The Dissociation of Benzene (C_6H_6), Pyridine (C_5H_5N) and Cyclohexane (C_6H_{12}) by Electron Impact

A. Hustrulid, P. Kusch* and John T. Tate
Department of Physics, University of Minnesota, Minneapolis, Minnesota
(Received September 2, 1938)

The dissociation of C_6H_6, C_5H_5N, and C_6H_{12} by electron impact has been investigated with a mass spectrograph. Four doubly charged and thirty-one singly charged positive ions were observed in the dissociation of benzene. The relative abundance, for electrons of 72 volts energy, and the appearance potential are given for each ion. The first and second ionization potentials of benzene are 9.8 ± 0.1 and 17.2 ± 1.0 volts, respectively. The ionization potential of C_5H_5N is 9.8 ± 0.2 volt and of C_6H_{12}, 11.0 ± 0.2 volt. In each of the three vapors, certain of the ions resulting from the dissociation process have a doublet character. The components have a constant energy separation independent of magnetic field. The components also have different appearance potentials. The interpretation given is that these particular ions are formed by two different processes, one of which imparts a *definite* amount of kinetic energy to the ion.

INTRODUCTION

THE pioneer work of Smyth[1] and more recent studies[2-4] have shown that the identification with a mass spectrograph of the ions formed by electron impact in vapors is capable of giving valuable information about the molecular structure of these vapors. Directly observable are the nature (M/e value) of the ion formed, the minimum electronic energy which must be imparted to the molecule to produce this ion, and the relative probability, for any particular electron energy of impact, of forming ions of various kinds. In addition, a second experiment such as Lozier's[5] may determine the kinetic energy acquired by the ion in the dissociation process. As has been illustrated in previous work, observations of this kind may, when coupled with known thermochemical data, lead to new information about such things as heats of dissociation of the molecule, and of the molecular ion, ionization potentials of the molecule, of the molecular ion, and of the fragments into which the molecule may dissociate. Indirectly it is often possible to estimate bond energies of various kinds.

The purpose of the present paper is to describe the results obtained in an investigation of the dissociation of benzene (C_6H_6) and of related molecules under electron impact. The structure of the benzene molecule has been extensively studied by physical and chemical means. It was hoped that the appearance potentials and the probabilities of formation of the various ions produced in benzene might be interpreted in terms of the known structure of benzene and thus lead to some general guiding principle for the interpretation of the observed appearance potentials and probabilities of formation of ions produced from other complicated molecules under electron impact. In this hope we have been largely disappointed. The results, though interesting in themselves, have not been amenable to satisfactory interpretation in terms of known characteristics of the benzene molecule.

Previous studies of the dissociation of benzene by electron impact have been made by Linder,[6] and Friedlander and Kallman.[7] Conrad[8] studied the decomposition of benzene in a positive ray tube.

THE MASS SPECTROGRAPH

The apparatus is similar to that described by Nier.[9] The essential difference is that the filament is enclosed and has a separate pumping lead. The purpose of the housing around the filament is

* Now at Columbia University.
[1] For references to earlier work see Smyth, Rev. Mod. Phys. **3**, 347 (1931).
[2] Smith, Phys. Rev. **51**, 263 (1937).
[3] Kusch, Hustrulid and Tate, Phys. Rev. **52**, 843 (1937).
[4] Hipple, Phys. Rev. **53**, 530 (1938).
[5] Lozier, Phys. Rev. **46**, 268 (1934).

[6] Linder, Phys. Rev. **41**, 149 (1932).
[7] Friedlander and Kallman, Zeits. f. physik. Chemie **B17**, 265 (1932).
[8] Conrad, Trans. Faraday Soc. **30**, 215 (1934).
[9] Nier, Phys. Rev. **50**, 1041 (1936).

to prevent products of dissociation at the filament from diffusing back into the ionizing region. That the differential pumping system apparently fulfilled the purpose of preventing products of thermal dissociation from diffusing back into the ionizing region is evidenced by the fact that the character of the mass spectrum remained the same over rather wide ranges of pressure in the ionizing chamber. The metal parts of the apparatus were built entirely of Nichrome V with Pyrex tubing for supports and insulators.

Before assembly the metal parts were baked out in a vacuum quartz furnace. After assembly the whole apparatus was enclosed in an oven and baked out at 350°C for 36 hours. The residual pressure in the tube after this treatment, as determined by an ionization gauge, was less than 5×10^{-7} mm Hg.

A large water-cooled solenoid whose axis was parallel to the main tube, surrounded the entire apparatus and could give a magnetic field of 3000 gauss in the region of the analyzer. The resolving power was such that it was possible to detect the mercury isotopes separated by one atomic mass unit at 200. Although no careful observations were made, it was estimated that the background between the peaks was approx-
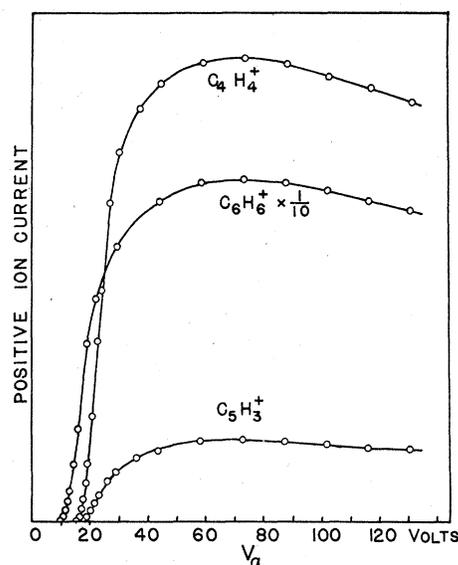

FIG. 1. Efficiency of formation of $C_6H_6^+$, $C_5H_3^+$ and $C_4H_4^+$ as a function of electron energy (V_a).

imately one-half the average peak height when using the maximum available magnetic field.

STUDY OF BENZENE

Mallinckrodt's thiophene-free benzene was fractionally crystallized five times. About one-half of the end product was then distilled off under reduced pressure and the remaining portion placed in a bulb connected to the ionizing region of the mass spectrograph by a fine capillary. The bulb could be maintained at any desired temperature. With the source at 0°C, the combined rate of leak and pumping speed was such as to give a pressure of about 10^{-4} mm Hg in the main tube. The only observed ions which could not reasonably be assumed to originate from dissociation of the benzene were those due to water. These peaks were at all times of *very low* intensity. A few of the peaks observed in this investigation had such M/e values that they might conceivably be due to CO, CO_2 or other vapors often observed as impurities in mass spectrographs. Since the intensity of any questionable peaks, for example, $M/e = 28$, was the same function of pressure as that of peaks undoubtedly due to benzene, it is safe to say that these peaks arose from the dissociation of benzene

TABLE I. *Ions formed in benzene by electron impact. Their appearance potentials and relative abundances are for electrons of 72 volts energy.*

M/e	Ion	Appearance Potential (volts)	Abundance	M/e	Ion	Appearance Potential (volts)	Abundance
78	$C_6H_6^+$	9.8±0.1	100.0	15	CH_3^+		0.01
77	$C_6H_5^+$	14.5±0.3	15.2	14	CH_2^+		0.02
76	$C_6H_4^+$	15.0±0.3	4.6	13	CH^+		0.03
75	$C_6H_3^+$	21.9±0.5	1.7	12	C^+		0.05
74	$C_6H_2^+$	23.9±0.5	4.0				
73	C_6H^+	33.7±0.5	1.3	2	H_2^+		0.15
72	C_6^+	41.9±2.5	0.2	1	H^+		0.2
63	$C_5H_3^+$	16.8±0.3	2.6	39½	$C_6H_6^{++}$	27.0±1.0	1.8
62	$C_5H_2^+$	19.1±0.5	0.6	38½	$C_6H_5^{++}$	30.4±2.5	0.18
61	C_5H^+	27.4±1.0	0.5	37½	$C_6H_3^{++}$	39.8±2.5	0.42
60	C_5^+	44.0±2.5	0.2	30½	C_6H^{++}		0.015
52	$C_4H_4^+$	15.5±0.3	13.5	39'	$C_3H_3^+ + KE$	>39	0.3
51	$C_4H_3^+$	18.5±0.3	15.7	38'	$C_3H_2^+ + KE$	>39	0.4
50	$C_4H_2^+$	18.3±0.5	13.3	37'	$C_3H^+ + KE$	>39	0.2
49	C_4H^+	27.6±1.0	2.1				
48	C_4^+	40.4±2.5	0.3	27'	$C_2H_3^+ + KE$	>39	0.09
39	$C_3H_3^+$	16.1±0.3	6.6	26'	$C_2H_2^+ + KE$	>39	0.14
38	$C_3H_2^+$	23.0±0.5	3.6*	25'	$C_2H^+ + KE$	>39	0.03
37	C_3H^+	27.4±1.0	2.5*				
36	C_3^+	45.0±3.0	0.3	15'	$CH_3^+ + KE$	29±3	0.1
28	$C_2H_4^+$		0.2	14'	$CH_2^+ + KE$		0.003
27	$C_2H_3^+$	21.1±1.0	1.3	13'	$CH^+ + KE$		0.002
26	$C_2H_2^+$	17.9±1.0	1.1	12'	$C^+ + KE$		0.002
25	C_2H^+	27.1±3.0	0.14				
24	C_2^+		0.03				

* Includes $C_6H_4^{++}$ and $C_6H_2^{++}$.

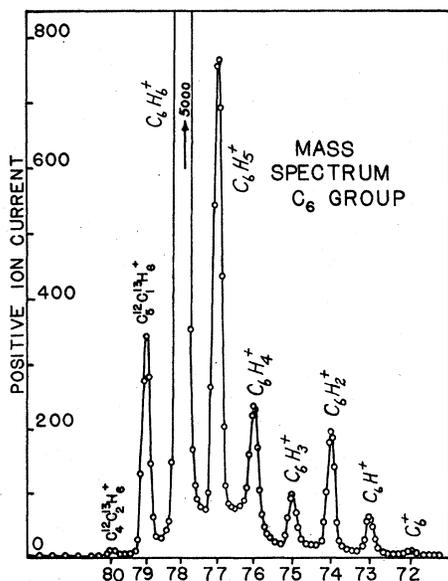FIG. 2. Mass spectrum of ions with M/e values from 80 to 72.

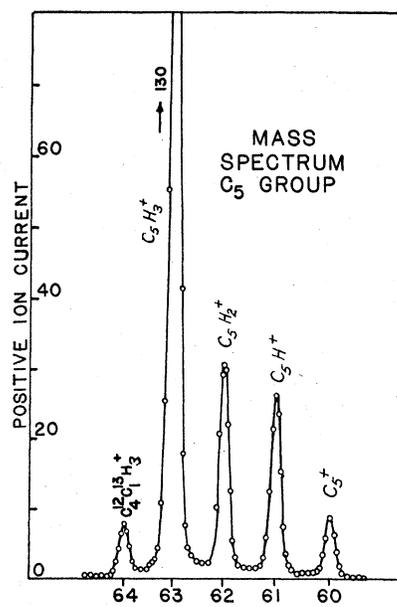FIG. 3. Mass spectrum of ions with M/e values from 64 to 60.

FIG. 4. Mass spectrum of ions with M/e values from 53 to 48.

and that impurities did not exist in important amounts.

Table I gives a summary of the results obtained for benzene. The nature of the ions, their appearance potentials, if determined, and their relative probabilities of formation for incident electrons of 72 volts energy are tabulated. The primed M/e values refer to rather sharp peaks on the high mass side of the corresponding peaks without primes. No integral M/e values could be assigned to these peaks by a simple comparison with the known M/e values of neighboring peaks. The evidence for associating these peaks with the M/e values assigned to them in Table I will be reviewed later. Suitable corrections to the abundances have been made for the presence of the carbon isotope of mass 13. It is possible that peaks caused by doubly charged ions of even mass (e.g. $C_4H_4^{++}$) coincide with some of the peaks of lower mass ($C_2H_2^+$), but this is unlikely since no doubly charged ions of odd mass (e.g. $C_4H_3^{++}$) were observed except for the C_6 group. In that case, the ions $C_6H_6^{++}$, $C_6H_5^{++}$, $C_6H_3^{++}$, C_6H^{++} were definitely observed but the ions $C_6H_4^{++}$ and $C_6H_2^{++}$, if they exist, coincide with $C_3H_2^+$ and C_6H^+. A search was made for negative ions, but none was found.

The ionization potential of benzene was found to be 9.8 ± 0.1 volt. Boucher[10] and Friedlander and Kallman[7] have obtained the values 9.6 ± 0.1 volt and 9.5 volts, respectively by direct measurement. Price and Wood[11] give the value 9.19

[10] Boucher, Phys. Rev. 19, 189 (1922).
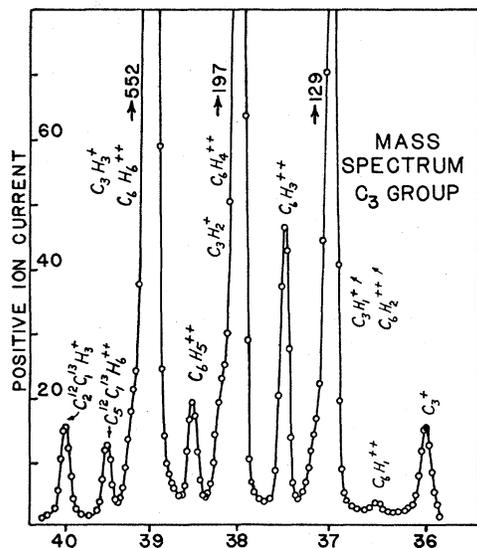[11] Price and Wood, J. Chem. Phys. 3, 439 (1935).

FIG. 5. Mass spectrum of ions with M/e values from 40 to 36.

±0.005 volt obtained from spectroscopic evidence. The present determination of the ionization potential was made by admitting a mixture of benzene and mercury vapor to the mass spectrograph and observing the ion current as a function of electron energy near the threshold energy. The pressure was adjusted to give approximately the same slope to the curves for benzene and mercury. This method of estimating the ionization potential eliminates much of the uncertainty caused by contact potential and velocity distribution of electrons. The variation in the individual measurements of the ionization potential of benzene is much less than would seem to be the case from the probable error given here. The true ionization potential may differ from the observed one because of factors depending on the velocity distribution of electrons and the limiting sensitivity of the amplifier.

Price and Wood[11] also predict 11.7±0.3 volt for the second ionization potential of benzene. The value obtained in the present work is 17.2 ±1.0 volt. The value given by Price and Wood[11] is incompatible with the present observations.

The appearance potentials of ions other than $C_6H_6^+$ were determined by comparison with the ionization potential of benzene. The only appearance potentials found in the literature, other than the ionization potential, are those given by

Friedlander and Kallman.[7] Their values in volts are as follows: $C_6H_4^+$, 18.5; $C_6H_2^+$, 25; and $C_2H_2^+$, 18. They give only upper or lower limits for the appearance potentials of the other ions which they identified.

Figure 1 gives sample curves for the relative efficiencies of formation of the more abundant ions as a function of the electron energy. It is observed that they are of the usual form. The curves for the other ions are similar.
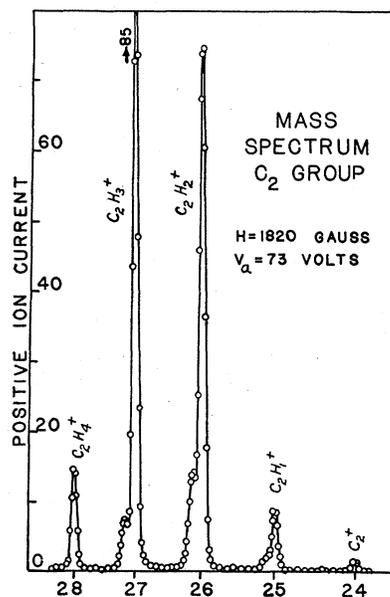

FIG. 6. Mass spectrum of ions with M/e values from 28 to 24.

Figures 2–7 inclusive show a typical mass spectrum for values of M/e from 80 to 12. These curves have not been corrected for small differences in electron current or gas pressure in going from one group to the next. The ions H_2^+ and H^+ were also found as given in Table I. A striking feature of the mass spectrum curves is that some of the peaks appear as doublets as shown in Figs. 6, 7 and 8. The component on the high mass side is the less intense one, except in the case of CH_3^+ where, it is many times more intense than the component of apparently lower mass. The actual abundance of these "high mass" ions is considerably greater than the values given in Table I arrived at by measuring the peak heights, if they are ions with initial kinetic energy as interpreted in the following discussion, because

the solid angle from which these ions are collected is a small fraction of 4π steradians.

The difference in the accelerating potential required to focus an ion peak and the satellite of the peak on to the exit slit of the analyzer is constant regardless of the magnetic field which is used. Since the total accelerating potential which is required to focus is smaller at low than at high magnetic fields, the satellite is more nearly resolved from the main peak at low magnetic fields, even though the general resolution increases with the magnetic field. This effect is indicated for the peaks of $M/e = 26$ and 27 in Figs. 6, 8(a) and 8(b) observed with magnetic fields of 1820, 1065 and 1320 gauss, respectively. The satellites of the peaks in the C_3 group, shown in Fig. 5, may, in the same way, be resolved from the main peak by suitably decreasing the magnetic field. No integral M/e

FIG. 7. Mass spectrum of ions with M/e values from 15 to 12.

value may then be assigned to the satellite peaks, but it is reasonable to assign the same M/e value to these peaks as to the main peaks from which they are separated by a constant energy difference.

The appearance potentials of the ions of the satellite peaks are, in general, higher than those of the ions of the main peaks. This is shown in Fig. 8(b) and 8(c) where the 26 and 27 peaks have been observed for different energies of the

electrons producing the dissociation but for otherwise identical experimental conditions. No careful determination was made of the appearance potentials of the satellite peaks because of the low general resolution when the field was low enough to resolve the satellite peaks from the main peaks.

It seems reasonable to suppose that the satellite peaks are not ghosts produced by the mechanical and electrical arrangement of the mass spectrograph. The satellites of neighboring peaks bear no constant intensity relationship to the main peaks, and the peak caused by N_2^+ which appears in the same region as peaks which possess satellite, shows no trace of a satellite.

The satellite peaks are believed to be caused by ions to which the dissociation process has imparted a large kinetic energy lying within a *small* range. It can be shown that ions having kinetic energies in a small range will give a peak on the high mass side of the peak for ions of no kinetic energy. The momenta of the ions upon dissociation will be distributed over large angles, but only the momenta lying within the angle defined by the entrance slits of the analyzer will
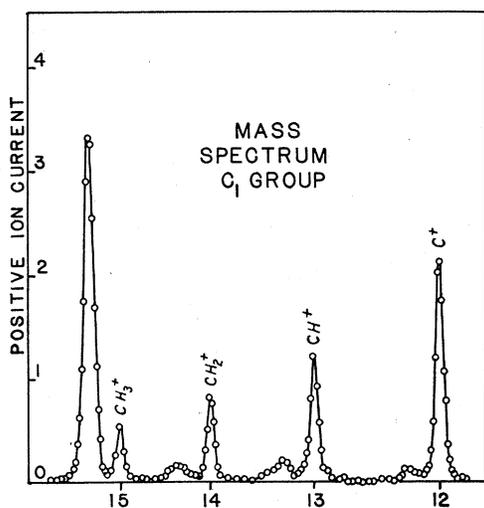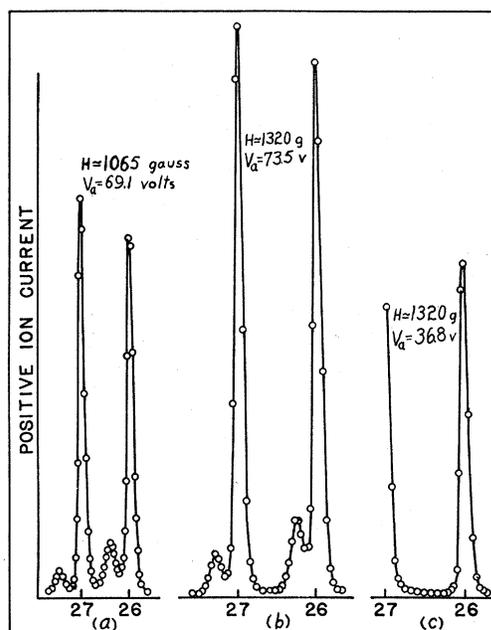

FIG. 8. Mass spectrum of ions with M/e values 26 and 27 for different values of magnetic field and different values of accelerating potentials (V_a) applied to electrons.

contribute to the observed peaks. If ions acquire a range of kinetic energy in the dissociation process, the peak caused by the ions will be broadened on the high mass side of the peak corresponding to no kinetic energy. If only a small proportion of the ions have an appreciable kinetic energy, they will appear as a foot on the high mass side of the peak. Such an effect has been observed by Tate, Smith and Vaughan,[12] and by Nier and Hanson[13] for H^+.

The most reasonable hypothesis which may be advanced for the occurrence of these peaks with their satellites is that the ion in question may be produced by at least two distinct dissociation processes. When the ions are produced by one of these processes, they acquire a large kinetic energy which is manifested by a displacement of the peak from its ideal position. The high appearance potentials which are associated with the ions corresponding to the satellite peaks suggest that these ions may be produced by the spontaneous dissociation into several parts of a large doubly charged ion which is extremely unstable. Such a spontaneous dissociation would require the conservation of momentum; this in turn requires that the lighter of two ions carry away more kinetic energy than the heavier of the two ions. A rough measurement of the kinetic energies showed that this condition is qualitatively obeyed.

While it is true that the appearance of the whole mass spectrum is rather surprising, certain features of the mass spectrum are of particular interest. For a group consisting of ions containing a constant number of carbon atoms (6, 5, 4 or 3) and a variable number of hydrogen atoms, the probability of formation of each ion decreases regularly with a decrease in the number of hydrogen atoms. Significant exceptions occur in the case $C_6H_3^+$ which is less abundant than both $C_6H_4^+$ and $C_6H_2^+$, and in the case of $C_4H_4^+$, $C_4H_2^+$ which have an approximately equal abundance. The group containing 5 carbon atoms is much weaker than the groups containing 6, 4, or 3 carbons and the ions $C_5H_5^+$ and $C_5H_4^+$ are entirely absent. The doubly charged ion $C_6H_3^{++}$ has, however, a relatively large intensity.

Pyridine[14]

Because pyridine (C_5H_5N) is chemically similar to benzene, a brief study of the ions produced from it by electron impact was made. The mass spectrograph is unable to distinguish between the ions $C_nH_m^+$ and $C_{n-1}H_{m-2}N^+$ and, therefore, no careful study was made of the relative abundance of the ions and of their appearance potentials.

The mass spectrum of the ions produced by the dissociation of pyridine has the same general features as that of the ions produced from benzene. The ionization potential was found to be 9.8 ± 0.2 volt, the same as that of benzene within the limits of error. The abundance of the group of ions containing 5 carbons or 4 carbons and one nitrogen atom is extremely low. The low abundance of such ions is much more pronounced in the case of pyridine than in the case of benzene. It is not possible to determine whether ions containing 5 carbon atoms and 4 or 5 hydrogen atoms are produced, because the ions may not be identified uniquely.

As in the case of benzene, the ion $C_5H_3N^+$ is less abundant than either of the ions $C_5H_2N^+$ and $C_5H_4N^+$. The group of ions containing 4 carbons or 3 carbons and one nitrogen is relatively much more abundant than the corresponding group for benzene. The intensity of the peak caused by ($C_4H_4^+ + C_3H_2N^+$) is about the same as that of the peak caused by $C_5H_5N^+$.

Peaks which possessed satellites were observed in the C_2 or CN group of peaks. Apparently the same conditions which give rise to ions of high kinetic energy in the dissociation of benzene exist for the dissociation of pyridine.

Cyclohexane

The ions observed as dissociation products of cyclohexane (C_6H_{12}) under electron impact and the relative abundances at an electron energy of 72 volts are tabulated in Table II. In addition to the ions tabulated there, the ions $C_6H_3^{++}$, $C_6H_5^{++}$, $C_6H_7^{++}$ and $C_6H_9^{++}$ were observed. Other doubly charged ions may be produced which are masked by singly charged ions of an

[12] Tate, Smith and Vaughan, Phys. Rev. 48, 525 (1935).
[13] Nier and Hanson, Phys. Rev. 50, 722 (1936).

[14] Professor Lauer of the Chemistry Department kindly supplied us with samples of pyridine and cyclohexane.

TABLE II. *Nature and relative abundances of ions formed in cyclohexane by electrons with 72 volts energy.*

ION	$n=6$	5	4	3	2	1	0
$C_nH_{12}^+$	100.						
$C_nH_{11}^+$	5.9	1.2					
$C_nH_{10}^+$	0.4	1.2					
$C_nH_9^+$	0.6	46.4	3.8				
$C_nH_8^+$	0.2	3.6	223.				
$C_nH_7^+$	0.8	5.1	78.	42.			
$C_nH_6^+$	1.2	0.5	13.	77.	1.0		
$C_nH_5^+$	1.2	1.0	8.4	155.	15.6		
$C_nH_4^+$	0.1	0.1	2.4	11.7	13.3	0.2	
$C_nH_3^+$	0.1	0.6	5.3	50.2	27.6	3.0	
$C_nH_2^+$	0.3	0.3	3.9	4.2	3.4	0.3	
C_nH^+	0.1	0.2	0.5	2.2	0.2	0.1	—
C_n^+	0.2					0.1	—

equal M/e. The abundance values given in Table II have been corrected for the presence of the carbon isotope of mass 13.

The peak for $C_2H_4^+$ shows the presence of a satellite and thus indicates that the ion $C_2H_4^+$ may be produced by at least two different processes, in one of which the ion acquires a considerable kinetic energy.

The appearance potentials of only three ions were measured. The ionization potential of cyclohexane was found to be 11.0 ± 0.2 volt. The very abundant ions $C_4H_8^+$ and $C_3H_5^+$ were found to have appearance potentials of 11.7 ± 0.3 and 13.5 ± 0.3 volt, respectively.

A general appearance of the mass spectrum of the ions produced from cyclohexane differs markedly from that of the ions produced from benzene. The ions in the group containing 5 carbon atoms are less abundant than those in the groups containing 6, 4, and 3 carbon atoms, but the effect is less pronounced than in the case of benzene or pyridine. The ions $C_5H_5^+$ and $C_5H_4^+$, which were entirely absent in the case of benzene, do appear as dissociation products of cyclohexane. Their appearance in the present case precludes the possibility that they do not occur as dissociation products of benzene because of an inherent instability.

It is noteworthy that the ions $C_4H_8^+$ and $C_3H_5^+$ are much more abundant than the ion $C_6H_{12}^+$. This is contrary to the more usual case observed in electron impact experiments where the probability of ionization alone is greater than the probability of ionization plus dissociation. However, this agrees with the results of Hipple[4] in a study of ethane and Stewart and Olson[15] in a study of propane and butane.

[15] Stewart and Olson, J. Am. Chem. Soc. **53**, 1236 (1931).

DISCUSSION

Paucity of thermochemical and spectroscopic data and of work on simpler molecules prohibits the making of a satisfactory analysis of the processes by which the ions are formed. If one assumes, however, that the ring structure is maintained and that all free valences are taken care of by formation of double bonds or removal of a valence electron, something can be said about the possible processes. The sole test which is available to check the analysis will be the value obtained for the ionization potential of the new ion. The appearance potential of an ion which lacks one or more of the atoms of the parent molecule is the sum of three quantities: a dissociation energy, an ionization potential and the total minimum excitational and mutual kinetic energy with which the products can dissociate or $A=D+I'+E+K.E.$ The minimum excitational and kinetic energy with which the products dissociate is usually small and one may define a new quantity I, which is nearly equal to I', by $A-D=I$. This new I must have a value which is reasonable for the ionization potential of hydrocarbons and, therefore, should be in the range 9.0 to 15.0 volts.

For example:

$$I'(C_6H_6) = 9.8 \text{ volts}$$
$$I'(C_6H_{12}) = 11.0 \text{ volts} \Big\} \text{Present work}$$
$$I'(C_5H_5N) = 9.8 \text{ volts}$$

$$I'(CH_4) = 13.1 \text{ volts} - \text{Smith}[2]$$
$$I'(C_2H_2) = 11.2 \text{ volts} - \text{Tate, Smith and Vaughan}[12]$$
$$I'(C) = 11.2 \text{ volts}$$
$$I'(H) = 13.5 \text{ volts}$$

Since A has been measured for many of the ions, a value of I may be obtained by calculating D. In making this calculation it will be assumed that the bond energies are additive.

Pauling and Sherman[16] and Dietz[17] have computed the bond energies as they occur in organic molecules. Such determinations for bonds involving carbon must always be made from thermochemical data, and these are in doubt by the uncertainty in the heat of sublimation of

[16] Pauling and Sherman, J. Chem. Phys. **1**, 606 (1933).
[17] Dietz, J. Chem. Phys. **3**, 58 (1935).

TABLE III. *Calculated values of the heats of dissociation, D, for various processes and the corresponding values of the ionization potentials for the organic radicals involved.*

PROCESS $C_6H_6 \rightarrow$	DISSOCIATION ENERGY, D.	IONIZATION POTENTIAL OF RESULTING RADICAL
$C_6H_5^+ + H$	4.0 volts	10.5 volts
$C_6H_4^+ + 2H$	5.5 volts	9.5 volts
$C_6H_3^+ + 3H$	9.4 volts	12.5 volts
$C_6H_2^+ + 4H$	10.9 volts	13.0 volts
$C_6H^+ + 5H$	15.0 volts	18.7 volts
$C_6^+ + 6H$	16.5 volts	25.4 volts

carbon, $L(C)$. In considering the dissociation of benzene one is, however, interested only in the energy changes which occur when C_6H_6 is dissociated to a small extent into very similar forms. Such energy differences would not involve $L(C)$.

From the values given by Dietz for the bond energies, i.e., C—H bond = 3.97 volts, C—C bond = 3.17 volts and C=C bond = 5.65 volts,[18] D and I have been calculated for various dissociation processes of benzene and are given in Table III.

If it is assumed that the group of ions containing six carbons is produced by the removal of the hydrogen in atomic form and that the ion itself is ring-shaped with no free valences, reasonable values are obtained for the ionization potentials of C_6H_5, C_6H_4, C_6H_3 and C_6H_2 as is shown in Table III. The same reasoning gives values which are higher than might be expected for C_6H and C_6. These values cannot be reduced on the basis of the above picture, since as much energy as possible has been taken up as dissociation energy. Several possibilities occur as an explanation. The ionization potentials of C_6 and C_6H may actually be higher than the ionization potentials of stable hydrocarbons; the binding energies calculated from data on stable hydrocarbons may not be applicable to these hydro-
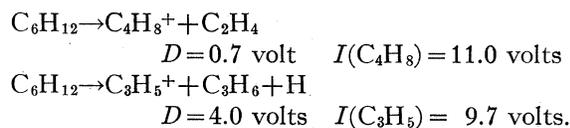
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[18] The values 4.0, 3.2 and 5.7 have been used in the calculation.

carbons which are not chemically known; or the picture of the ion may be inaccurate.

If a dissociation process which will give reasonable values of the ionization potentials for the first members of the group is assumed for any other group, the same sort of discrepancy is observed. If the ions C_nH^+ and C_n^+ are to have reasonable ionization potentials, the neutral fragments which are produced must be much smaller than they are in the case of $C_nH_2^+$, $C_nH_3^+$. That this result is not entirely due to uncertainties in the calculation is manifested by the fact that an inspection of the appearance potentials in Table I indicates a sudden increase in the appearance potential for C_nH^+ and C_n^+.

It may be seen from an inspection of the experimental data and from a few simple calculations that when the ions $C_5H_3^+$, $C_5H_2^+$, $C_4H_4^+$, $C_4H_3^+$, $C_3C_3^+$ and $C_3H_2^+$ are formed the dissociation is not very extensive. The un-ionized portion of the molecule probably leaves as a single large fragment and as many hydrogen atoms as cannot be easily attached to the carbons of the fragment. This conclusion is not in accord with one which Smith[2] has made about the simpler hydrocarbon, methane, that of all the possible dissociation processes, those which require the greatest minimum energy actually occur.

In the same way as above one can make the calculations for the ions of cyclohexane for which the appearance potentials have been determined.

$C_6H_{12} \rightarrow C_4H_8^+ + C_2H_4$

$\qquad D = 0.7$ volt $I(C_4H_8) = 11.0$ volts

$C_6H_{12} \rightarrow C_3H_5^+ + C_3H_6 + H$

$\qquad D = 4.0$ volts $I(C_3H_5) = 9.7$ volts.

These processes seem very likely to be the correct ones because in either case the compounds involved are known and stable and the ionization potentials for the new radicals have reasonable values.