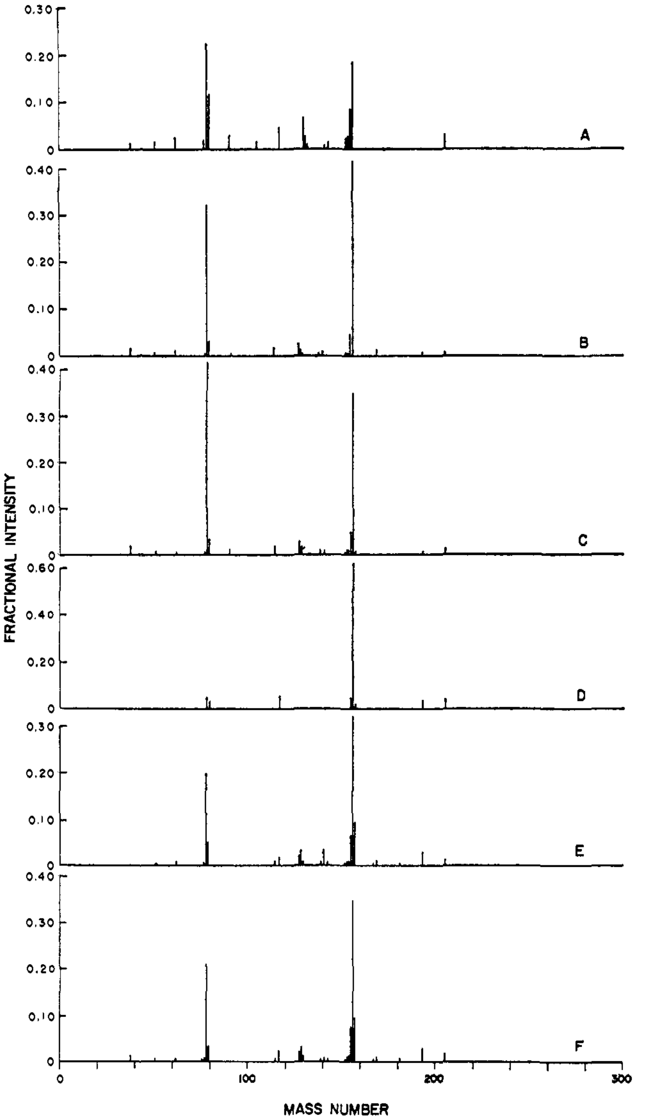

Figure 1. Comparison of distributions of ionic species in benzene for various energies of ionizing electrons: (A) source pressure P_s = 0.040 torr, electron energy E_e = 80 eV; (B) P_s = 0.051 torr, E_e = 400 eV; (C) P_s = 0.043 torr, E_e = 1000 eV; (D) P_s = 0.304 torr, E_e = 80 eV; (E) P_s = 0.310 torr, E_e = 400 eV; (F) P_s = 0.300 torr, E_e = 1000 eV. The intensities of each species in this figure, as well as those shown in other figures of this paper, have been corrected for naturally occurring C^{13}.

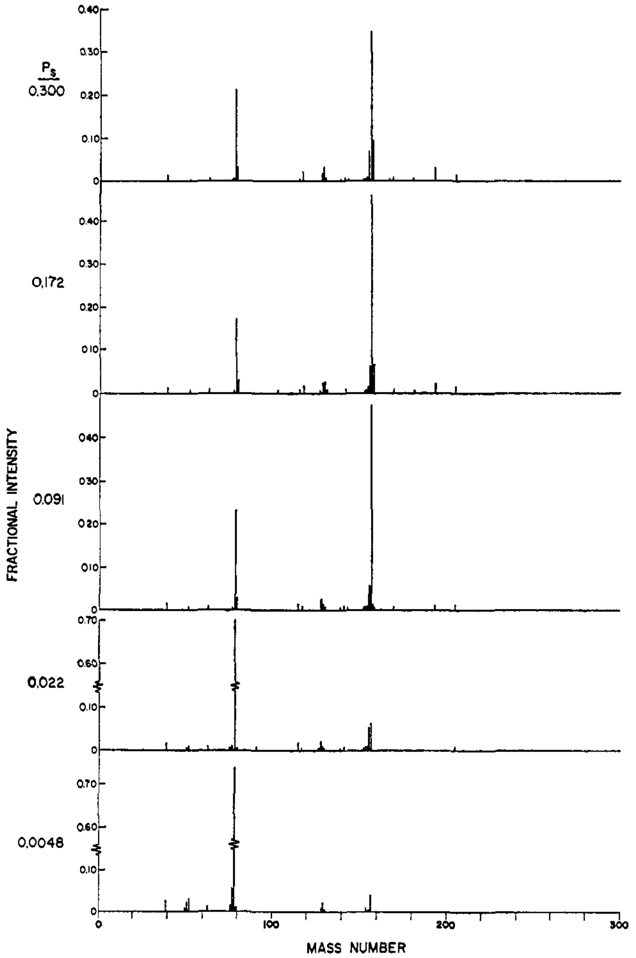

Figure 2. Histograms of mass spectra of positively charged species in gaseous benzene at several source pressures (P_s) (torr). The energy of the ionizing electrons was 1 keV.

collisions with gas molecules between the entrance slit of the source chamber and the critical region adjacent to the ion exit slit may affect the relative yields of primary ions in this region, and consequently the over-all "high-pressure" mass spectra could be dependent on the initial energy of the electron beam. To study this possible difficulty we recorded the spectra of positively charged ionic species in benzene for the mass range from 12 to 360 amu over the pressure range from $\sim 5 \times 10^{-3}$ to 0.32 torr when the bombarding energies were 80, 400, and 1000 eV. Representative spectra at source pressures in the vicinity of 0.045 torr and of 0.30 torr are presented in histogram form in Figure 1. The pattern observed with 80-eV electrons is seen to differ from those at the higher electron energies, but 400- and 1000-eV electrons appear to give very similar spectra of ionic fragments.

Although more than 200 different positively charged fragments from benzene are identified as the source pressure is varied, the spectrum is dominated by relatively few species. This may be seen in the set of histograms (Figure 2) of mass spectra observed (with 1-keV electrons) at a number of pressures. The principal ions at very low pressures are the parent $C_6H_6^+$ (mass 78), several of its primary dissociation products, *e.g.*, $C_6H_5^+$, $C_3H_3^+$, $C_5H_3^+$, and $C_5H_4^+$, and the products, notably $C_6H_7^+$, $C_9H_8^+$, $C_{10}H_9^+$, $C_{12}H_{12}^+$, and $C_{12}H_{13}^+$, of ion–molecule reactions with benzene. But as the pressure increases, the polymeric species become much more intense, with the dimer $C_{12}H_{12}^+$ standing out as by far the dominant secondary ion. Note, however, that $C_6H_6^+$ remains an important species even at source pressures of 0.20 torr and above, although the abundances of the other primary ionic fragments, particularly $C_6H_5^+$, of benzene have decreased. Ions containing a larger number of carbon atoms appear as the pressure is increased, for example, $C_{15}H_{13}^+$ and $C_{16}H_{13}^+$, but trimers of benzene (C_{18} species) were detected in only very small yield. The characteristic behaviors with pressure of the normalized intensities of several of the more intense ions (Figure 3) show that the yields of dimers tend to remain invariant or to decrease slightly at higher pressures. In addition, $C_6H_5^+$ behaves like a typical reactive primary species, indicating that this ion is not also formed by hydride-ion transfer from a benzene molecule to the $C_6H_6^+$ parent. Evidence for proton transfer to benzene is shown by

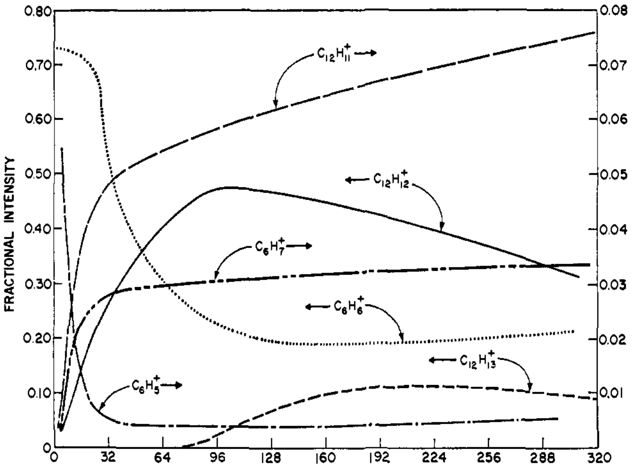

Figure 3. Behaviors of normalized intensities of dominant ions as functions of the benzene pressure in the source.

the presence and behavior of the $C_6H_7^+$ ion, but the reaction appears to be of minor importance in gaseous benzene.

Total reaction cross sections of many of the primary and secondary species with benzene vapor were estimated (in the manner described in detail in a previously published work[5c]) from the slopes of the linear portions of the curves of log (fractional intensity) plotted against pressure. The reactivities so determined for the more prominent ions (those whose relative abundances exceeded 1% at some source concentration) are listed in Table I. One sees that the cross sections measured with the 400-eV bombarding electrons are in quite good agreement with those for the 1000-eV electrons, but in a few cases large differences exist between these values and the corresponding ones measured with electrons of 80-eV energy. The data taken at the 80-eV bombardment energy tended to be more scattered than those observed with the more energetic electrons, and so the values of the cross sections listed in Table I for the 400- and 1-KeV electrons are considered to be the more reliable. The reactivities of the primary species are larger but within the same order of magnitude as collisional cross sections calculated from gas kinetic theory, but those of the secondaries range from being about a factor of 2 smaller than the ones for the primaries to being below the limit of sensitivity of the method.

Table I. Total Reaction Cross Sections of Ions in Benzene

Species	Electron energy, eV		
	80	400	1000
	$\sigma^t \times 10^{-16}$ cm^2 molecule^{-1}		
$C_3H_3^+$	17	3.2	5.3
$C_4H_2^+$	150	170	174
$C_4H_3^+$	96	128	97
C_4H_4	170	157	102
$C_5H_5^+$	31	30	58
$C_6H_4^+$	53	123	123
$C_6H_5^+$	56	90	117
$C_6H_6^+$	78	31	21
$C_6H_7^+$	5	<0.1	<0.1
$C_9H_7^+$	17	11	15
$C_{10}H_9^+$	9	<0.1	<0.1
$C_{10}H_{10}^+$	<1	<0.1	<0.1
$C_{12}H_{11}^+$	<1	<0.1	<0.1
$C_{12}H_{12}^+$	<1	2.4	3.2

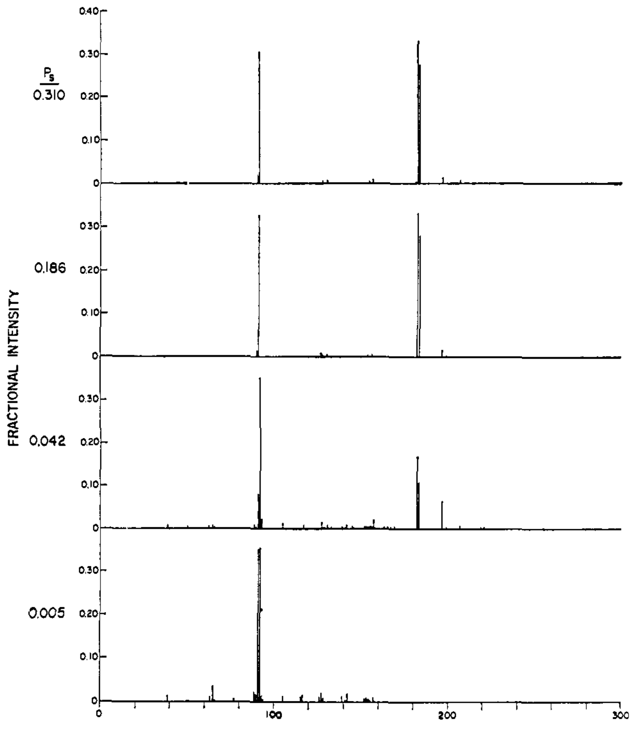

Figure 4. Histograms of mass spectra of positive species in gaseous toluene at several pressures (P_s) (torr) in the source chamber of the mass spectrometer.

2. Toluene. The general features of the mass spectra of C_6H_6 appear to be repeated in toluene as the source pressure is progressively increased from 0.005 to 0.31 torr (Figure 4). At the lowest pressure the pattern consists principally of the two primary ions $C_7H_7^+$ (mass 91) and $C_7H_8^+$, but several other primaries are in evidence: $C_6H_5^+$, $C_5H_5^+$, $C_5H_3^+$, and $C_3H_3^+$, as examples. But several secondary species are also produced in small yield at this pressure, *e.g.*, $C_8H_9^+$, $C_9H_8^+$, $C_{10}H_7^+$, $C_{11}H_{10}^+$, and $C_{12}H_{13}^+$. When the pressure is increased, several characteristic changes in the spectra of ions take place.

(a) The relative abundance of the parent, $C_7H_8^+$, remains constant, although the other primary species virtually disappear. When the pressure of toluene is 0.31 torr, the $C_7H_7^+$ is the only primary fragment present, and its yield is only a small fraction of that at 0.005 torr.

(b) Accompanying the disappearance of the primary ions are dramatic enhancements of the yields of the dimeric species $C_{14}H_{15}^+$ and $C_{14}H_{16}^+$.

(c) Most of the other secondary products, fairly prominent at the lower source pressures, decrease markedly in intensity as the concentration of gas becomes greater.

As a consequence of these changes the mass pattern at the higher pressures appears to be very simple, consisting mainly of the species $C_7H_8^+$, $C_{14}H_{15}^+$, and $C_{14}H_{16}^+$. Nevertheless, approximately 200 ionic species were recorded, but the great majority of them possessed such low yields that they do not stand out in the histograms of Figure 4.[21a]

A number of phenomena occurring in the source chamber are illustrated by the characteristic pressure-dependent functions of the fractional intensities of the several species plotted in Figure 5. The ions $C_5H_5^+$ and $C_7H_7^+$ decay exponentially, in keeping with the behavior of reactive primary species, but the parent ion $C_7H_8^+$ appears to behave like a secondary species that becomes unreactive at higher pressures. Clearly, it is being formed by processes other than by initial electron impact, and/or it is stabilized against unimolecular dissociation by collisions with toluene molecules. The products $C_{14}H_{15}^+$ and $C_{14}H_{16}^+$ of the addition of $C_7H_7^+$ and $C_7H_8^+$, respectively, to toluene molecules are seen to be unreactive with this molecule. Further evidence for the nonreactivity of these dimers comes from the absence of the corresponding trimers $C_{21}H_{23}^+$ (mass 275) and $C_{21}H_{24}^+$ (mass 276) among the ions in the spectra observed at the highest concentrations of toluene in the source.

Total reaction cross sections of the important primary and secondary ions in gaseous toluene were obtained from the linear slopes of the curves of log (fractional yield) *vs.* source pressure. Those for species with yields greater than 1% at maximum are collected in Table II.

Table II. Total Cross Sections for Reactions of Positive Ions with Toluene

Species	$\sigma^t \times 10^{-16}$ cm^2 molecule^{-1} [a]	Species	$\sigma^t \times 10^{-16}$ cm^2 molecule^{-1} [a]
$C_3H_3^+$	36	$C_{10}H_8^+$	23
$C_5H_3^+$	21	$C_{11}H_7^+$	33
$C_5H_5^+$	43	$C_{11}H_{10}^+$	26
$C_7H_5^+$	37	$C_{12}H_{13}^+$	17
$C_7H_6^+$	67	$C_{14}H_{14}^+$	<0.1
$C_7H_7^+$	44	$C_{14}H_{15}^+$	<0.1
$C_7H_9^+$	42	$C_{14}H_{16}^+$	<0.1

[a] Electron energy = 400 eV.

Discussion

The behaviors of ionized benzene and toluene at progressively higher concentrations of gas show distinctive similarities. When the pressure is low, the parent species are prominent along with some of the same ions formed from unimolecular dissociations of the two parents: $C_6H_5^+$, $C_5H_3^+$, and $C_3H_3^+$. In addition, some of the products of reactions of the primary ions with the respective gas are identical, *e.g.*, $C_9H_9^+$ and $C_{12}H_{13}^+$, but the dramatic similarity occurs at the higher source pressures, where both spectra are relatively simple and are dominated by dimers $C_{12}H_{11}^+$, $C_{12}H_{12}^+$, and $C_{12}H_{13}^+$ in gaseous benzene and $C_{14}H_{15}^+$ and $C_{14}H_{16}^+$ in toluene. From the linear increases in abundances of the $C_{12}H_{11}^+$ and $C_{12}H_{12}^+$ species at the lower source pressures (Figure 3), it appears probable that these ions are produced by simple persistent or "sticky" collisions of primary ions with benzene molecules, and the collision complexes do not require further deexciting collisions for stabilization.

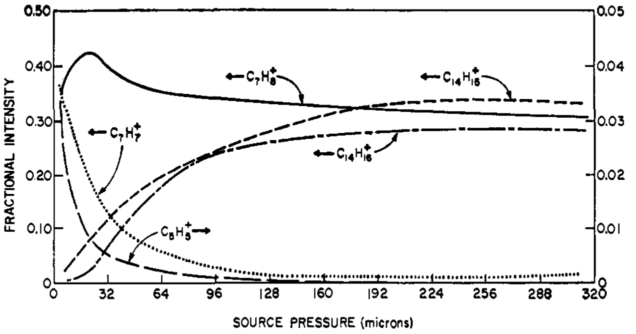

Figure 5. Variations of normalized intensities of prominent ionic species with increasing concentration of toluene.

$$C_6H_6^+ + C_6H_6 \longrightarrow C_{12}H_{12}^+ \qquad (1)$$

$$C_6H_5^+ + C_6H_6 \longrightarrow C_{12}H_{11}^+ \qquad (2)$$

Reaction 2 has been established previously by Henglein,[18] but it may be somewhat surprising that he did not observe reaction 1. Perhaps the much higher concentrations of gas in our experiments favored reactive collisions of excited $C_6H_6^+$ ions before they could radiate. Again from Figure 3, the species $C_{12}H_{13}^+$ is formed by a process higher than bimolecular, and since $C_6H_7^+$ is not the precursor ion (its abundance is too low and it appears unreactive with benzene; *cf.* Figure 3), it seems likely that a hydrogen atom transfer to $C_{12}H_{12}^+$ is involved.

$$C_{12}H_{12}^+ + C_6H_6 \longrightarrow C_{12}H_{13}^+ + C_6H_5 \qquad (3)$$

Reaction 3 can account for a large fraction of the decrease in abundance of $C_{12}H_{12}^+$ ion above the source pressure of 100 μ.

The $C_{14}H_{15}^+$ product observed in gaseous toluene appears to be also produced by a bimolecular association process, as shown by the linear increase of its abundance with source pressure in the lower range (Figure 5), but $C_{14}H_{16}^+$ behaves somewhat like a tertiary ion and thus requires a further collision for its formation. It is suggested that a persistent collision occurs when $C_7H_7^+$ hits a toluene molecule, but the $C_{14}H_{16}^+$ is the result of two consecutive reactions.

$$C_7H_8^+ + C_7H_8 \longrightarrow [C_{14}H_{16}^+]^* \xrightarrow{C_7H_8} C_{14}H_{18}^+ \qquad (4)$$

From their very small reaction cross sections (Tables I and II), the dimeric species react further only slightly if at all. However, many of the C_8^+ to C_{13}^+ ions (most of low abundance) were found to have higher total reaction cross sections in toluene than in benzene. It may be suggested that these species disappear more readily through charge exchange with toluene than with benzene, the process being favored in the former gas by the 18-kcal/mole lower heat of formation of the $C_7H_8^+$ ion relative to that of $C_6H_6^+$. It is of interest to note that the $C_7H_7^+$ fragment from toluene, called the "tropylium" ion and known to possess a seven-carbon-atom ring structure,[22] is observed here to be quite

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[21a] NOTE ADDED IN PROOF. Recent studies by Mr. Louis G. Pobo on gaseous toluene ionized by 2-MeV protons in another high-pressure mass spectrometer in our laboratory have confirmed the efficient formation of the dimeric species $C_{14}H_{15}^+$ and $C_{14}H_{16}^+$. Small yields of trimeric and quadrimeric ions were also found.

[22] S. Meyerson and P. N. Rylander, *J. Chem. Phys.*, 27, 901, 1116 (1957); P. N. Rylander, S. Meyerson, and H. M. Grubb, *J. Am. Chem. Soc.*, 79, 842 (1957).

reactive toward toluene molecules, though it has been thought to be a rather stable cation.[23] Furthermore, the continuing high yields of the $C_6H_6^+$ and $C_7H_8^+$ parent ions at high pressures, in contrast to the markedly diminished intensities of other primary species, suggest that the former are either being stabilized by collision against unimolecular dissociation or are being generated by charge exchange between other primary ions and the bulk gas. Both processes should reduce the yields of secondary and tertiary products initiated by these primary ions and, indeed, the data show this. It is also possible, as mentioned above, that some of the higher order species can also charge exchange with benzene and toluene molecules, and this may be the reason for the reduction in intensity of the tertiary species of mass 197 in the toluene mass pattern. Rudolph and Melton[20] have already presented evidence for the occurrence of charge exchange between $C_2H_2^+$ and C_6H_6 in mixtures of acetylene and benzene ionized by α particles in their mass spectrometer.

The introductory section of this paper stated that Barker[17] had previously studied ion–molecule reactions in gaseous benzene and toluene, but the data reported by him were taken at a source pressure of 1.91×10^{-3} torr, and they were only on the relative yields of secondary products in the mass range from 89 to 155. Since his conditions, such as pressure and electric field, differed from ours, only rough comparisons of the observations are possible. While Barker finds the most abundant ions in benzene to be $C_{10}H_8^+$, $C_{12}H_{11}^+$, $C_9H_7^+$, $C_{10}H_7^+$, and $C_{12}H_9^+$ (in decreasing order of intensity), the measurements at 4.8×10^{-3} torr (Figure 2), the low end of our pressure range, show that the prominent ions in the same mass range (and again in decreasing order of yield) are $C_{10}H_9^+$ (mass 129), $C_9H_7^+$, $C_{10}H_8^+$, $C_{12}H_{10}^+$, $C_{12}H_{11}^+$, and $C_{10}H_{10}^+$. Thus, the main products are the same or differ by one hydrogen atom. But of greater importance is our finding of a fair abundance of $C_6H_7^+$ (mass 79) as the pressure of benzene in the source is increased. Barker specifically looked for this species at his low pressures by reducing the ionizing voltage where both masses 78 (the parent ion $C_6H_6^+$) and 79 could be readily measured and found that the ratio of intensities of $C_6H_7^+$ to $C_6H_6^+$ was independent of pressure. He consequently concluded that the proton-transfer reaction from $C_6H_6^+$ to a benzene molecule does not take place, as would be predicted from an endothermicity of 48 kcal/mole calculated for this reaction between ground-state species. The prominence of the protonated benzene in our studies indicates that proton-transfer reactions involving one or more primary ions and benzene molecules do occur. Excited $C_6H_6^+$ and $C_2H_3^+$ are two possible reactant species.

For toluene Barker lists $C_{10}H_8^+$, $C_9H_7^+$, $C_9H_8^+$, $C_{10}H_9^+$, $C_{11}H_7^+$, and $C_{11}H_{10}^+$ as the principal product ions. These are to be compared with $C_{10}H_7^+$, $C_{11}H_{10}^+$, $C_{10}H_8^+$, $C_9H_8^+$, $C_9H_7^+$, and $C_{11}H_7^+$ found by us at 5×10^{-3} torr (Figure 4). The agreement is quite good, although the orders of importance of the species differ.

With but one exception, and this a very important difference, our observations agree quite well with the recent results of Field, Hamlet, and Libby:[19] (*a*) the important primary and secondary ions up through $C_{12}H_{12}^+$ appear to be the same; (b) the fractional yields of the primary fragment ions, notably $C_6H_5^+$, $C_5H_4^+$, $C_3H_3^+$, etc., decrease greatly, due, in some cases, to electron-transfer reactions with benzene to give $C_6H_6^+$; and (c) proton transfer to give $C_6H_7^+$ occurs in the irradiated benzene. But, contrary to their results, we find a sizable drop of the intensity of the $C_6H_6^+$ parent as the pressure increases and a much larger yield of $C_{12}H_{12}^+$ at the higher source pressures—0.32 as against 0.024 at 0.300–0.335 torr. Our data, then, suggest that the $C_6H_6^+$ ion reacts fairly readily with a benzene molecule to form the dimer ion, and, in sharp contrast to the conclusion of Field, *et al.*, this ionic reaction should be important in the radiation chemistry of benzene. From comparison of the yields of $C_{12}H_{12}^+$ in pure benzene and C_6H_6–Xe mixtures, they conclude that the $C_6H_6^+$ reactant must be in an excited state to form the dimer ion. To account for the difference in the observations, then, it would appear necessary to suppose that a much higher concentration of excited $C_6H_6^+$ ions are produced in our experiments than in theirs. Although it is possible that the energies of the collisionally degraded electrons in the critical region of ionization adjacent to the ion exit slit may have been higher in our work, it is not clear that this should account for a higher yield of excited benzene ions. Certainly, the differences in repeller field, exit slit dimensions, and ion path length or ion residence time in the source chambers of the two mass spectrometers cannot explain the discrepancy. As a consequence, we are at a loss to rationalize the great difference in behavior of the $C_6H_6^+$ species in the two studies.

In the discussion of his paper on ionic reactions in acetylene, Munson[24] mentions briefly that he observed $C_6H_6^+$ ions to be relatively inert toward benzene molecules, but that $C_2H_2^+$ fragments from dissociation of the parent are quite reactive toward this molecule. The first observation is contrary to our results, for appearance of the $C_{12}H_{12}^+$ species at higher pressures in our experiments must have occurred because of reaction of a $C_6H_6^+$ primary ion. In addition, the abundance of the $C_6H_6^+$ decreases to about one-third of its yield at the lowest pressures as the concentration of benzene is raised (Figure 2). The leveling off of its relative intensity is best explained by collisional deexcitation of the primary species and production of $C_6H_6^+$ by charge exchange of benzene molecules with other primary species such as $C_2H_2^+$, these reactions taking place concurrently with reaction of $C_6H_6^+$ with benzene to produce $C_{12}H_{12}^+$. It is of interest, in this regard, that dimeric as well as monomeric benzene cations have recently been observed by electron spin resonance in γ-irradiated benzene on silica gel at 77°K.[25] The probability of stabilizing the $C_{12}H_{12}^+$ by collisional deexcitation should have been enhanced by the very high density of benzene in this solid system.

The radiolysis of gaseous or liquid benzene produces hydrogen, methane, acetylene, ethylene, and ethane as the principal volatile products, but the total yield of all these products accounts for only 7–16% of the ben-

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zene consumed.[26–29] The bulk of the radiolyzed benzene is converted to a yellow, viscous, liquid "polymer," which consists of 18.8% C_{12} compounds, namely biphenyl, phenylcyclohexadiene, phenylcyclohexene, and nonaromatic bicyclic molecules such as dicyclohexadienes, 57.6% C_{18} hydrogenated terphenyl compounds, and the remainder substances containing more than 18 carbon atoms.[30–33] (Biphenyl and phenylcyclohexadiene have also been found after a glow discharge in benzene vapor.[34]) Both the viscosity and molecular weight increase with the absorbed energy, while the number of double bonds per benzene molecule converted decreases. Yet the *G* value for polymer formation remains constant over the range of dosage used.[29] Furthermore, the LET effect on the yield of polymer is much smaller than that for production of H_2 and C_2H_2.[32]

All the foregoing characteristics of the polymer and of its formation are consistent with its being formed at least partially *via* an ion–molecule mechanism. Our finding of a prominent $C_{12}H_{12}^+$ product species relatively unreactive with benzene suggests the following sequence of reactions leading to the formation of the dimers observed in conventional radiolysis

$$C_6H_6 \rightsquigarrow [C_6H_6^+] \qquad (5)$$

$$[C_6H_6^+] + C_6H_6 \longrightarrow C_{12}C_{12}^+ \qquad (6)$$

$$C_{12}H_{12}^+ + e^- \left\{ \begin{array}{ll} \longrightarrow C_{12}H_{10}\ (\text{biphenyl}) + H_2 & (7) \\ \longrightarrow C_{12}H_{12}\ (\text{phenylcyclohexadiene}) & (8) \\ \longrightarrow [C_{12}H_{12}]^* \xrightarrow{C_6H_6} C_{12}H_{14} & (9) \\ \qquad (\text{phenylcyclohexene}) & \end{array} \right.$$

The fact that the average molecular weight increases and *G*(polymer) remains constant as the dosage is raised may be explained by the reactions of $C_6H_6^+$ and $C_{12}H_{12}^+$ ions with the products of prior irradiation, *i.e.*, biphenyl, phenylcyclohexene, and phenylcyclohexadiene. Clearly, the ionic mechanism proposed above, which should not exhibit a linear energy-transfer effect, is in contrast and alternative to the mechanism of competing first- and second-order reactions of excited benzene molecules put forth by Burns and Reed[32] to account for the LET effect. It also differs from proposals[30,31,33] that the polymer is built up by reactions of excited C_6H_6 and free radicals. The finding by MacLachlan and McCarthy[31] that iodine scavenger quenches the formation of C_{12} compounds, except for biphenyl, while yielding iodobenzene is not inconsistent with the ionic mechanism proposed here, because I_2 readily scavenges electrons, and negatively charged iodine would, therefore, be at the site of the neutralization of the $C_{12}H_{12}^+$ ion.

Similar to the behavior of benzene under radiation, liquid toluene is converted mainly to "polymer."[35] A very complex mixture of products is found, including the dimers bibenzyl, dimethylbiphenyls, benzyltoluene, and phenyltoluene, as well as higher molecular weight compounds.[31,36] An ionic mechanism analogous to eq 5–9 may be written to account for the transformation, by way of prominent $C_{14}H_{15}^+$ and $C_{14}H_{16}^+$ intermediates observed in our experiments, of toluene molecules to these dimers. The ionic mechanism suggested here should be operating in competition with the free-radical mechanism, involving benzyl and tolyl radicals, proposed by Hoigne and Gäumann.[36,37] The formation of phenyltolylmethanes, which amount to 20% of the dimer products in their experiments and whose formations are insensitive to iodine scavenging, may be accounted for by neutralization of $C_{14}H_{15}^+$ and $C_{14}H_{16}^+$ by a free electron or I_2^-.

$$\begin{array}{lll} C_{14}H_{15}^+ + e^- \longrightarrow & CH_3C_6H_4CH_2C_6H_5 + H & (10) \\ \qquad + I_2^- \longrightarrow & \qquad + HI + I & (11) \\ C_{14}H_{16}^+ + e^- \longrightarrow & \qquad + H_2 & (12) \\ \qquad + I_2^- \longrightarrow & \qquad + 2HI & (13) \end{array}$$

It should be noted that this mechanism avoids the necessity of assuming radical–radical combination in the spurs of the ionizing electrons to account for the behavior of the phenyltolylmethanes.[37] Finally, since the *G*(polymer) value remains constant with increasing dosage while those of several of the dimers decrease,[36] the latter may be converted to trimers and quadrimers by their reactions with $C_7H_8^+$, $C_{12}H_{15}^+$, and $C_{12}H_{16}^+$, resulting from later radiation action.

The data of Figure 4 reveal that no transmethylation, such as

$$C_7H_8^+ + C_7H_8 \left\langle \begin{array}{l} \nearrow C_8H_{10}^+ + C_6H_6 \\ \searrow C_8H_{11}^+ + C_6H_5 \end{array} \right. \qquad (14)$$

occurs. Consequently, polymethylbenzenes (*e.g.*, xylenes) would not be expected as products of ionic reactions taking place in the radiolysis of toluene. Recently, Wilzbach and Kaplan[38] have measured very low yields of xylenes relative to that of polymer from the γ radiolysis of gaseous toluene.

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