

Dissociative Channels for the Production of Positive Ion Fragments by Electron Impact on Benzene

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Uma geometria de colisão de feixes cruzados de elétrons e moléculas é usado na medida de valores relativos de seção de choque e limiares de energias na produção de vários íons positivos, por colisão de elétrons com benzeno. Estes limiares são também calculados pela diferença dos calores totais de formação dos produtos menos os dos reagentes. Os valores de formação são também calculados pelo método MNDO. Pela comparação dos dois valores de limiar conseguimos prever os possíveis canais de dissociação. Vinte e dois fragmentos de íons positivos foram observados.

A crossed electron and molecular beam collision geometry has been used to measure relative values of cross sections and threshold energies for the production of various positive ions by electron impact on benzene. These thresholds are also calculated by subtracting the total heat of formation of products from the total heat of formation of reactants. The heats of formation are obtained by performing Modified Neglect of Differential Overlap (MNDO) calculations. By comparing the two threshold values we have been able to predict the various possible channels of dissociation. In all, twenty two positive ion fragments are observed.

Key words: benzene; electron impact; dissociative channels; MNDO.

Introduction

Recently there has been a great interest in the electron impact dissociation and ionization properties of organic molecules such as methane and benzene because of their applications in the field of plasma deposition^{1,2} of diamond-like films. However, a closer look at the literature shows that for benzene not much cross-section information is available. Relative values of abundances of various ion fragments have been published only for 70 eV electron impact energy³. The threshold energies for the production of ionic fragments have been published for a few selected species. They have been determined by a variety of techniques such as photo-ionization⁴, retarding potential⁵, and electron impact⁶. Although the various channels through which benzene dissociates to pro-

duce $C_6H_6^+$, $C_6H_5^+$, $C_6H_4^+$, $C_4H_4^+$, $C_3H_3^+$, $C_2H_2^+$ have been estimated by Natalis and Franklin⁶ there are 16 other fragments, seen in our mass spectrum, for which these data are not available.

We, therefore, undertook the study of electron impact properties of benzene. We measured the values of appearance energies and relative abundances of species for electron impact energies ranging from threshold to 500 eV. Threshold energies for twenty two ionic fragments were experimentally determined. Heats of formation of all ionic fragments were computed quantum mechanically from which the various channels of dissociation were characterized. In the following, the experimental apparatus and the method of data acquisition

are described, details on the computational procedure are provided, and the results are discussed.

Experimental Apparatus and Method

A detailed description of the experimental apparatus and method of data acquisition has been published previously⁷. Briefly, it consists of an electron gun which generates a pulsed electron beam of desired energy and of widths of about 100 ns. This beam crosses at 90 degrees a beam of benzene molecules which is produced by flowing the benzene vapor through a capillary array. A pair of wire meshes of about 95% transmission are placed at 90° to both beams. An electrical pulse of about 50 V/cm is applied between these meshes to extract the ions from the collision region. The sequence of the electron beam pulse and the electrical pulse is such that at the time when the electron beam is present in the collision region the voltage on the wire meshes is at the ground potential (0 volts). However, as soon as (within about 100 ns) the electron beam interaction (duration of about 100 ns) is over the extraction pulse of a few micro-seconds width is applied to the wire meshes. This sequence of application of pulses ensures the collection of all ions, even of those which are born with high kinetic energies. These extracted ions are then focused at the entrance aperture of a quadrupole mass spectrometer by the help of an Einzel lens. The quadrupole selects an ion of a particular mass. At the exit end of the mass spectrometer a charged particle detector is placed. Each detected ion produces an electrical pulse which passes through a discriminator and an amplifier. The number of these pulses per second gives a measure of intensity of ions produced as a result of electron collisions with benzene. This number is stored in a multichannel scalar either as function of ionic mass for a fixed electron impact energy or as a function of electron impact energy for a fixed ionic mass. Thus, two different types of spectra are accumulated. The former are called cracking patterns and the latter are excitation function curves. The cracking patterns provide relative values of ion abundances (which are proportional to the relative values of cross sections) for the various electron impact energies. The excitation functions are used to obtain appearance potentials of the ionic fragments. Excitation function curves recorded for 0 to 50 eV electron impact energy range are used to determine the threshold energies where the ion of a particular mass begins to appear. In the present work the energy spread of the electron beam was estimated to be about 0.5 volts. Therefore, in the threshold region instead of observing a sharp rise in the ion signal a gradual rise is seen. The threshold energy was obtained by extrapolating the linear portion of this curve near the rise from zero to the zero ion intensity. The energies were calibrated using the excitation function curve for $C_6H_6^+$ for which the threshold energy of 9.25 eV is well known⁸.

The response of the system as a function of charge to mass ratio was determined by measuring the mass spectra of a commercially prepared mixture of gases (He, Ne, Cl₂, Ar, and Kr) of known concentrations. In addition, this was verified by employing the technique described by Krishnakumar and Srivastava⁷. This response profile was used to calculate the relative abundances for the ionic fragments of benzene as a function of electron impact energy.

Calculation of Threshold Energies

Quantum mechanical calculations were carried out using the AMPAC program available from the Quantum Chemistry Program Exchange⁹. This program was used to compute heats of formation and optimized cationic geometries using MNDO Hamiltonians for self consistent field calculations with a restricted Hartree-Fock (RHF) method. In some cases (see **Results and Discussion**) the RHF method was substituted for the unrestricted Hartree-Fock method in order to achieve self-consistency of the field. The program was developed by Michael Dewar and his group out of the University of Texas, Austin, and gives heats of formation of hydrocarbon cations, on average, within 0.25 eV from the measured values¹⁰. The largest deviation was for CH_3^+ (0.69 eV), otherwise all deviations were within 0.50 eV.

Threshold energies were estimated using the heats of formation of benzene and its fragments. Heats of formation of the cationic fragments were computed quantum mechanically and those of benzene and the neutral fragments were those reported in the literature, as reported below. The heats of formation are as follows: for benzene⁸ (0.86 eV), linear C_3H_3 ¹¹ (3.56 eV), cyclic C_3H_3 ¹² (4.55 eV), C_2H_4 ¹³ (0.54 eV), C_2H_3 ¹⁴ (2.75 eV), C_2H_2 ¹³ (2.36 eV), C_2H ¹² (5.85 eV), C_2 ¹³ (8.62 eV), CH_4 ¹³ (-0.77 eV), CH_3 ¹⁶ (1.51 eV), CH_2 ¹⁷ (4.03 eV), CH ¹⁵ (6.17 eV), C ¹⁷ (7.43 eV), and H ¹⁸ (2.26 eV). No reliable data for the heats of formation are available for the neutral species, C_3 , C_3H , and C_3H_2 and therefore, processes leading to their formation were not considered. This results in a gap in the analysis of threshold energies for only two of the cationic species, namely $C_3H_3^+$ and $C_3H_2^+$ (see **Results and Discussion**). No branched ionic isomers were considered.

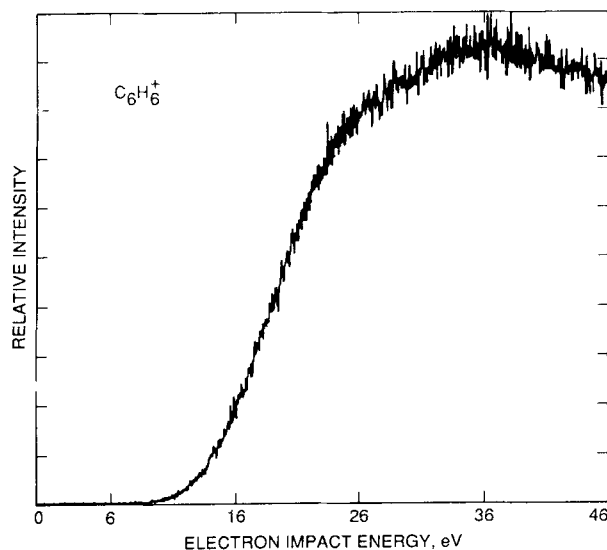


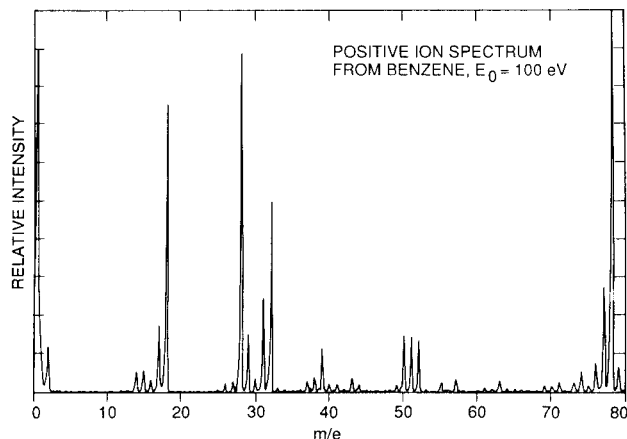
Figure 1. The uncorrected cracking pattern for benzene with an electron impact energy of 100 eV. Several peaks, such as the one at mass number = 18, are due to impurities.

Table 1. Threshold energies of the dissociative ionization products in eV.

Mass Number	Formula of Ionic Fragment	Present work	Previous work	Method ^a	Ref.
78	C ₆ H ₆ ⁺		9.24	Many studies	8
77	C ₆ H ₅ ⁺	13.9	14.1 13.8	RPD PI	5 4
76	C ₆ H ₄ ⁺	13.9	14.1 14.2	EI RPD	6 5
75	C ₆ H ₃ ⁺	18.5			
74	C ₆ H ₂ ⁺	24.2			
73	C ₆ H ⁺	24.3, 29.7 ^b	29.0	RPD	5
72	C ₆ ⁺	22.37 ^c			
63	C ₅ H ₃ ⁺	16.9	15.7	RPD	5
62	C ₅ H ₂ ⁺	18.1			
61	C ₅ H ⁺	20.4			
60	C ₅ ⁺	15.36 ^c			
52	C ₄ H ₄ ⁺	15.6	14.5	RPD	5
51	C ₄ H ₃ ⁺	19.7	17.6	RPD	5
50	C ₄ H ₂ ⁺	20.0	17.5	RPD	5
49	C ₄ H ⁺	27.5			
48	C ₄ ⁺	17.31 ^c			
39	C ₃ H ₃ ⁺	17.7	14.7	RPD	5
38	C ₃ H ₂ ⁺	22.8			
37	C ₃ H ⁺	25.0			
36	C ₃ ⁺	17.32 ^c			
27	C ₂ H ₃ ⁺	20.5	19	RPD	5
26	C ₂ H ₂ ⁺	20.4	18.6 19	EI RPD	6 5

^a The abbreviations are RPD: retarding potential difference, PI: photoionization, EI: electron impact.

^b Although generally a strong signal, a weak signal at low energy is apparent. It could be background.

**Figure 2.** The excitation spectrum from 0 to 50 eV for benzene with detection set at $m/e = 78$.

Results and Discussion

Over 100 ionic isomers have been considered in this study. For convenience, a nomenclature was devised. Consider 5113. The first number gives the number of carbons, i.e. 5. The next series of numbers indicates the position of the hydrogen on the 5-carbon chain. Thus, two hydrogens are on C-1, the end carbon, and one hydrogen is in the third position, namely [CH₂ - C - CH - C - C]⁺. A "C" preceding the first number indicates a cyclic structure.

Figure 1 shows the mass spectrum or cracking pattern for benzene with an electron energy of 100 eV. Other cracking patterns were measured for 20, 40, and 75 eV. Figure 2 shows a representative excitation spectrum for mass number 78. The threshold energies for 22 ionic fragments were measured with an accuracy of 0.5 eV and are listed in Table 1.

MNDO calculations using a restricted Hartree-Fock procedure were performed for most possible isomers of each fragment. For some ions (5224, 5225, C511, C513, C4112, C41, 3122), this procedure failed to yield a self-consistent field and an unrestricted Hartree-Fock procedure was used for them. The heats of formation derived from these calculations were used to predict some of the more likely structures for most of the ionic fragments formed at the threshold energies. For example, the threshold energy for C₆H₄⁺ was measured to be 13.9 eV. By employing the known heats of formation of benzene and monatomic hydrogen, and the heats of formation of the ortho-, meta- and para-forms of C₆H₄⁺ computed quantum mechanically, one can estimate the minimum energies required to form the ionic species from benzene. Thus

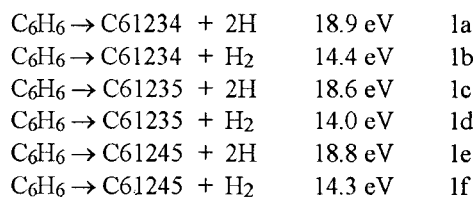


Table 2. Computed Energies for selected ionization processes

Ionic Fragment	Threshold Energy, eV	Ionic Isomer	Other Product(s)	Computed Energy for Process, eV
(C ₆ H ₅ ⁺) ^a	13.9	C612345	H	13.7
(C ₆ H ₄ ⁺) ^a	13.9	C61234	H ₂	14.4
		C61245	H ₂	14.3
		C61235	H ₂	14.0
(C ₆ H ₃ ⁺) ^a	18.5	C6123	H ₂ + H	18.9
		C6124	H ₂ + H	19.1
		C6135	H ₂ + H	19.3
(C ₆ H ₂ ⁺) ^a	24.2	C613	H ₂ + 2H	24.1
		C614	H ₂ + 2H	24.3
		C612	H ₂ + 2H	24.2
(C ₆ H ⁺) ^{a,b}	24.3	C61	2H ₂ + H	25.0
(C ₆ H ⁺) ^{a,b}	29.7	C61	H ₂ + 3H	29.6
(C ₅ H ₃ ⁺)	16.9	5112	CH ₃	16.1
		5114	CH ₃	16.5
		5235	CH ₃	16.5
		5125	CH ₃	16.7
		5111	CH ₃	17.9
		5113	CH ₃	17.9
(C ₅ H ₂ ⁺)	18.1	C513	CH ₄	18.2
		523	CH ₄	18.7
		524	CH ₄	19.0
		515	CH ₃ + H	17.7
		515	CH ₂ + H ₂	18.0
(C ₅ H ⁺)	20.4	52	CH ₄ + H	20.8
		52	CH ₃ + H ₂	20.8
		41224	C ₂ H ₂	15.5
		C41123	C ₂ H ₃	15.5
		41234	C ₂ H ₂	15.6
		C41124	C ₂ H ₂	15.7
		41123	C ₂ H ₂	16.1
		41112	C ₂ H ₂	16.5
(C ₄ H ₃ ⁺)	19.7	4113	C ₂ H ₂ + H	19.0
		C4123	C ₂ H ₂ + H	19.6
		4112	C ₂ H ₂ + H	20.0
		4224	C ₂ H ₂ + H	20.0
		4123	C ₂ H ₂ + H	20.3
		C4112	C ₂ H ₃	19.3
		C4113	C ₂ H ₂	19.3
		4111	C ₂ H + H ₂	19.8
		4113	C ₂ H + H ₂	20.3
		4114	CH ₃ + C	20.6
(C ₄ H ₂ ⁺)	20.0	412	C ₂ H ₂ + H ₂	19.9
		C413	C ₂ H ₂ + H ₂	20.4
		C412	C ₂ H ₂ + H ₂	20.7
		423	C ₂ H ₂ + H ₂	20.8
		414	C ₂ H ₂ + 2H	20.1
		411	C ₂ H ₃ + H	20.3
		413	C ₂ H ₃ + H	20.9
		423	C ₂ H ₄	19.0
		422	C ₂ H ₄	20.8
(C ₄ H ₂ ⁺)		414	CH ₄ + C	19.9
		414	2CH + H ₂	19.4
(C ₄ H ⁺)	27.5	41	C ₂ H ₂ + 3H	26.5
		41	CH ₃ + CH + C	27.3
		41	CH ₂ + CH + H ₂	27.6
		41	2CH ₂ + H	27.8
		41	C ₂ + 2H ₂ + H	28.4
		41	C ₂ H + H ₂ + 2H	27.8
		42	C ₂ H ₃ + 2H	27.3
		C41	C ₂ H ₃ + 2H	28.2
		C41	C ₂ H + 2H ₂	26.7

Ionic Fragment	Threshold Energy, eV	Ionic Isomer	Other Product(s)	Computed Energy for Process, eV
(C ₃ H ₃ ⁺)	17.7	3123	HC ≡ C - CH ₂	18.0
		3112	cyclopropenyl radical	17.8
(C ₃ H ₂ ⁺)	22.8	311	C ₂ H ₄ + C	22.8
		C312	C ₂ H ₄ + C	22.8
		312	C ₂ H ₄ + C	23.5
		311	C ₂ H ₃ + CH	23.8
		C312	C ₂ H ₃ + CH	23.8
		312	C ₂ H ₂ + CH ₂	21.9
		313	C ₂ H ₂ + CH + H	23.4
		313	C ₂ H ₂ + C + H ₂	22.5
		313	C ₂ H + CH ₃	22.1
		C312	C ₂ H ₂ + CH ₃	22.2
		312	C ₂ H + CH ₃	22.8
		311	C ₂ + CH ₄	22.7
		312	C ₂ + CH ₄	23.4
		312	cyclopropenyl radical	22.3
		C311	cyclopropenyl radical	22.6

a Only hexacyclic ionic fragments were considered.

b Both possible threshold energies are considered (see Table 1). However, it is felt that the one at higher energy, 29.7 eV, is probably the correct one.

Considering the uncertainties of 0.5 eV each in the electron impact measurement and the MNDO calculation, it is strongly suggested that at threshold, H₂, rather than 2H is formed although it is not possible to determine which ionic isomer forms. In most cases, it is possible to provisionally rule out the formation of several ionic isomers. For example, for the species, C₅H₃⁺, 21 isomers were investigated, and only six were considered possible (see Table 2). Table 1 gives the results of this procedure for all ionic species excluding C₆⁺, C₅⁺, C₄⁺, C₃⁺, and those lighter than C₃H₂⁺ for which the number of possibilities is so large that predictions of likely isomers are impossible. All processes with computed energies within 1.0 eV of the threshold energy of the ionic fragment are listed. Processes leading to the neutral species, C₃, C₃H, and C₃H₂, were not considered because of the unavailability of reliable heats of formation for these neutral species (see *Calculation of Threshold Energies*). Table 3 lists the number of possible isomers and sets of neutral products considered along with the number of possible paths and reasonable paths or channels based upon the 1-eV criterion.

Up to this point the most extensive study of the threshold energies for benzene was done by using the RPD technique (See Table 1). For the higher mass numbers, agreement between this work and the previous work is good. However, for the lower mass numbers, the previous study reports threshold energies consistently lower than the energies presented herein. The ensuing discussion will show that for mass numbers 77, 76, 73, 63 and 52, the use of previously determined values for threshold energies does not seriously alter the conclusions presented in Table 2 regarding likely ionic isomers and sets of neutral products. However, for mass numbers 51, 50 and 39, this is not the case. At this point the reason for the discrepancies must remain an open question.

$C_6H_6^+$

Momigny *et al.*¹⁹ have concluded that the decomposition of benzene by electron impact starts with production of $C_6H_6^+$ chain, $[CH_2 = CH - CH = CH - C \equiv CH]^+$, excluding the possibility of the formation of cyclic $C_6H_6^+$. The computed heats of formation of the linear and cyclic $C_6H_6^+$ fragments are 11.7 and 9.9 eV leading to estimates of threshold energies of 10.9 and 9.1 eV, respectively. The observed threshold energy of 9.25 eV⁸ for benzene leading to $C_6H_6^+$ would seem to eliminate the possibility of the production of the linear fragment at threshold. This, of course, does not preclude the possibility that the linear fragment forms at energies above threshold with some appreciable cross section. However, it is for this reason, namely the unlikeliness of the production of the linear fragment at threshold, that it was decided to consider only cyclic C_6 fragments.

 $C_6H_5^+$

Results for the threshold energies reported earlier differ by 0.2 eV or less from results reported herein (see Table 1).

 $C_6H_4^+$

Regardless of which hexacyclic ionic isomer is produced, the neutral product is almost certainly H_2 and not $2H$. The calculated threshold energies based upon the computed heats of formation for the ionic isomers and the heat of formation for $2H$ are all at least 4.7 eV above the measured threshold energy of 13.9 eV. It is not possible to choose among the three ionic isomers (see Table 2). Results from previous work agree to within 0.2 eV with results reported here (see Table I).

 $C_6H_3^+$

Regardless of which ionic isomer is produced at threshold, the neutral products are $H_2 + H$ rather than $3H$. The latter process leads to calculated threshold energies at least 5.0 eV above the measured value. One can see from Table 2 that one cannot choose among the three possible ionic isomers.

 $C_6H_2^+$

Although, as before, one cannot choose the ionic isomer (see Table 2), one can confidently choose a path leading to the neutral products $H_2 + 2H$ and eliminate the channels leading to $2H_2$ and $4H$ since they, at best, predict threshold energies that differ by at least 4.2 eV from the observed threshold energy

 C_6H^+

There is only one hexacyclic ionic fragment but three channels leading to neutral products $2H_2 + H$, $H_2 + 3H$, or $5H$. There is some uncertainty regarding the correct threshold energy (see Table 1). Depending upon which threshold energy is used, either path leading to $2H_2 + H$ or $H_2 + 3H$ is reasonable (see Table 2). Lifshitz and Reuben⁵ report a threshold energy of 29 eV, close to the higher value reported here. Using 29 eV in the analysis rather than 29.7 eV, does not alter the conclusion presented in Table 2.

 C_6^+

All completely deprotonated species show weak signals with low signal to noise ratio. In each of these cases, two

thresholds are apparent with the one at lower energy probably resulting from background.

 $C_5H_3^+$

There are 21 possible isomers for $C_5H_3^+$ leading from six possible channels. The only path that results in differences of 1.0 eV or less between measured and calculated threshold energies is the one leading to the neutral product, CH_3 . All other paths result in differences of greater than 1.5 eV. Lifshitz and Reuben⁵ found threshold energy to be 1.2 eV below that reported here (Table 1). It is instructive at this point to use the 1-eV criterion in conjunction with this previously determined value for the threshold energy to see how the conclusions drawn in Table 1 change. Use of the previously determined value would lead to the elimination of two of the ionic isomers (5111 and 5113) and lead to the same conclusion regarding the neutral products. This is a surprisingly minor consequence.

 C_5H^+

Eleven paths leading to four ionic isomers result in 44 possibilities of which only two meet the criterion. In both cases the ionic fragment is the one with the hydrogen attached to the C-2. The computed heat of formation of 52 is 20.2 eV, some 3.0 eV above the heat of formation for the ionic isomer with the next highest heat of formation, 53. The bond angles for isomer 52 are what one would expect from electrostatic arguments. All angles are *ca.* 180° except around the triply bonded carbon for which the angles are nearly trigonal. All carbon-carbon bond lengths are computed to be *ca.* 0.135 nm (double bonds) except for bond length between C_3 and C_4 which is 0.124 nm (triple bond).

 C_5^+

See comments under C_6^+ .

Table 3. Number of possible and likely paths.

Ionic Fragment	n_I Number of Possible Ionic Fragments	n_P Number of Possible sets of Neutral	Number of Possible paths ($n_I \times n_P$)	Number of Paths meeting the 1-eV Criterion
$(C_6H_5^+)^b$	1	1	1	1
$(C_6H_4^+)^b$	3	2	6	3
$(C_6H_3^+)^b$	3	2	6	3
$(C_6H_2^+)^b$	3	2	6	3
$(C_6H^+)^b$	1	3	3	1
$(C_5H_3^+)$	21	6	126	6
$(C_5H_2^+)$	12	9	108	5
(C_5H^+)	4	11	44	2
$(C_4H_4^+)$	19	9	171	7
$(C_4H_3^+)$	12	14	168	10
$(C_4H_2^+)$	9	21	189	11
(C_4H^+)	3	27	81	9
$(C_3H_3^+)$	7	24	168	2
$(C_3H_2^+)$	6	38	228	16

^a Based upon the 1-eV criterion (See text).

^b Only hexacyclic ionic fragments considered. (See text).

$C_4H_4^+$

Nine paths leading to 19 ionic fragments result in 171 possibilities of which only seven meet the criterion. All of the seven have C_2H_2 as the neutral product. Lifshitz and Reuben⁵ indicate a threshold energy of 1.1 eV below the value found here. It is again instructive to use the 1-eV criterion in conjunction with this previously determined value for the threshold energy to assess the conclusions reported in Table 2. Use of the earlier value leads to the removal of the cationic fragments, 41234 and 41123, and the addition of 4114 while leaving unchanged the conclusions regarding the nature of the neutral product.

 $C_4H_3^+$

14 paths leading to 12 ionic fragments result in 165 possibilities of which 10 meet the criterion. Lifshitz and Reuben⁵ report a threshold energy of 2.1 eV below the value reported here. Use of this previously reported value significantly alters the conclusions reported in Table 2. Application of the 1-eV criterion results in the inclusion of one new isomer (4124) and the exclusion of two isomers, C4112 and C4113, from Table 2. However, the paths or channels leading to particular ionic isomers differ in the two cases. For example, the current work has isomer 4111 in channels C_2H_2 and C_2H_3 . In the

current work, 14 channels were considered but only four meet the criterion. Use of the previously reported value leads to three of the four paths indicated in Table 2 and excludes the channel leading to products $CH_3 + C$.

 $C_4H_2^+$

Nine paths leading to twenty one ionic fragments result in 189 possibilities of which eleven meet the criterion. Lifshitz and Reuben⁵ report a threshold energy of 2.5 eV below the value reported here. Use of the 1-eV criterion for this previously reported value leads to only two possibilities, namely, 422 ($+ C_2H_2 + H_2$) and 413 ($+ C_2H_2 + H_2$).

 C_4H^+

Twenty seven paths leading to three ionic fragments result in 81 possibilities of which only nine meet the criterion. Six of the nine paths lead to the 41 isomer, the isomer with the lowest heat of formation by some 2.5 eV. The structure of 41 is what one would expect from electrostatic consideration, namely, all atoms are distributed nearly in a straight line. The carbon-carbon bond length between C-3 and C-4 is computed to be 0.136 nm (double bond) while the two other carbon-carbon bond lengths are computed to be ca 0.127 nm (between double and triple bond).

 C_4^+

See comments under C_6^+ .

 $C_3H_3^+$

The only neutral products that conform to the 1-eV criterion are the linear and cyclic forms of C_3H_3 . Lifshitz and Reuben⁵ indicate a threshold energy some 3.0 eV below the value reported herein. Using their value results in the formation of 3113 and C3123 (propargyl and cyclopropenyl cations) through the same channels predicted in this work, namely the formation of the neutral fragments, cyclic and linear C_3H_3 . The MNDO-computed heats of formation for the propargyl and cyclopropenyl cations were 11.5 and 11.8 eV, respectively, and compare well with those estimated experimentally by Lossing²⁰ (12.2 and 11.1 eV, respectively), which are supported by *ab initio* calculations²¹. The difference of 0.7 eV for each ion is slightly above what is normally encountered (within ca. 0.5 eV) but can be attributed to the size of the ions. MNDO calculations of heats of formation have been found to be less accurate for small ions¹⁰. In any event, using Lossing's values in no way vitiates our conclusion that neither the propargyl nor the cyclopropenyl cation is produced at threshold. This may be regarded as a somewhat surprising result considering the fact that MNDO predicts that the two most stable $C_3H_3^+$ ions are the propargyl and cyclopropenyl cations and that Lifshitz and Reuben's results seem to suggest the formation at threshold of either one or both of them. Although in general the results reported herein agree well with those of Lifshitz and Reuben, for $C_3H_3^+$ at least, there is strong disagreement. The partial pressures for benzene used by Lifshitz and Reuben⁵ were high, on the order of 10^{-4} Torr, and at these pressures ion molecule reactions can lead to uncertainties in derived threshold values. Indeed, the major goal of their work was the investigation of ion-molecule reactions. Earlier studies do not resolve the dispute. Values of 16.2, 17.0 eV²², and 16.4 eV²³ have been reported earlier and, whereas these values are closer to those reported here

Table 4. Relative abundances at various electron beam energies.

Mass	20 eV ^a	40 eV ^a	75 eV ^a	100 eV ^a
78	100 ^b	100 ^b	100 ^b	100 ^b
77	10	22	22	25
76	2	5	5	6
75	<1 ^c	2	2	2
74	<1	5	5	5
73	<1	1	2	2
72	<1	<1	<1	<1
63	<1	3	4	3
62	<1	<1	<1	<1
61	<1	<1	<1	1
60	<1	<1	<1	<1
52	5	14	16	13
51	1	19	15	14
50	<1	11	14	14
49	<1	2	1	2
48	<1	<1	<1	<1
39	2	11	11	11
38	<1	2	4	4
37	<1	<1	4	3
36	<1	<1	<1	<1
27	<1	3	2	3
26	<1	2	2	2

^a Electron beam energy.

^b The value of the abundance for mass number = 78 is arbitrarily set at 100 and all other abundances are related to it

^c The relative abundance could not be accurately determined but was estimated to be less than one.

than to those reported by Lifshitz and Reuben, they still disagree considerably with perhaps one exception (17.0 eV) from the results reported here. Clearly additional work is needed on the $C_3H_3^+$ - fragment. It is important to point out, however, that if our results are correct, they do not preclude the formation of either the propargyl nor the cyclopropenyl cations. It is possible that at threshold 3123 and/or 3112 form (see Table 2) and after some relaxation time convert to either of the aforementioned ions with subsequent release of energy. In fact, for the reaction, $3123 \rightarrow C_3H_3^+$, only ring closure is required. The possibility of such processes suggest some intriguing areas for future investigation.

$C_3H_2^+$

Thirty eight paths leading to six ionic fragments result in 228 possibilities of which 16 meet the criterion.

C_3H^+ , C_3^+ , $C_2H_3^+$, and $C_2H_2^+$

Because of the large number of channels for these species, no attempt was made to determine which channels were the most likely. All pertinent experimental information for these ions is furnished in Table 1.

Although space does not permit a detailed description of the computed geometries of all the ionic fragments, it is instructive to describe some general features. The angular disposition of bonds about carbon atoms normally are consistent with electrostatic considerations. Thus, 4-, 3-, and 2-coordinated carbons exhibit bond angles not far from 109° , 120° , and 180° respectively. For example the four bond angles about C-1 in 41112 are all $109 \pm 2^\circ$, the three bond angles about C-2 are all 120 ± 6 , and the bond angle about C-3 is 181° . It is a general observation that sp^2 -carbons exhibit the largest deviations from the predicted angles. Carbon-carbon bond lengths vary between 0.12 and 0.15 nm, the range expected from triple to single bonds. Normally carbon-carbon bond lengths between carbons of which one carbon is 4-coordinated are close to 0.15 nm. For unsaturated carbons, the bond lengths normally vary between 0.14 and 0.12 nm. Carbon-hydrogen bond lengths normally are 0.110 ± 0.006 nm regardless of the state of the carbon atom to which they are bonded.

Table 4 lists the abundances of all ionic fragments relative to mass number = 78, for electron impact energies of 20, 40, 75, and 100 eV. Most extra peaks evident in the mass spectrum shown in Figure 1 almost certainly result from impurities. For example, the intense peak at mass number = 18 is due to water. Others result from isotopes, e.g. mass number = 79.

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