Ion Chemistry of Several C_6 Molecules in the Gas Phase[1]

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Abstract: Ion-molecule reactions in gaseous *n*-hexane, cyclohexane, methylcyclohexane, benzene, toluene, ethylbenzene, and aniline were studied at source pressures in the range from 0.025 to 1.00 Torr in a proton beam-high pressure mass spectrometer. Dimerization and in some cases trimerization involving parent and fragment positive ions were prominent reactions in the aromatic compounds, but they were not observed in the aliphatic molecules investigated. H^-, H_2^-, and charge transfer, as well as condensation reactions, occurred in both types of molecules. The observations are correlated with the results of previous radiation-chemical studies of these compounds to arrive at ionic mechanisms for their transformation to other substances under the action of a radiation field.

A voluminous literature exists on the radiation chemistry of C_6 molecules and their derivatives, and several reviews of these studies have been written.[2-6] In addition to the formation of volatile products in relatively high yields, polymerization is often a prominent process provoked by the radiation. In these conventional experimental approaches, the effects of dose, irradiating agent, pressure, additives, etc., are correlated to arrive at the mechanisms by which the target compound is transformed. Often, reactions of ions created by the radiation field are postulated to account for the observations.

In contrast to the large number of investigations of gaseous and liquid C_6 compounds by the conventional technique of irradiation followed by product analysis, there are relatively few mass spectrometric studies in which the transient ionic reactants and products are observed directly, and the ionic mechanisms of radiation chemical action thereby established unambiguously. The techniques of "high-pressure" mass spectrometry have been utilized by Field, Hamlet, and Libby[7] for the investigation of ion-molecule reactions in benzene and benzene-rare gas mixtures, by Wexler and Clow[8] for benzene and toluene, and by Giardini-Guidoni and Zocchi[9] for benzene, toluene, and the three xylenes. Limited studies of ion chemistry involving these gaseous molecules have been reported by Barker,[10] Henglein,[11] Rudolph and Melton,[12] and Tiernan and Bhattacharya.[13] Since ionic processes are likely to play important roles in the radiation chemistry of the compounds, and the earlier high-pressure experiments[7-9] provided unequivocal evidence for ionic modes of polymerization of benzene and toluene, it was considered worthwhile to extend this technique to the investigation of the following gaseous molecules: ethylbenzene, aniline, *n*-hexane, cyclohexane, and methylcyclohexane. In addition, a few studies on benzene and toluene were carried out to verify the results for these compounds that were reported earlier. The experiments described here were performed with a proton beam-high pressure mass spectrometer, in which the primary ionization is caused by a beam of 2-MeV protons (from a Van de Graaff generator) which enters and leaves the source chamber through thin windows.

Experimental Section

A description of the proton beam-high pressure mass spectrometer has already been communicated,[14] and the machine will therefore not be described here. But an improved, versatile source chamber, a sketch of which appears in Figure 1, was constructed for these experiments. The proton beam entered and left the source through thin nickel foils (A and A′) 0.00025 cm thick and 0.34 cm in diameter, the foils being protected by heat-dissipating copper grids (Varian Associates, Palo Alto, Calif.). The protons, focused into a beam 1 × 2 mm before entering the source, were further collimated in the chamber by a knife-edge aperture (B) 0.48 mm high and 2.0 mm wide. A negative voltage on plate C containing a wider slit served to repel secondary electrons formed at the window and at the jaws of the beam-defining aperture. A third grounded plate D with a 2.0 × 5.0 mm slot shielded the main section of the chamber from the electric field of the electron repeller. After crossing the chamber the proton beam passed through two wide apertures C′ and D′, the first grounded and the second at negative potential to repress secondary electrons formed by the beam at the exit window. And on leaving the chamber, the protons were measured for intensity in a deep Faraday cup (E). The ionizing beam thus was very near the dimensions of the knife-edge aperture, and its midplane was 10 mm from the apertures (F) through which the ions left the source chamber. These apertures were four 0.0076-cm diameter holes, drilled in a line with adjacent holes 0.038 cm apart, in a 0.0025-cm thick nickel disk.

The gas to be studied entered the source through the tube H, and its pressure in the chamber was measured directly by means of a side tube (I) which extended from the chamber to a calibrated Baratron capacitance manometer (MKS Instruments, Inc., Lexington, Mass.). The pressure range investigated usually extended from 0.025 to 1.00 Torr. The gases were introduced into the spectrometer from an all stainless steel gas-handling line.

The temperature of the chamber could be varied and controlled between 22 and 100° by circulating a light mineral oil (Sargent Co., No. 13637 paraffin oil) through cavities L and L′, the oil being pumped and heated, if necessary, by a temperature bath and circulating system (Series 1280, Haake PolyScience Corp., Evanston, Ill.). However, in all the experiments reported here, the tempera-

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

[2] G. R. Freeman, *Radiat. Res. Rev.*, **1**, 1 (1968).

[3] J. W. T. Spinks, "An Introduction to Radiation Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1964.

[4] A. Chapiro, "Radiation Chemistry of Polymeric Systems," Interscience Publishers, New York, N. Y., 1962.

[5] G. G. Meisels in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Interscience Publishers, New York, N. Y., 1968.

[6] P. Ausloos and S. G. Lias, *Actions Chim. Biol. Radiations*, **11**, 1 (1967).

[7] F. H. Field, P. Hamlet, and W. F. Libby, *J. Amer. Chem. Soc.*, **89**, 6035 (1967); Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 13-18, 1969.

[8] S. Wexler and R. P. Clow, *J. Amer. Chem. Soc.*, **90**, 3940 (1968).

[9] A. Giardini-Guidoni and F. Zocchi, *Trans. Faraday Soc.*, **64**, 2342 (1968).

[10] R. Barker, *Chem. Ind.* (London), 233 (1960).

[11] A. Henglein, *Z. Naturforsch.*, *A*, 17, 34, 41 (1962).

[12] P. S. Rudolph and C. E. Melton, *J. Chem. Phys.*, 32, 586 (1960).

[13] T. O. Tiernan and A. K. Bhattacharya, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 13-18, 1969.

[14] S. Wexler, A. Lifshitz, and A. Quattrochi, "Ion-Molecule Reactions in the Gas Phase," Advances in Chemistry Series, No. 58, American Chemical Society, Washington, D. C., 1966, p 193.

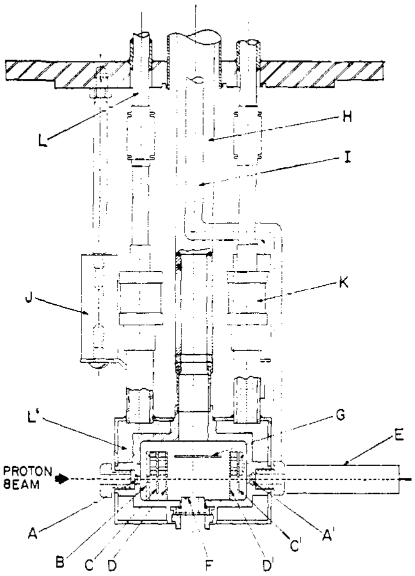

Figure 1. Drawing of the improved source chamber of the proton beam–high pressure mass spectrometer. The letters identify parts that are described in the text.

ture of the chamber was 22° as measured by an iron-constantan thermocouple.

The ions were driven from the source by a positive potential on the repeller plate G, and entered a Nier-type accelerating and focusing system. For most of the experiments a repeller field strength of 21.6 V/cm existed in the source.

Note that the entire source assembly was supported by a single flange, through which the gas inlet and pressure-measuring tubes, the heating fluid, and the electrical leads passed. The source was isolated electrically from ground by ceramic standoffs J and K.

Very high purity compounds were obtained in liquid form, and each was thoroughly outgassed before vapor was withdrawn for study. The stated purities were for benzene 99.999% (James Hinton Co., Valparaiso, Fla.); toluene 99.96%, cyclohexane 99.94%, ethylbenzene 99.90%, *n*-hexane 99.95% (Phillips Petroleum Co.); aniline 99.99% (Mallinckrodt Chemical Works); and methylcyclohexane 99.93% (Matheson Coleman and Bell Co.).

As in the earlier work, the mass spectra of positive ions in each gas were recorded in the range up to usually 260 mass units as a function of known source pressure of the compound. Each ion intensity was corrected for naturally occurring C^{13} and for dead time of the pulse amplification electronic system, the relative abundances of the species were calculated, and the spectra then plotted in histogram form. The yields of several of the more prominent species were also plotted as a function of source pressure. All these operations were performed by computer (CDC-3600).

Results

A. *n*-Hexane. The fractional yields of the various singly charged positive ions formed in *n*-hexane when bombarded by 2-MeV protons were determined as a function of discrete source pressures in the range from 0.025 to 1.00 Torr. At the lower gas concentrations there were relatively few primary ions produced by the proton impact on normal hexane, mainly the parent, $C_6H_{14}^+$ (mass 86), the dominant fragment $C_6H_{13}^+$, $C_6H_{12}^+$, $C_5H_{11}^+$, $C_4H_9^+$, and $C_4H_8^+$; some of these had reacted with *n*-hexane to give $C_7H_9^+$, $C_7H_{10}^+$, and $C_{10}H_{21}^+$ in very low yields. As the pressure in the source was raised, the intensities of the primary ions other than that of $C_6H_{12}^+$ rapidly decreased, with the concomitant appearance of products of low yield at many mass positions up to 260 atomic units. As shown in Figure 2, which presents the behaviors of the more prominent ions found in *n*-hexane, the abundances of the species $C_6H_{13}^+$, $C_6H_{12}^+$, and $C_5H_{11}^+$ initially increased as the source pressure was raised, before they decreased exponentially. The behaviors are indicative of secondary processes giving rise to these normally primary fragment ions. Apparently, H^- and H_2^- transfer from *n*-hexane molecules to primary ionic fragments occurs readily. Also, dissociative charge transfer giving $C_5H_{11}^+$ and a CH_3 radical must be a common reaction. At about 100 μ pressure, another important reaction appears to be

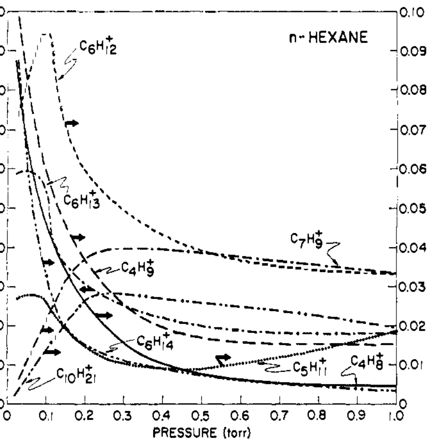

Figure 2. Characteristic dependences of several of the prominent positive ions in *n*-hexane on its pressure in the source chamber.

$$C_6H_{13}^+ + C_6H_{14} \longrightarrow C_{10}H_{21}^+ + C_2H_6 \qquad (1)$$

Beginning with 200 μ a steady state became evident, as shown by the invariance of the pattern as the concentration of gas was increased. The ionic species then appeared in groups which differed in mass by a CH_2 unit. Some evidence that the ions appear to be formed by attachment of a hexane molecule to an ionic fragment comes from the observation that a sharp decrease occurred in the abundances of ions with masses above 206. The change took place just where two C_6H_{14} units would be required to join a C_2-fragment ion. However, there was no evidence for formation of a dimer ion, such as $C_{12}H_{28}^+$, or a trimer product in *n*-hexane at any source pressure over the range studied.

B. Cyclohexane. In contrast to the few ionic reactions observed in *n*-hexane, cyclohexane exhibited mass patterns showing many distinctive, efficient ion–molecule reactions. The variations with source pressure of several of the some 20 prominent ionic species observed are presented in Figure 3. One sees that positive ions with masses equal to or less than that of C_6H_{12} decreased in intensity as the source pressure was raised, up to about 400 μ. At the same time, several very abundant species with massses above that of the parent appeared, namely, $C_7H_9^+$ (mass 93), $C_8H_9^+$, $C_{10}H_{19}^+$, $C_{11}H_{19}^+$, $C_{11}H_{20}^+$, $C_{11}H_{25}^+$, $C_{14}H_{19}^+$, $C_{14}H_{23}^+$, $C_{14}H_{24}^+$, $C_{15}H_{30}^+$, $C_{16}H_{35}^+$, and $C_{18}H_{34}^+$. Note that the positive ions larger than $C_{11}H_{20}^+$ must be at least tertiary species, and indeed the shapes of the fractional abundance–pressure curves indicate that they are of this kinetic order. The relative importance of the ionic products in the cyclohexane spectrum shifted to those of higher masses with increasing source pressure up to 0.40 Torr. However, the dimer $C_{12}H_{24}^+$ from reaction of the parent ion with cyclohexane was absent, as was

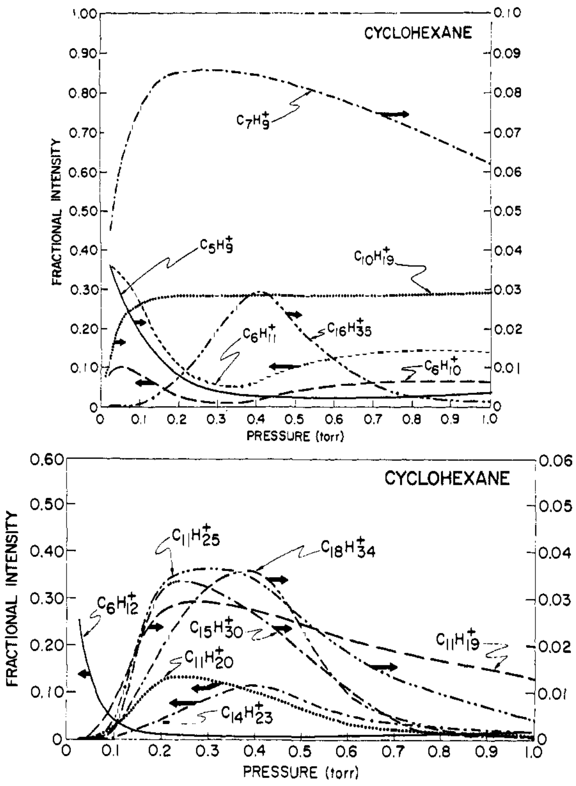

Figure 3. Pressure-dependent variations of the yields of the dominant positive ions in cyclohexane.

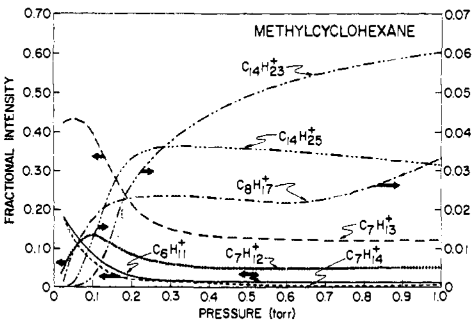

Figure 4. Relative abundances of important ionic species in methylcyclohexane as functions of source concentration.

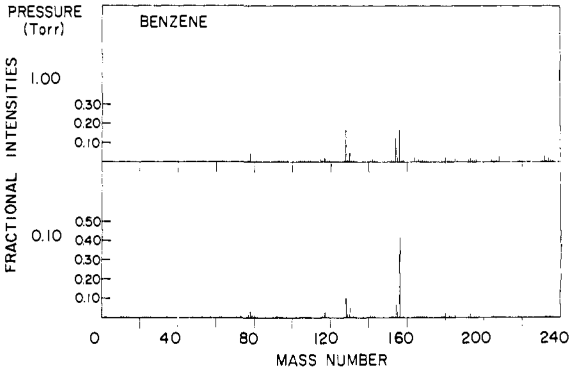

Figure 5. Spectra of positive ions found in gaseous benzene at two different concentrations in the source.

the trimer $C_{18}H_{36}^+$, although the tertiary species $C_{18}H_{34}^+$ was observed. Apparently, as in the case of *n*-hexane, simple polymerization by "sticky" collisions of the parent or other primary ions with the gas molecules does not occur in cyclohexane. Plausible condensation-type reactions, with the elimination of H_2 and small hydrocarbon fragments, may be written to account for the formation of all the prominent products. A discussion of these reactions will be given later in this paper.

When the source pressure reached about 0.60 Torr, a steady-state condition took place, with the appearance of many groups of ions, the adjacent groups differing by about a CH_2 unit. The fragments whose masses exceeded 201 had intensities only one-third or less than those of masses less than this value. This division appears to suggest that reactions in which two cyclohexane molecules are involved with $C_3H_n^+$ and higher weight ions are of much lower probabilities than those involving only one gas molecule. Three of the primary ions, $C_6H_{10}^+$, $C_6H_{11}^+$, and $C_6H_{12}^+$, rose in yield in the range from 0.40 to 1.00 Torr, after decreasing below the lower pressure. This characteristic is probably the result of H_2^-, H^-, and electron-transfer processes, respectively.

C. Methylcyclohexane. The behavior of methylcyclohexane under proton irradiation showed characteristics similar to those of *n*-hexane as the gas concentration was raised. The dominant primary species $C_7H_{14}^+$ (mass 98), $C_7H_{13}^+$, and $C_6H_{11}^+$, as well as those of lower abundance (*e.g.*, $C_6H_{10}^+$, $C_5H_{10}^+$, $C_5H_9^+$, $C_5H_8^+$, $C_5H_7^+$, $C_4H_8^+$, $C_4H_7^+$, and $C_3H_3^+$) dropped off rapidly, with the formation in small yields of secondary and tertiary products with masses up to 287 atomic units (Figure 4). The most prominent of these products were $C_8H_{17}^+$ (mass 113), $C_{14}H_{25}^+$ (193), and $C_{14}H_{23}^+$ (191). As in *n*-hexane, this aliphatic hydrocarbon did not form dimer products by persistent collisions with the parent ion or other primary species. Only condensation and hydrogen-transfer reactions appeared to be taking place. Plausible reactions to account for the occurrence of the main products are

$$C_7H_{14}^+ + C_7H_{14} \longrightarrow C_8H_{17}^+ + C_6H_{11} \quad (2)$$

$$C_7H_{13}^+ + C_7H_{14} \longrightarrow C_{14}H_{25}^+ + H_2 \quad (3)$$

$$\longrightarrow C_{14}H_{23}^+ + 2H_2 \quad (4)$$

$$C_nH_m^+ + C_7H_{14} \longrightarrow C_7H_{12}^+ + C_nH_{m+2} \quad (5)$$

And, again, the establishment of a steady-state condition was evident at higher source pressures, as shown by the invariance of the mass pattern. The groups of ions were, as in the other hydrocarbons, separated by approximately a CH_2 group, and there were sharp decreases in yields of the products when a second gas molecule was eventually required for reaction with the primary species formed by the proton ionization. A competing reaction was hydride ion transfer, as indicated by the high and constant yield of $C_7H_{13}^+$ above 0.30 Torr (Figure 4).

D. Benzene. Because the ionic reactions in gaseous benzene have already been investigated in detail at this laboratory in experiments with an electron gun,[8] as well as by others,[7,9–13] the spectra of benzene only at source pressures of 0.10 and 1.00 Torr were recorded. The spectra at both pressures (Figure 5) were relatively simple, being dominated by four or five species. Even at 0.10 Torr the parent ion $C_6H_6^+$ (mass 78) was relatively small, while products of ion–molecule reactions were present in high yields, *e.g.*, $C_{10}H_8^+$ (128), $C_{10}H_{10}^+$ (130),

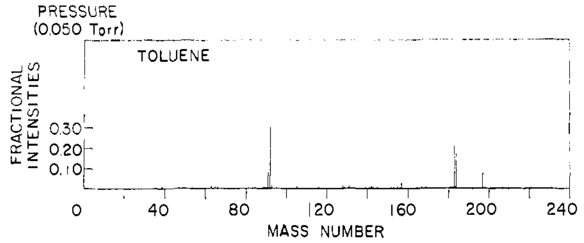

Figure 6. Mass pattern of ionic species in toluene at 50 μ source pressure.

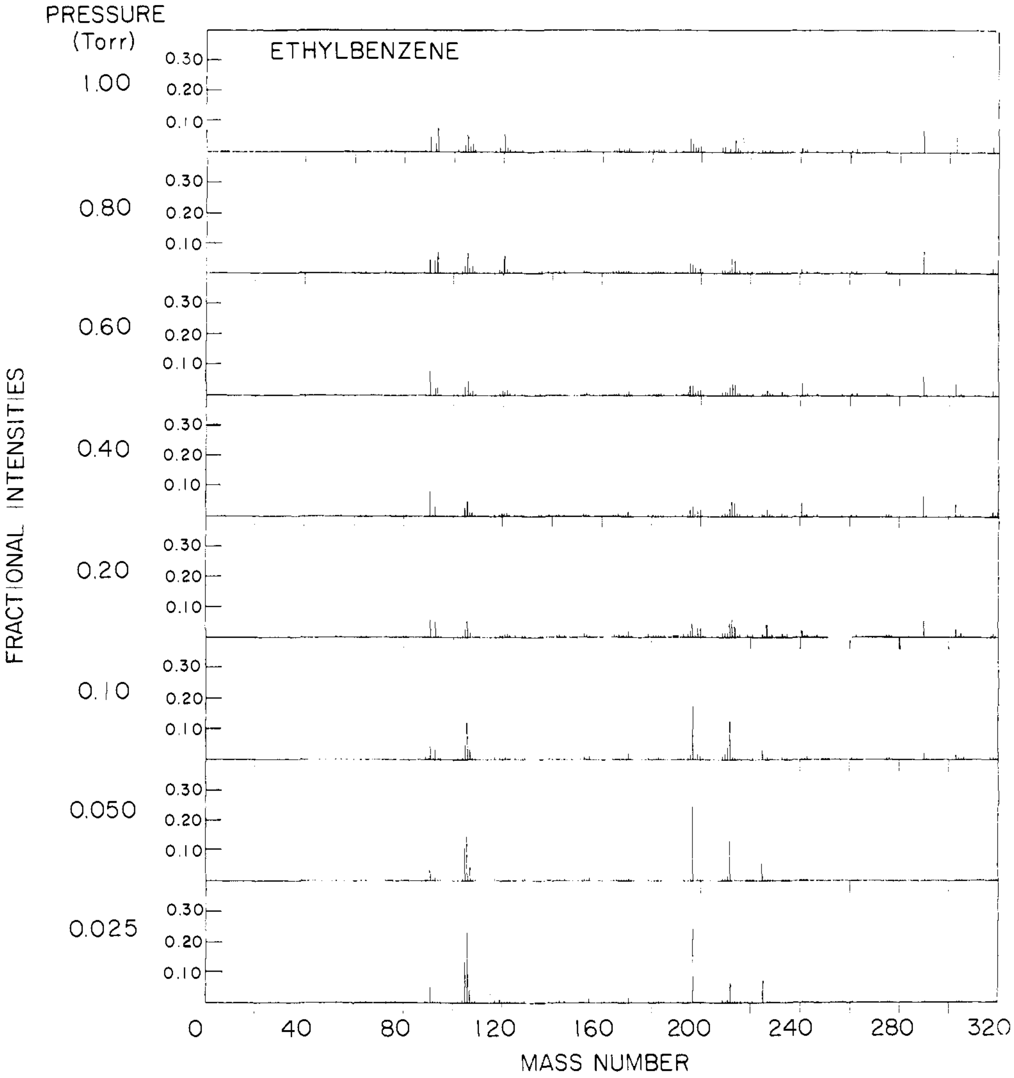

Figure 7. Histogram presentation of the mass spectra of positive ions in ethylbenzene observed with increasing source pressures in the range from 0.025 to 1.00 Torr. The prominent ionic species are identified in the text.

$C_{12}H_{10}^+$ (154), $C_{12}H_{11}^+$ (155), and $C_{12}H_{12}^+$ (156). The appearance of the mass pattern remained about the same at the higher gas pressure. However, the two spectra are not strictly comparable because the repeller field strengths were 64.8 V/cm and 17.2 V/cm at the lower and higher pressures, respectively. It is quite evident that dimerization of $C_6H_6^+$ to give $C_{12}H_{12}^+$ especially, as well as $C_6H_5^+$ to form $C_{12}H_{11}^+$, are very important processes in gaseous benzene. Small yields of the trimers $C_{18}H_{18}^+$ and $C_{18}H_{16}^+$ were also observed. Many ion–molecule reactions other than polymerization also occurred, as shown by the complex spectra of ions of low yield. The fact that the parent ion $C_6H_6^+$ increased in abundance with pressure while the other primary species essentially disappeared confirms the phenomena of charge exchange from fragment ions to benzene molecules that was observed in the earlier work.

E. Toluene. Only the mass spectrum at 50-μ source pressure was measured for gaseous toluene, just as a check on the extensive studies reported.[8,9] As the histogram plot in Figure 6 shows, the toluene spectrum, like that of benzene, was relatively simple, consisting at this concentration mostly of the five ionic species $C_7H_7^+$ (mass 91), $C_7H_8^+$ (92), $C_{14}H_{15}^+$ (183), $C_{14}H_{16}^+$ (184), and $C_{15}H_{17}^+$ (197). Thus, there is strong evidence for the formation of the dimer ion $C_{14}H_{16}^+$ as well as for the attachment of a toluene molecule to $C_7H_7^+$. But trimers were not found at this pressure. In addition to the important reactions cited, numerous other ion–molecule reactions gave rise to a complex spectrum of species of very low abundance.

F. Ethylbenzene. The histogram presentations of the mass spectra of proton-bombarded ethylbenzene as a function of increasing source pressure are given in Figure 7. The parent, $C_8H_{10}^+$ (mass 106), and its prin-

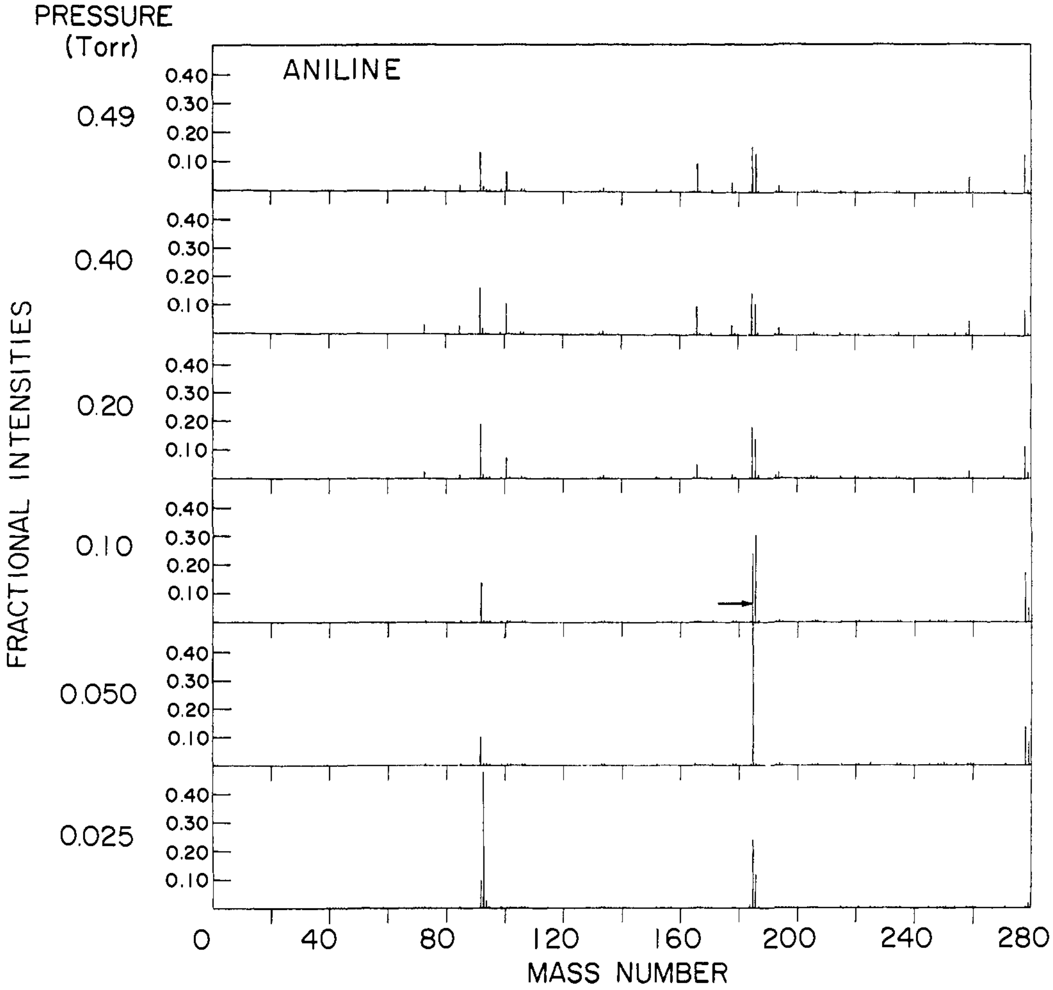

Figure 8. Relative yields of ions in aniline in the pressure range from 0.025 to 0.49 Torr.

cipal primary fragment $C_8H_9^+$ (105), became less intense as the pressure was raised from 25 to 200 μ, but then remain constant in yield. However, $C_7H_9^+$ (93) and $C_7H_7^+$ (91) increased in abundance, suggesting that these nominally primary ions are also formed by secondary processes. In addition, there were several other primary species of very low abundance, ranging from $C_3H_3^+$ (39) to $C_8H_8^+$ (104).

The reduction of the primary ions was accompanied by the appearance of several secondary and tertiary ions in high abundance. Of importance was the dimer, $C_{16}H_{20}^+$ (mass 212), which was formed from association of the parent $C_8H_{10}^+$ with an ethylbenzene molecule, and which, from the appearance of its abundance–pressure curve, was also quite reactive with ethylbenzene. The principal competing reaction to dimer formation appeared to be

$$C_6H_5C_2H_5^+ + C_6H_5C_2H_5 \longrightarrow C_{15}H_{17}^+ (197) + CH_3 \quad (6)$$

The $C_8H_9^+$ (105) ion also attached to a gas molecule to form $C_{16}H_{19}^+$ (211). A small amount of the trimer, $C_{24}H_{30}^+$ (mass 318 and probably $(C_6H_5C_2H_5)_3^+$), was also produced under the conditions of the experiment. The trimer was probably formed from the dimer in competition with the prominent reactions that led to $C_{22}H_{26}^+$ (290) + C_2H_4 and $C_{23}H_{27}^+$ (303) + CH_3. All three ionic products (the trimer $C_{24}H_{30}^+$, $C_{22}H_{26}^+$, and $C_{23}H_{27}^+$) did not react further with the substrate gas. The principal secondary product, $C_{15}H_{17}^+$, other than the dimer reacted readily (its abundance dropped rapidly at pressures above 50 μ) with an ethylbenzene molecule to give probably $C_{17}H_{21}^+$ (225) + C_6H_6. The species with mass 225 must be due to an impurity in the ethylbenzene, because its relative abundance behaved like that of a primary ion, decaying exponentially with increasing source pressure. $C_{15}H_{16}^+$ (196) was a secondary ion of moderate yield, while $C_{16}H_{21}^+$ (213) and $C_{16}H_{22}^+$ (214) appeared to be tertiary species, formed possibly by H and H_2 transfer, respectively, to the dimer. These species were unreactive toward ethylbenzene, as shown by the invariance of their yield–pressure plots above ~0.40 Torr. Other higher order products of some importance were $C_{23}H_{29}^+$ (305) and $C_{24}H_{32}^+$ (320).

Beginning at 200 μ the pattern of ionic masses generally remained the same in appearance with increasing source pressure, with the tertiary species $C_{22}H_{26}^+$ (290) and $C_{23}H_{27}^+$ (303) standing out.

G. Aniline. Aniline was ionized by protons in pressure steps from 25 to 490 μ, the upper limit being its vapor pressure at 22°. The data for the positively-charged species are presented in Figure 8. Several features of the ion chemistry of aniline are indicated by the pressure-dependent variations of their abundances.

(a) Of the two primary ions that are found in high yield, namely $C_6H_5NH_2^+$ (mass 93) and $C_6H_5NH^+$ (92), the latter is also produced in a secondary process.

(b) Both the molecule–ion $C_6H_5NH_2^+$ and the protonated aniline ion, $C_6H_5NH_3^+$ (94), react rapidly with the gas, with formation of a product spectrum that is composed of relatively few species.

(c) Obviously, polymerization occurs readily in ionized gaseous aniline. The dimer $(C_6H_5NH_2)_2^+$ (mass 186) and the trimer $(C_6H_5NH_2)_3^+$ (279) are products with high abundances.

(d) Both $C_6H_5NH^+$ and $C_6H_5NH_3^+$ also readily attach to aniline molecules to form $(C_6H_5NH_2 \cdot C_6H_5NH)^+$ (mass 185) and $(C_6H_5NH_2 \cdot C_6H_5NH_3)^+$ (187), respectively, and from the forms of their curves of abundances as functions of increasing pressure, these products attract another aniline to yield the respective trimers, $[(C_6H_5NH_2)_2 \cdot C_6H_5NH]^+$ (278) and $[(C_6H_5NH_2)_2 \cdot C_6H_5NH_3]^+$ (280).

(e) Prominent secondary products other than those already mentioned are $C_8H_5^+$ (mass 101) and $C_{12}H_8N^+$ (166), these probably being the products of the competitive reactions

$$C_6H_5NH_2^+ + C_6H_5NH_2 \longrightarrow C_8H_5^+ + NH_3 + C_2H_4 + C_2H_2 \quad (7)$$

$$\longrightarrow C_{12}H_8N^+ + NH_3 + H + H_2 \quad (8)$$

These two also appear to attach themselves to aniline molecules, with the creation of $(C_6H_5NH_2 \cdot C_8H_5)^+$ (194) and $(C_6H_5NH_2 \cdot C_{12}H_8N)^+$ (259), respectively. $C_8H_5^+$ probably also reacts with aniline to give $C_{14}H_{10}^+$ (178).

The pattern of positively charged species did not change above 200 μ pressure. Several ions of low abundance (masses 193, 205, 206, 215, 220, 234, 248–251, and 271) also were present in the gas.

Discussion

With the exception of aniline, the compounds whose ionic reactions were observed in this work have been the subject of numerous radiation–chemical investigations. Particularly, the C_6 molecules *n*-hexane, cyclohexane, and benzene have been studied and restudied, mainly because of the structural similarity of the latter two and the protective behavior of benzene. It is the intent in this section to review briefly the results of these studies, with each compound taken separately, and then to attempt to correlate where possible our high-pressure measurements with the published results, in order to aid in establishing the ionic mechanisms that may be responsible for the major products, especially the "polymer," that are formed on irradiation of each substance.

A. *n*-Hexane. Radiation of *n*-hexane converts this molecule principally to H_2, C_2H_4, C_2H_6, C_3H_8, C_4H_{10}, and higher weight compounds through at least C_{12}.[15–17] Although radical scavengers such as propylene, I_2, and cyclohexene greatly reduce, but do not eliminate, the yields of H_2, C_4H_{10}, and the C_7–C_{12} hydrocarbons,[18] the formation of C_1–C_3 products is not affected by these scavengers. By assuming the primary ion distribution of *n*-hexane observed in a mass spectrometer, hydride-ion transfer reactions of thirteen primary fragments, *i.e.*

$$R^+ + C_6H_{14} \longrightarrow \underset{\substack{\downarrow \\ \text{dissociation}}}{RH} + C_6H_{13}^+ \quad (9)$$

and neutralization of $C_6H_{13}^+$ to give cyclohexane, Futrell[16] was able to calculate *g* values for the main products of radiolysis remarkably close to those measured experimentally. The condensation reaction

$$C_6H_{14}^+ + C_6H_{14} \longrightarrow C_{12}H_{26}^+ + H_2 \quad (10)$$

was suggested by Williams[19] to account for the dimeric products. But Hardwick,[20] on the other hand, proposed a free radical mechanism in which ion–molecule reactions play a very small role.

Our "high-pressure" spectra of proton-irradiated *n*-hexane show that $C_6H_{13}^+$ is indeed the dominant ion, but its demise along with the formation of $C_{10}H_{21}^+$ as the source pressure is raised indicates that it must react with hexane

$$C_6H_{13}^+ + C_6H_{14} \longrightarrow C_{10}H_{21}^+ + C_2H_6 \quad (11)$$

Accordingly, the $C_6H_{13}^+$ would be too short lived to undergo electron neutralization, as suggested by Futrell.[16] Furthermore, reaction 11 is also a mode of formation of ethane, in addition to one of the type indicated by eq 9, and since this reaction would not be affected by scavengers, it would be consistent with Dewhurst's observations on the behavior of C_1–C_3 product yields in their presence.[18] Moreover, we find no strong evidence for the ion $C_{12}H_{26}^+$ that Williams[19] has postulated as the ionic intermediate in the production of dimer. Indeed, only H^-, H_2^-, and dissociative charge transfer involving fragment ions of *n*-hexane to give $C_6H_{13}^+$, $C_6H_{12}^+$, and $C_5H_{11}^+$, respectively, were found (Figure 2), along with reaction 11 and those leading to a large number of ionic species of low abundance. The nondescript character of the hexane spectra at intermediate and higher source pressures leads us to the conclusion that ionic modes of production of the observed products involve the hydride-transfer reactions suggested by Futrell, H_2^- and charge transfer, many ion–molecule reactions of the type illustrated in eq 11, and electron neutralization of many different ions. No preferred ionic pathway to formation of polymer is indicated by our data.

B. Cyclohexane. From the numerous investigations (often leading to conflicting conclusions) of the behavior of cyclohexane under the action of a radiation field,[21–26] the principal products (in order of decreasing yield) are H_2, C_2H_4, C_2H_6, cyclohexene, dicyclohexyl, C_4 hydrocarbons, C_3H_6, C_3H_8, CH_4, and C_2H_2. The ethylene and acetylene were thought to be produced chiefly by dissociation of excited neutral molecules, while the lower alkanes were considered to be formed from reactions of primary fragment ions and free radicals. Propylene was probably the result of a neutralization process. Since scavenging with HI and I_2 left a yield of H_2 from charge neutralization equal to that of the parent $C_6H_{12}^+$ ion in the primary mass pattern, Theard[25] thought this hydrogen and cyclohexene were the products of electron-$C_6H_{12}^+$ recombination. But the data from isotopic studies[24] suggested that half the

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(15) H. A. Dewhurst, *J. Amer. Chem. Soc.*, **83**, 1050 (1961).

(16) J. H. Futrell, *ibid.*, **81**, 5921 (1959).

(17) R. A. Back and N. Miller, *Trans. Faraday Soc.*, **55**, 911 (1959).

(18) H. A. Dewhurst, *J. Phys. Chem.*, **62**, 15 (1958).

(19) T. F. Williams, *Trans. Faraday Soc.*, **57**, 755 (1961).

(20) T. J. Hardwick, *J. Phys. Chem.*, **64**, 1623 (1960).

(21) J. M. Ramaradhya and G. R. Freeman, *J. Chem. Phys.*, **34**, 1726 (1961); *Can. J. Chem.*, **39**, 1769 (1961).

(22) P. J. Dyne, J. Denhartog, and D. R. Smith, *Discussions Faraday Soc.*, 135 (1963).

(23) J. Blachford and P. J. Dyne, *Can. J. Chem.*, **42**, 1165 (1964).

(24) J. Milhaud and J. Durup, *Compt. Rend.*, **260**, 6363 (1965).

(25) L. M. Theard, *J. Phys. Chem.*, **69**, 3292 (1965).

(26) K. H. Jones, *ibid.*, **71**, 709 (1967).

ethane and one-tenth of the propane were the eventual result of H^- and H_2^- transfer, respectively. Other experiments with $c\text{-}C_6H_{12}$ + $c\text{-}C_6D_{12}$ mixtures[27] gave evidence that 25% of the H_2 was formed by unimolecular detachment, 40% from H-atom reactions, and the remainder by ion–molecule reactions, for example

$$C_6H_{12}^+ + c\text{-}C_6H_{12} \longrightarrow C_6H_{13}^+ + c\text{-}C_6H_{11} \qquad (12)$$

$$C_6H_{13}^+ + e^- \longrightarrow c\text{-}C_6H_{11} + H_2 \qquad (13)$$

Since the yield of dicyclohexyl increased, those of H_2 and cyclohexene reduced at most slightly, and those of C_1–C_3 compounds fell greatly when the pressure was raised,[26] excited ionic species (probably $C_6H_{12}^+$), whose dissociation was quenched at the higher pressures, were believed to be involved in the mechanism of the radiation chemistry of cyclohexane.

But Dyne and Jenkinson[28] concluded from their irradiations of $c\text{-}C_6H_{12}$ with added I_2 or benzene that a single excited state of cyclohexane is the precursor of H_2, while Freeman[29] and Hamill[30] claimed that there are two distinct activated species. More recent work[31] showed that H_2, cyclohexane, and bicyclohexyl are the principal products at high dose rate. Other studies demonstrated that benzene acts as an energy or charge acceptor and not as an electron scavenger.[29,32]

The consensus of opinion at present appears to be that the $C_6H_{12}^+$ parent ion from the effect of radiation on cyclohexane is very stable toward reaction with the molecule[33] and is neutralized either by electron or charge transfer. The main products, H_2, cyclohexane, and bicyclohexyl, are the result of the instability of the freshly neutralized $C_6H_{12}^+$ species as well as primary excited molecules and subsequent H-atom and cyclohexyl radical reactions.[34] However, a part (possibly large) of cyclohexane is converted to a nonvolatile residue,[35] and higher weight products such as tetracyclohexyl must be postulated to obtain a material balance.[36] In addition, the yields of products obtained from irradiation of the vapor are significantly different from those in the liquid, with carbon–carbon bond rupture being much more frequent in the gas.[37]

Our observation of the growth of abundances of some twenty ionic species with masses greater than the parent, along with marked decreases in the yields of the primary ions, with rising pressure of cyclohexane (Figure 3) indicates that many of the products observed in the conventional radiolysis of cyclohexane may be the neutral components of the products of ion–molecule reactions. For, in illustration, one may write the following reasonable reactions to account for many of our observed ionic species

$$C_6H_{11}^+ + C_6H_{12} \longrightarrow C_7H_9^+ + C_3H_8 + C_2H_6 \qquad (14)$$

$$\longrightarrow C_8H_9^+ + 2C_2H_6 + H_2 \qquad (15)$$

$$\longrightarrow C_{10}H_{19}^+ + C_2H_4 \qquad (16)$$

$$C_6H_{12}^+ + C_6H_{12} \longrightarrow C_{11}H_{19}^+ + CH_3 + H_2 \qquad (17)$$

$$\longrightarrow C_{11}H_{20}^+ + CH_4 \qquad (18)$$

$$C_6H_{12}^+ + 2C_6H_{12} \longrightarrow C_{18}H_{34}^+ + H_2 \qquad (19)$$

$$C_{11}H_{19}^+ + C_6H_{12} \longrightarrow C_{14}H_{19}^+ + 2H_2 + C_3H_8 \qquad (20)$$

$$\longrightarrow C_{14}H_{23}^+ + C_3H_8 \qquad (21)$$

$$C_{11}H_{25}^+ + C_6H_{12} \longrightarrow C_{15}H_{30}^+ + C_2H_5 + H_2 \qquad (22)$$

$$2C_2H_5 \longrightarrow C_4H_{10} \qquad (23)$$

These reactions could account for the nonscavengeable H_2, ethane, or propane. Thus, it is probable that these two alkanes are formed by this mechanism instead of or in addition to the H^- and H_2^- transfer reactions suggested by Milhaud and Durup.[24] Note that we find no evidence for the $C_6H_{13}^+$ ion, which Nevitt and Remsberg[27] postulate as the ionic intermediate in the formation of H_2 and cyclohexyl radicals, and in contrast to the conclusions of Ausloos[33] and Dyne,[34] we observe the $C_6H_{12}^+$ ion to be reactive with cyclohexane.

The rather large abundances of high-weight ions, such as the tertiary species $C_{18}H_{34}^+$, $C_{15}H_{30}^+$, $C_{14}H_{19}^+$, $C_{14}H_{23}^+$, and $C_{16}H_{35}^+$, in irradiated cyclohexane (Figure 3) suggest that these may be of importance in the production of cyclohexane, bicyclohexyl, and "polymer." If stable toward further reaction with cyclohexane, some of these ions could on electron recombination give cyclohexene and bicyclohexyl. Or if reactive, some may lead to the ever-present "polymer."

C. Methylcyclohexane. Holtslander and Freeman[38,39] studied the radiation chemistry of methylcyclohexane extensively. The main products of γ radiolysis of the vapor were H_2, CH_4, C_2H_4, C_3H_6, $c\text{-}C_6H_{12}$, and C_7H_{12}. A dimer, $C_{14}H_{16}$, appeared in moderate yield. However, attempts at a material balance revealed that there was an excess of 4.8 *G* units of H_2, which indicated that the missing carbon-containing compounds were probably polymers. Indeed, a nonvolatile residue was found in the cells after an irradiation. Similar to the behavior of cyclohexane, carbon–carbon bond rupture was much more prevalent in the gas than in the liquid, but the hydrogen yields were nearly the same.

From studies which involved the effects of electron, positive ion, and free radical scavengers, Holtslander and Freeman arrived at the following mechanism of radiolytic conversion of methylcyclohexane

	G value	
$C_7H_{14} \longrightarrow M_1^+, M_2^+, N^+, e^-$	4.4	(24)
$\longrightarrow C_7H_{14}^+ + e^-$	3.1	(25)
$C_7H_{14}^* \longrightarrow C_7H_{13} + H$	1.5	(26)
$\longrightarrow C_7H_{12} + H_2$	1.6	(27)
$M_1^+ + e^- \longrightarrow$ H + product	2.1	(28)
$M_2^+ + e^- \longrightarrow$ no H or H_2	1.3	(29)
$N^+ + e^- \longrightarrow$ no H or H_2	1.0	(30)
$H + C_7H_{14} \longrightarrow H_2 + C_7H_{13}$	3.6	(31)

The *G* values estimated for the products of the respective

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(27) T. D. Nevitt and L. P. Remsberg, *J. Phys. Chem.*, **64**, 969 (1960).

(28) P. J. Dyne and W. M. Jenkinson, *Can. J. Chem.*, **38**, 539 (1960); **39**, 2163 (1961).

(29) G. R. Freeman, *J. Chem. Phys.*, **33**, 71 (1960); *Can. J. Chem.*, **38**, 1043 (1960).

(30) L. J. Forrestal and W. H. Hamill, *J. Amer. Chem. Soc.*, **83**, 1535 (1961).

(31) A. W. Boyd, C. Willis, O. A. Miller, and A. E. Rothwell, "Radiation Chemistry—II," Advances in Chemistry Series, No. 82, American Chemical Society, Washington, D. C., 1968, p 456.

(32) M. Burton and W. N. Patrick, *J. Phys. Chem.*, **58**, 421 (1954).

(33) R. D. Doepher and P. Ausloos, *J. Chem. Phys.*, **42**, 3746 (1965).

(34) P. J. Dyne, *Can. J. Chem.*, **43**, 1080 (1965).

(35) J. M. Ramaradhya, unpublished results.

(36) Reference 4, p 80.

(37) J. M. Ramaradhya and G. R. Freeman, *J. Chem. Phys.*, **34**, 1726 (1961).

(38) W. J. Holtslander and G. R. Freeman, *Can. J. Chem.*, **45**, 1649, 1661 (1967).

(39) G. R. Freeman, *Radiat. Res. Rev.*, **1**, 1 (1968).

reactions are listed along each equation. Although the identities of the ions M_1^+, M_2^+, and N^+ were unknown, they were claimed to be unreactive with methylcyclohexane, and thereby were sufficiently long lived to undergo electron recombination. The authors stated that M_1^+ probably includes the parent ion, $C_7H_{14}^+$, and it is the only species to give H_2 on neutralization, while either M_1^+ or M_2^+ probably includes $C_7H_{13}^+$. M_1^+ and M_2^+ together comprise 75% of the positive ions in the gas, and they both react with ND_3 by a proton-transfer reaction that leads to formation of HD and D_2. Methane and cyclohexene were considered to be produced by the reactions

$$C_7H_{14} \rightsquigarrow C_7H_{14}^{+*} + e^- \qquad (32)$$

$$\downarrow$$

$$C_6H_{11}^+ + CH_3 \qquad (33)$$

$$C_6H_{11}^+ + C_7H_{14} \longrightarrow C_6H_{12} + C_7H_{13}^+ \qquad (34)$$

$$CH_3 + C_7H_{14} \longrightarrow CH_4 + C_7H_{13} \qquad (35)$$

while the dimer and part of the cyclohexene resulted from radical–radical recombination

$$C_7H_{13} + C_7H_{13} \longrightarrow C_{14}H_{26} \qquad (36)$$

$$\longrightarrow C_7H_{12} + C_7H_{14} \qquad (37)$$

Finally, the polymer was thought to be the product of secondary processes involving methylcyclohexene and the dimer or their precursors.

Our mass spectrometric results (Figure 4) show that, except possibly for $C_7H_{12}^+$, all the primary ions of methylcyclohexane react with the gas. The increase in intensity of $C_7H_{12}^+$ with pressure suggests its formation by a H_2^- transfer reaction from $C_6H_{11}CH_3$ to fragment ions, as indicated by eq 5, but it too is reactive. There is no evidence in our data for long-lived $C_7H_{14}^+$ or $C_7H_{13}^+$, sufficiently stable to be neutralized by electron recombination. Since $C_6H_{11}^+$ is a prominent fragment in the mass pattern at lower source pressures, and it must arise from unimolecular dissociation of the excited parent, the methyl radical accompanying the formation of $C_6H_{11}^+$ must also be in high abundance. Consequently, reactions 33 and 35 are a probable mode of formation of methane.

But the reactivity of the prominent primary species $C_6H_{11}^+$, $C_7H_{14}^+$, and $C_7H_{13}^+$ to give a great variety of ionic products, especially $C_8H_{17}^+$, $C_{14}H_{25}^+$, and $C_{14}H_{23}^+$, would make it appear that the latter and not the former species are among the long-lived M_1^+, M_2^+, and N^+ intermediates postulated by Holtslander and Freeman. An alternative suggestion is that $C_7H_{13}^+$ rather than $C_7H_{14}^+$ is the H_2-producing precursor, and it does so *via* the ion–molecule reactions 3 and 4 and not by electron recombination (eq 28). This proposal is consistent with the production of HD and D_2 when ND_3 is added to methylcyclohexane, because of the probable proton transfer reaction to the ammonia that competes with reactions 3 and 4. The methylcyclohexene isomers measured in high yield by Holtslander and Freeman may be accounted for by electron neutralization of $C_8H_{17}^+$.

The dimer observed by these workers, assumed to be dimethylcyclohexyl, may be the product of hydride transfer to the secondary product $C_{14}H_{25}^+$ in our mass patterns, but the dimer could also be $C_{14}H_{24}$ resulting from hydrogen atom elimination following neutralization of $C_{14}H_{25}^+$. It is interesting that these authors found two C_{14} compounds among their gas-chromatographic products. The second dimer may very well be $C_{14}H_{22}$, from neutralization of $C_{14}H_{23}^+$ (formed through eq 4). The polymer found by them may, at least in part, be the end result of continuing ion–molecule reactions of ionic products observed by us, the chains being terminated by electron neutralization.

D. Benzene and Toluene. A detailed discussion of the radiation chemistry of benzene and toluene was included in a recent report from this laboratory,[3] and a correlation of high-pressure mass spectral data with this chemistry was given there. The present results obtained with the proton spectrometer confirm the earlier work, as well as that of Giardini-Guidoni and Zocchi,[9] and are convincing evidence for the importance of dimeric ions in the radiolysis of these aromatic compounds. The agreement with the work of Giardini-Guidoni and Zocchi extends to a tertiary species in toluene, identified in our studies as $C_{15}H_{17}^+$ (mass 197) but given the assignment $C_{15}H_{16}^+$ (mass 196) in theirs. Quite probably, the entity observed in both experiments is the same species.

However, in contrast to the previous electron impact investigations,[8] the results we have obtained with the proton spectrometer show that charge transfer from fragment ions to benzene, and proton transfer to give $C_6H_7^+$ and $C_{12}H_{13}^+$, are much less probable in the latter instrument. Possibly, the negatively-charged space charge well existing in the ion source when an electron beam is used to ionize the gas holds the ions in the reactive region a longer time than in the absence of such a well when protons are employed. Electron transfer is quite sensitive to the velocity of the ionized species.[40]

E. Ethylbenzene. A thorough investigation of the γ radiolysis of gaseous ethylbenzene, as well as benzene, toluene, and the xylenes, was very recently completed by Wilzbach and Kaplan,[41] who found that the aromatic molecules were remarkably less resistant to radiation as vapors than when in a condensed state. The prominent identifiable products were (in order of decreasing G values) C_2H_6, H_2, C_2H_2, CH_4, C_2H_4, C_6H_6, and $C_6H_5CH_3$. But the ethylbenzene was converted overwhelmingly to a "polymer," which accounted for 68% of the hydrocarbon consumed. Methane, ethylene, and ethane were markedly enhanced in irradiated ethylbenzene over toluene, while C_2H_2 was reduced, observations that are evidence for the former products originating in the side chain attached to the benzene ring. Xylenes, ethyltoluenes, and propylbenzenes were also formed, but in lower yields. Although much of their data may be explained by assuming that the precursors of the products are excited target molecules, the fact that the yields are so much higher in the gas phase, that C_2H_2 is formed in moderate amount, and that ring hydrogens are replaced by methyl groups Wilzbach and Kaplan found difficult to account for on the basis of this postulate.

The high-pressure mass spectral results for ethylbenzene (Figure 7) indicate that ion–molecule reactions play important roles in the gas phase radiation chemistry of this aromatic compound. Efficient formation of dimers and trimers as well as high-molecular weight products of condensation reactions, for example

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(40) See, for example, E. W. McDaniel, "Collision Phenomena in Ionized Gases," John Wiley & Sons, Inc., New York, N. Y., 1964, pp 251–261.

(41) K. E. Wilzbach and L. Kaplan, ref 31, p 134.

$C_{23}H_{27}^+$, $C_{23}H_{29}^+$, and $C_{24}H_{32}^+$, are definite evidence for ion–molecule reaction mechanisms leading to the appearance of polymeric substances. Further, the lower hydrocarbon products and the benzene derivatives found by Wilzbach and Kaplan are neutral products accompanying several of the prominent ions observed, species which probably arise from the following plausible reactions

$$C_6H_5C_2H_5^+ + C_6H_5C_2H_5 \longrightarrow C_{15}H_{16}^+ + CH_4 \quad (38)$$

$$\longrightarrow C_{15}H_{17}^+ + CH_3 \quad (39)$$

$$CH_3\cdot + CH_3\cdot \longrightarrow C_2H_6 \quad (40)$$

$$C_{15}H_{17}^+ + C_6H_5C_2H_5 \longrightarrow C_{17}H_{21}^+ + 3C_2H_2 \quad (41)$$

$$\longrightarrow C_{17}H_{21}^+ + C_6H_6 \quad (42)$$

$$(C_6H_5C_2H_5)_2^+ + C_6H_5C_2H_5 \longrightarrow C_{22}H_{26}^+ + C_2H_4 \quad (43)$$

$$C_6H_5C_2H_4^+ + C_6H_5C_2H_5 \longrightarrow C_7H_7^+ + C_6H_5C_3H_7 \quad (44)$$

$$\longrightarrow C_7H_7^+ + C_6H_5CH_3 + C_2H_4 \quad (45)$$

F. Aniline. Apparently only a very limited amount of effort has been devoted to the radiolysis of aniline.[42–44] The main products of γ irradiation of the liquid were benzene, pyridine, the three isomeric picolines, and six isomeric lutidines. Expansion of the aniline molecule to a seven-membered ring followed by reversion to a pyridine structure was suggested as the mechanism of formation of pyridine and the picolines.[42] A positive ion, considered to be $C_6H_5NH_2^+$, has been identified in nanosecond pulse radiolysis of aniline.[44]

The growth of the $C_6H_5NH^+$ ion (mass 92) in the aniline high-pressure spectrum (Figure 8) as the concentration of gas is increased shows that it is produced mainly in chemical processes, the most likely of which are

$$C_6H_5NH_2^+ + C_6H_5NH_2 \longrightarrow C_6H_5NH^+ + \underset{\text{(pyridine)}}{C_5H_5N} + CH_3 \quad (46)$$

$$\longrightarrow C_6H_5NH^+ + \underset{\text{(picoline)}}{C_6H_7N} + H \quad (47)$$

Thus, pyridine and the picolines should be neutral components of the products of rather rapid ion–molecule reactions in gaseous aniline. Furthermore, protonated aniline $C_6H_5NH_3^+$ (mass 94) must be the ionic product of a very rapid proton transfer reaction, since even at a source pressure of 25 μ this species is a very prominent member of the spectrum. The neutral component of this reaction is probably the $C_6H_5NH\cdot$ radical, which on combination with another such entity yields azobenzene and hydrogen. Another probable mode of producing H_2 is by means of the reaction

$$C_6H_5NH_2^+ + C_6H_5NH_2 \longrightarrow C_{12}H_8N^+ + NH_3 + H_2 + H \quad (48)$$

But the outstanding characteristic of the behavior of gaseous aniline ionized and excited by proton bombardment is ionic polymerization—the rapid build-up of dimers and trimers of $C_6H_5NH^+$, $C_6H_5NH_2^+$, $C_6H_5NH_3^+$, and of the secondary ions $C_8H_5^+$ (mass 101) and $C_{12}H_8N^+$ (166). Because of limitations in the resolving power of our mass spectrometer, measurements could only be extended up to 280 atomic units. Undoubtedly, the polymerization continues to higher mass ions, whose neutralization should give rise to "polymer." The clustering of aniline molecules to ions observed by us is another example of the attachment to gaseous ions of molecules with high permanent and induced dipole moments, a phenomenon extensively studied by Kebarle and his students in ammonia and water vapor.[45–50]

G. Conclusions. Attachment of molecules to ions in the gas phase (dimerization, trimerization, etc.) appears to be a characteristic of aromatic molecules. The phenomenon is not observed in the straight chain or cyclic aliphatic analogs of aromatic compounds. The π-electron structure of the aromatic rings probably absorbs the energy available from the exoergic ion–molecule reaction, preventing the usual dissociation of the intermediate complex. This type of polymerization may be considered another illustration of the stability of aromatic systems toward radiation action.

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(42) O. S. Pascual and L. S. Bonoan, *Philippines Nucl. J.*, 1, 53 (1966); AINSE Radiation Chemistry Conference, Sydney, Australia, Oct 1963.

(43) O. S. Pascual, *Chemist's Quart.*, 6, 20 (1964).

(44) R. Cooper and J. K. Thomas, *J. Chem. Phys.*, **48**, 5103 (1968).

(45) S. K. Searles and P. Kebarle, *J. Phys. Chem.*, 72, 742 (1968).

(46) A. M. Hogg and P. Kebarle, *J. Chem. Phys.*, **43**, 449 (1965).

(47) A. M. Hogg, R. M. Haynes, and P. Kebarle, *J. Amer. Chem. Soc.*, **88**, 28 (1966).

(48) P. Kebarle, S. K. Searles, A. Zolla, J. Scarborough, and M. Arshadi, *ibid.*, **89**, 6393 (1967).

(49) P. Kebarle, R. M. Haynes, and J. G. Collins, *ibid.*, **89**, 5753 (1967).

(50) P. Kebarle, "Mass Spectrometry in Inorganic Chemistry, Advances in Chemistry Series, No. 72, American Chemical Society, Washington, D. C., 1968, p 24.