The Effect of Molecular Structure on Ionic Decomposition. I. An Electron Impact Study of Seven C_8H_8 Isomers

J. L. Franklin and S. R. Carroll

Contribution from the Department of Chemistry, Rice University, Houston, Texas 77001. *Received April 14, 1969*

Abstract: The ionization and fragmentation processes of seven C_8H_8 isomers (styrene, cyclooctatetraene, cubane, benzocyclobutene, barrelene, and *syn*- and *anti*-tricyclo[4.2.0.0^{2,5}]-3,7-octadiene) were determined. Reasonably complete fragmentation schemes were constructed through the use of metastable and energetic data. The structures of many of the fragment ions were postulated by comparing their heats of formation with that of other ions of corresponding mass to charge ratio. Where there were no experimentally determined heats of formation available for comparison, the heats of formation of the ions were compared to values calculated by the group equivalent method for various structures. It was found in some instances that more than one structure was energetically feasible.

The mass spectrum of a compound is expected to reflect both its composition and its structure. Nevertheless, it has been known for many years that the various isomers of paraffin, olefin, and cycloparaffin hydrocarbons give mass spectra that differ in only minor quantitative ways. One normally finds with a family of isomers that an ion of a given composition that is important in the spectrum of one compound will be important in the spectra of the other isomers as well. Similarly, studies by Meyerson[1] have shown that various C_7H_8 compounds give similar mass spectra and, further, that ions of a given composition from these isomers appear to be formed from a common activated state and have similar heats of formation. Similar observations were made by Von Brunt and Wacks[2] in a study of naphthalene and azulene.

In view of these results one would expect similar behavior from certain classes of isomers. However, it appeared of interest to measure the spectra and appearance potentials of ions from several isomeric compounds of widely different structure as well as of different chemical type. With this in mind, we have measured the mass spectra and the appearance potentials of the following compounds: C_8H_8, styrene, cyclooctatetraene, phenylcyclobutene, bicyclo[2.2.2]octatriene, *syn*- and *anti*-tricyclo[4.2.0.0^{2,5}]-3,7-octadiene, and cubane. These compounds differ extensively in both structure and chemical type and thus fit our requirements well.

Experimental Section

The mass spectra and appearance potential data were obtained primarily by means of a Consolidated Electrodynamics Corp. mass spectrometer, Type 21-701. The design of this instrument has been discussed in the literature[3] as well as its applications to problems similar to this study.[4,5]

The appearance potential data reported were evaluated by the EVD method of Warren.[6] Also, whenever possible the EVD results are compared to retarding potential difference (RPD) measurements obtained on a Bendix Model 12 Time-of-Flight mass spectrometer with a 180-cm flight tube. The theory of operation of this instrument has also been outlined in the literature.[7-12] For both the EVD and RPD appearance potentials, the data listed are an average of several determinations. The EVD ionization potential data are reproducible to ±0.05 eV and for the appearance potentials of the strong fragment ions, about ±0.10 eV. However, for some of the less intense ions or those produced by tertiary decompositions the reproducibility drops to about ±0.20 eV. For all of the ionization potentials and the ions produced by primary decompositions the accuracy is about ±0.10 eV (or on the order of the reproducibility), but for the weaker ions and the tertiary decompositions the accuracy could be as low as ±0.30–0.40 eV. This can be attributed to the large amounts of excess energy involved in these decompositions. This latter factor will be discussed later.

An attempt was made to measure translational energy and relate it to the excess energy involved in the transition. The method used[13] cannot measure the excess translational energy of a decomposition of a polyatomic molecule involving the loss of H or H_2 because the resulting ion possessed only a small fraction of the excess energy. The theory developed by Haney and Franklin[13] for relating the measured translational energy to the total excess energy involved in transition was not applicable to our secondary decompositions. With the above limitations we could hope to determine accurately the excess energy of only the process producing the $C_8H_6^+$ ion. However, experimental difficulties were encountered even with this ion. With the exception of cyclooctatetraene, the $C_8H_6^+$ peaks were severely distorted so that measurements of translational energy were only approximate. However, the translational energy measurements were good enough to permit correcting the appearance potential and ion heat of formation by this amount for several of the processes, and these corrections are shown in the tables.

The styrene and CO_2 were obtained from Matheson, Inc., and the cyclooctatetraene from Aldrich Chemical Co. Cubane was supplied by Professor Philip E. Eaton of the University of Chicago, *syn*- and *anti*-tricyclooctadiene by Professor Rowland Pettit from the University of Texas, barrelene by Professor H. E. Zimmerman from the University of Wisconsin, and benzocyclobutene by Professor R. B. Turner of Rice University.

Qualitative Features of the Mass Spectra

The relative intensities of the major ions in the mass spectra of the compounds studied are illustrated in Tables I–VII. Complete spectra may be obtained from Scientific Documentation Centre, Ltd., Dumferline, Fife, United Kingdom. In addition, the decomposition modes confirmed by metastable transition are also listed in these tables. The modes for which a metasta-

---

[1] H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, pp 453–527.

[2] R. J. Von Brunt and M. E. Wacks, *J. Chem. Phys.*, **41**, 3195 (1964).

[3] H. C. Voorhies, C. F. Robinson, L. G. Hall, W. M. Brubaker, and C. E. Berry, *Advan. Mass Spectry.*, **1**, 44 (1959).

[4] J. L. Franklin and A. Mogenis, *J. Phys. Chem.*, **71**, 2820 (1967).

[5] P. Natalis and J. L. Franklin, *ibid.*, **69**, 2935, 2943 (1965).

[6] J. W. Warren, *Nature*, **165**, 810 (1950).

[7] A. E. Cameron and C. D. F. Eggers, *Rev. Sci. Instr.*, **19**, 605 (1948).

[8] R. S. Gohlke, *Anal. Chem.*, **31**, 535 (1959).

[9] D. B. Harrington, *Advan. Mass Spectry.*, **1**, 249, (1959).

[10] P. M. Hierl, Doctoral Thesis, Rice University, June 1967.

[11] H. S. Katzenstein and S. S. Friedland, *Rev. Sci. Instr.*, 26, 324 (1955).

[12] W. C. Wiley and I. H. McLaren, *ibid.*, 26, 1150 (1955).

[13] M. A. Haney and J. L. Franklin, *J. Chem. Phys.*, 43, 4093 (1968).

Table I. Appearance Potentials of Styrene (CVDS)[a]

Ion	m/e	Rel abundance	AP, eV	Excess transl energy	Observed metastable transitions $[m^*]$	Observed metastable transitions	Neutrals	Exptl ΔH_f, kcal/mole
$C_8H_8^+$	104^+	100.0	8.46 ± 0.10	...	...	...	...	232
$C_8H_7^+$	103^+	39.0	12.41 ± 0.10	...	...	...	H	271
$C_8H_6^+$	102^+	69.0	12.72 ± 0.10	...	...	...	H_2	330
$C_6H_6^+$	78^+	24.1	12.30 ± 0.10 12.38 ± 0.05[b]	0.28	58.5	$104^+ = 78^+ + 26$	C_2H_2	262[c]
$C_6H_5^+$	77^+	11.9	16.02 ± 0.10	...	57.6	$103^+ = 77^+ + 26$	$H + C_2H_2$	300
$C_5H_3^+$	63^+	9.1	17.74 ± 0.10	0.09	44.6	$89^+ = 63^+ + 26$	$CH_3 + C_2H_2$	357
$C_4H_4^+$	52^+	15.7	17.25 ± 0.15	0.07	34.7	$78^+ = 52^+ + 26$	$2C_2H_2$	325
$C_4H_3^+$	51^+	44.9	19.61 ± 0.10	0.06	33.8	$77^+ = 51^+ + 26$	$H + 2C_2H_2$	328
$C_4H_2^+$	50^+	18.8	19.85 ± 0.25 20.22 ± 0.10[b]	0.07	56.6 32.9 48.1	$102^+ = 76^+ + 26$ $76^+ = 50^+ + 26$ $52^+ = 50^+ + 2$	$H_2 + 2C_2H_2$	384[c]
$C_3H_3^+$	39^+	23.0	14.90 ± 0.10	0.07	...	...	...	...

[a] Registration number, Scientific Documentation Centre, Ltd. [b] RPD. [c] Calculated using EVD AP value.

Table II. Appearance Potentials of 1,3,5,7-Cyclooctatetraene (CDVR)[a]

Ion	m/e	Rel abundance	AP, eV	Excess transl energy	Observed metastable transitions $[m^*]$	Observed metastable transitions	Neutrals	Exptl ΔH_f, kcal/mole
$C_8H_8^+$	104^+	100.0	8.06 ± 0.10	...	...	...	...	257
$C_8H_7^+$	103^+	56.4	10.90 ± 0.10	...	...	...	H	270
$C_8H_6^+$	102^+	10.7	11.70 ± 0.10	...	...	...	H_2	341
$C_8H_6^+$	78^+	76.5	9.70 ± 0.12[b] 10.36 ± 0.10	0.07	58.5	$104^+ = 78^+ + 26$	C_2H_2	239[c] 256[d]
$C_6H_5^+$	77^+	39.1	14.58 ± 0.10	...	57.6	$103^+ = 77^+ + 26$	$H + C_2H_2$	301
$C_5H_3^+$	63^+	15.1	16.41 ± 0.15	0.15	44.6	$89^+ = 63^+ + 26$	$CH_3 + C_2H_2$	358
$C_4H_4^+$	52^+	28.0	15.10 ± 0.10[b] 15.22 ± 0.25	0.11	34.7	$78^+ = 52^+ + 26$	$2C_2H_2$	308[c]
$C_4H_3^+$	51^+	69.9	18.16 ± 0.25	0.08	33.8	$77^+ = 51^+ + 26$	$H + 2C_2H_2$	327
C_4H_2	50^+	37.8	17.11 ± 0.10[b] 17.34 ± 0.45	0.12	56.6 32.9	$102^+ = 76^+ + 26$ $76^+ = 50^+ + 26$	$H_2 + 2C_2H_2$	354[c]
$C_3H_3^+$	39^+	55.9	13.40 ± 0.10	...	...	...	...	...

[a] Registration number, Scientific Documentation Centre, Ltd. [b] RPD. [c] Calculated using RPD AP value. [d] Calculated using EVD AP value.

Table III. Appearance Potentials of Cubane (CDVQ)[a]

Ion	m/e	Rel abundance	AP, eV	Excess transl energy[b]	Observed metastable transitions[b] $[m^*]$	Observed metastable transitions[b]	Neutrals	Exptl ΔH_f, kcal/mole
$C_8H_8^+$	104^+	17.2	8.64 ± 0.10				...	348
$C_8H_7^+$	103^+	100.0	8.96 ± 0.10				H	303
$C_8H_6^+$	102^+	9.1	8.92 ± 0.10				H_2	354
$C_6H_6^+$	78^+	90.2	9.00 ± 0.10				C_2H_2	302
$C_6H_5^+$	77^+	31.6	10.93 ± 0.10				$H + C_2H_2$	294
$C_5H_3^+$	63^+	12.0	13.60 ± 0.10				$CH_3 + C_2H_2$	375
$C_4H_4^+$	52^+	37.6	12.88 ± 0.15				$2C_2H_2$	337
$C_4H_3^+$	51^+	39.0	14.96 ± 0.10				$H + 2C_2H_2$	333
$C_4H_2^+$	50^+	25.7	14.33 ± 0.20				$H_2 + 2C_2H_2$	371
$C_3H_3^+$	39^+	51.4	10.01 ± 0.10				...	...

[a] Registration number, Scientific Documentation Centre, Ltd. [b] There was insufficient compound for metastable and excess translational energy measurements.

ble decomposition was not observed were established where possible by the energetics involved in the processes and are justified in the discussion of each ion. Figure 1 is a breakdown pattern for the formation of all of the principal ions. In so far as our data permit the determination, all of the seven compounds studied break down in accordance with this pattern. Although there are differences in the relative intensities of a given ion from various source molecules, the route by which the ion is formed seems to be the same regardless of the structure of the parent molecule. With the exception of cubane, all of the spectra of the C_8H_8's have several doubly charged ions appearing from mass 52.5 (for the doubly charged parent isotope ion) down to about 30 mass units. The $C_8H_8^{3+}$ from styrene was the only triply charged ion detected.

Table IV. Appearance Potentials of Barrelene (CDVP)[a]

Ion	m/e	Rel abundance	Ap, eV	Excess transl energy[b]	Observed metastable transitions[b] [m^*]		Neutrals	Exptl ΔH_f, kcal/mole
$C_8H_8^+$	104^+	84.2	7.95 ± 0.10				. . .	245
$C_8H_7^+$	103^+	52.1	10.63 ± 0.10				H	255
$C_8H_6^+$	102^+	7.33	11.97 ± 0.20				H_2	338
$C_8H_6^+$	78^+	100.0	10.50 ± 0.10				C_2H_2	250
$C_6H_5^+$	77^+	40.6	14.49 ± 0.10				$H + C_2H_2$	299
$C_5H_3^+$	63^+	14.5	16.11 ± 0.10				$CH_3 + C_2H_2$	346
$C_4H_4^+$	52^+	40.6	15.31 ± 0.20				$2C_2H_2$	307
$C_4H_3^+$	51^+	97.0	18.04 ± 0.10				$H + 2C_2H_2$	318
$C_4H_3^+$	50^+	45.5	17.20 ± 0.30				$H_2 + 2C_2H_2$	350
$C_3H_3^+$	39^+	73.7	13.64 ± 0.25				. . .	. . .

[a] Registration number, Scientific Documentation Centre, Ltd. [b] There was insufficient compound for metastable and translational energy measurements.

Table V. Appearance Potentials of Benzocyclobutene (CDVO)[a]

Ion	m/e	Rel abundance	AP, eV	Excess transl energy	Observed metastable transitions [m^*]		Neutrals	Exptl ΔH_f, kcal/mole
$C_8H_8^+$	104^+	82.8	8.74 ± 0.05[b] 8.82 ± 0.10	. . .	. . .	. . .	. . .	244[c]
$C_8H_7^+$	103^+	42.2	11.94 ± 0.10	. . .	. . .	. . .	H	265
$C_8H_8^+$	102^+	7.47	11.84 ± 0.10[b] 12.33 ± 0.30	. . .	. . .	. . .	H_2	315[c]
$C_6H_6^+$	78^+	64.1	11.55 ± 0.10	0.30	58.5	$104^+ = 78^+ + 26$	C_2H_2	247
$C_6H_5^+$	77^+	31.6	15.58 ± 0.10	. . .	57.6	$103^+ = 77^+ + 26$	$H + C_2H_2$	295
$C_5H_3^+$	63^+	21.0	17.34 ± 0.10	0.20	44.6	$89^+ = 63^+ + 26$	$CH_3 + C_2H_2$	350
$C_4H_4^+$	52^+	9.22	16.01 ± 0.15	0.19	34.7	$78^+ = 52^+ + 26$	$2C_2H_2$	298
$C_4H_3^+$	51^+	100.0	18.68 ± 0.10	0.18	33.8	$77^+ = 51^+ + 26$	$H + 2C_2H_2$	308
$C_4H_2^+$	50^+	44.8	17.69 ± 0.30	0.05	56.6 32.9	$102^+ = 76^+ + 26$ $76^+ = 50^+ + 26$	$H_2 + 2C_2H_2$	340
$C_3H_3^+$	39^+	14.7	14.16 ± 0.15	0.11	. . .	. . .	. . .	. . .

[a] Registration number, Scientific Documentation Centre, Ltd. [b] RPD. [c] Calculated using RPD value.

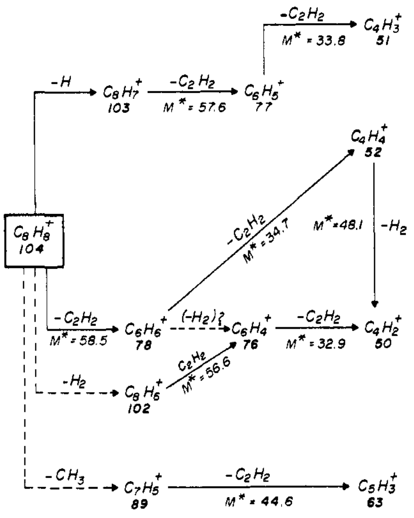

Figure 1. Fragmentation pattern.

Results

Ionization Potentials. The experimental ionization potentials of the C_8H_8 isomers are listed in Table VIII along with the available values from the literature. Our experimental values are in good agreement with these two previously determined values. The experimental ionization potentials are also compared to values calculated by Franklin's extension[14] of Hall's[15] group orbital method. The agreement of the calculated and experimental values is about ±0.2 eV with the exception of barrelene and cubane, and for these compounds the deviation is less than 0.40 eV. The agreement between the experimental values and the calculated estimations is remarkable considering the widely different structures involved.

Appearance Potentials. The appearance potentials of the ions with relative intensity greater that 5–10% are given in Tables I–VII. The metastable transitions leading to individual ions, the measured excess translational energy, and the neutrals assumed in calculating the ionic heats of formation are indicated. The values of the heats of formation of the neutrals used in the calculation of the ionic heats of formation are given in Table IX. The structure of the fragment ions is discussed below with emphasis on possible rearrangements.

$C_8H_7^+$ Ion. The P − 1 ion is observed in fair abundance with all of these compounds. One would like to ascertain the position in each molecule from which the hydrogen atom is lost. This is of course impossible with cubane and cyclooctatetraene. The only certain way of obtaining such information with the remaining compounds is by labeling with deuterium at the appropriate positions. Unfortunately, the preparation of such labeled compounds was beyond the scope of this work and only one such study was found in the literature.

---

(14) J. L. Franklin, *J. Chem. Phys.*, 22, 1034 (1954).

(15) G. G. Hall, *Proc. Roy. Soc.* (London), 205a, 541 (1951); *Trans. Faraday Soc.*, 49, 113 (1953).

Table VI. Appearance Potentials of *syn*-Tricyclooctadiene (CDVN)[a]

Ion	m/e	Rel abundance	AP, eV	Excess transl energy[b]	Observed metastable transitions[c] $[m^*]$	Neutrals	Exptl ΔH_f, kcal/mole
$C_8H_8^+$	104+	13.7	8.20 ± 0.10	...		...	297
$C_8H_7^+$	103+	63.5	9.12 ± 0.10	...		H	266
$C_8H_6^+$	102+	8.33	10.03 ± 0.10	...		H_2	339
$C_6H_6^+$	78+	100.0	9.09 ± 0.10	0.29		C_2H_2	257
$C_6H_5^+$	77+	37.6	12.41 ± 0.10	...		$H + C_2H_2$	288
$C_5H_3^+$	63+	15.2	14.07 ± 0.10	0.24		$CH_3 + C_2H_2$	340
$C_4H_4^+$	52+	41.7	13.85 ± 0.10	0.13		$2C_2H_2$	316
$C_4H_3^+$	51+	65.9	16.38 ± 0.10	0.10		$H + 2C_2H_2$	323
$C_4H_2^+$	50+	44.9	15.80 ± 0.10	0.14		$H_2 + 2C_2H_2$	360
$C_3H_3^+$	39+	87.7	11.87 ± 0.15	...		...	...
$C_3H_2^+$	38+	15.4	16.91 ± 0.10	...		...	...

[a] Registration number, Scientific Documentation Centre, Ltd. Note: The *syn* and *anti* isomers were recorded together and have the same registration number. [b] The values of the *anti* isomer are used for this compound. [c] There was insufficient compound available to make these measurements.

Table VII. Appearance Potentials of *anti*-Tricyclooctadiene (CDVN)[a]

Ion	m/e	Rel abundance	AP, eV	Excess transl energy	Observed metastable transitions[b] $[m^*]$	Neutrals	Exptl ΔH_f, kcal/mole
$C_8H_8^+$	104+	10.5	8.27 ± 0.10	...		...	299
$C_8H_7^+$	103+	59.2	9.13 ± 0.10	...		H	266
$C_8H_6^+$	102+	7.62	9.86 ± 0.10	...		H_2	335
$C_6H_6^+$	78+	100.0	9.01 ± 0.10	0.29		C_2H_2	255
$C_6H_5^+$	77+	32.1	12.59 ± 0.10	...		$H + C_2H_2$	292
$C_5H_3^+$	63+	13.4	14.36 ± 0.10	0.24		$CH_3 + C_2H_2$	346
$C_4H_4^+$	52+	36.5	13.90 ± 0.10	0.13		$2C_2H_2$	317
$C_4H_3^+$	51+	59.5	16.41 ± 0.10	0.10		$H + 2C_2H_2$	323
$C_4H_2^+$	50+	40.3	16.78 ± 0.10	0.14		$H_2 + 2C_2H_2$	383
$C_3H_3^+$	39+	75.4	11.95 ± 0.10	...		...	...
$C_3H_2^+$	38+	13.4	17.00 ± 0.35	...		...	...

[a] Registration number, Scientific Documentation Centre, Ltd. Note: The *syn* and *anti* isomers were recorded together and have the same registration number. [b] There was insufficient compound available to make these measurements.

Table VIII. Ionization Potentials

		Ionization potential, eV			
		This work		Literature	
Compound	Ion	Measd	Calcd[a]		
Styrene	$C_8H_8^+$	8.46 ± 0.10	8.6	8.47 ± 0.02[21]	(PI)[c]
Cyclooctatetraene	$C_8H_8^+$	8.06 ± 0.10	8.1	7.99 ± 0.02[21]	(PI)
Benzocyclobutene	$C_8H_8^+$	8.82 ± 0.10	8.6	...	
		8.74 ± 0.05[b]			
Barrelene	$C_8H_8^+$	7.95 ± 0.10	7.6	...	
Cubane	$C_8H_8^+$	8.64 ± 0.10	9.0	...	
syn-Tricyclooctadiene	$C_8H_8^+$	8.20 ± 0.10	8.0	...	
anti-Tricyclooctadiene	$C_8H_8^+$	8.27 ± 0.10	8.0	...	

[a] Calculated using Franklin's group orbital method.[14] [b] Measured by RPD. [c] PI = photoionization.

Quinn and Mohler[16] obtained mass spectra with 50–75-V electrons on α-, β-, and *p*-deuteriostyrene and on α,β,β-trideuteriostyrene. Their results showed approximately random loss of deuterium and hydrogen in forming the $C_8H_7^+$ ion. They suggested that the ion formed a cyclooctatetraene ring which dissociates with random loss of deuterium and hydrogen. However, since the observed loss is not completely random, there may be other modes of fragmentation. Further, since no low voltage studies were reported, it is not known whether the H and D loss remains random as onset is approached.

The difference in the resonance energies of cyclooctatetraene and styrene is 1.6 eV,[17] and the difference in energy required to remove a hydrogen to form the P − 1 ion from these compounds is 1.5 eV. This difference can result from either the destruction of resonance in styrene or gain in resonance energy by cyclooctatetraene in forming an aromatic nucleus. The removal of a hydrogen from ethylene, 1,3-butadiene, and propadiene requires 13.9,[18] 12.2,[4] and 12.2 eV,[4] respectively. In all three cases this is considerably more energy than is necessary to remove an H from cyclooctatetraene. Thus it seems very likely that, in losing an H atom, cyclooctatetraene forms an ion with an aromatic or other very

---

(16) E. I. Quinn and F. L. Mohler, *J. Res. Natl. Bur. Std.*, 62, 39 (1959).

(17) G. W. Wheland, "The Theory of Resonance and Its Application to Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1944.

(18) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957.

Table IX. Neutral Heats of Formation

Neutral	ΔH_f, kcal/mole	Ref sources
Styrene	37	20
Cyclooctatetraene	71	20
Benzocyclobutene	42[a]	*c*
Barrelene	62[a]	20
Cubane	149	19
syn-Tricyclooctadiene	108[b]	
anti-Tricyclooctadiene	108[b]	
H_2	0	
H	52.1	*d*
CH_3	33.2	*d*
C_2H_2	54.2	*e*

[a] Heat of hydrogenation used in conjunction with the group equivalent method. [b] Calculated by the authors using Franklin's group equivalent method.[20] [c] B. J. Mallon, Ph.D. Thesis, Rice University, 1967. [d] D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. Bailey, and R. H. Schumm, National Bureau of Standards Technical Note 270-1, U. S. Government Printing Office, Washington, D. C., 1965. [e] "JANAF Thermochemical Tables," The Dow Chemical Co., Midland, Mich., 1960.

stable structure. The 12.4 eV required to remove the first hydrogen from styrene apparently is the energy required to remove one from the side chain, but this is by no means certain.

Our energy measurements are not sufficient to distinguish the positions from which H atom is lost in the remaining compounds. However, if the above conclusion that cyclooctatetraene forms an aromatic ion when H atom is lost is valid, then the fact that $\Delta H_f(C_8H_7^+)$ from all of the compounds except cubane are approximately the same suggests that all except cubane form aromatic ions. The low appearance potential and very large strain energy of cubane (157 kcal/mole[19]) suggests that $C_8H_7^+$ from this source is formed with a great deal of excess energy and may not be aromatic.

In substantiation of these conclusions, we have estimated the relative heats of formation of open-chain and aromatic $C_8H_7^+$ ions. The heat of formation of 3,5-octadiene-1,7-diyne can be estimated using Franklin's group equivalent method.[20] The proton affinities of propadiene and 1,3-butadiene are estimated to be 193 and 186 kcal/mole, respectively, and, as will be seen later, the proton affinity of a linear ion of *m/e* 78 is approximately 200 kcal/mole. Using this latter value as a fair approximation of the proton affinity of an acyclic C_8H_6 compound, a heat of formation of about 305 kcal/mole for a linear ion of *m/e* 103 is estimated. Similarly, the heat of formation of a protonated phenylacetylene ion (*m/e* 103) in which the proton is either on the side chain or on the ring can be estimated using the heat of formation of phenylacetylene and the proton affinity of acetylene and benzene, respectively. The heat of formation of a protonated phenylacetylene ion is about 275 kcal/mole with the proton on the ring and approximately 290 kcal/mole when it is on the side chain. With the exception of cubane (303 kcal/mole), the heat of formation of the $C_8H_7^+$ ion from the remaining compounds is 260–270 kcal/mole. Quite naturally it is not possible to say conclusively that the $C_8H_7^+$ ion is the protonated ring structure, but we can say with at least some confidence that the resulting ion does not have a linear structure and probably most closely resembles a protonated phenylacetylene ion. Cubane with its higher heat of formation for this ion is probably acyclic, although the possibility of its being an excited protonated phenylacetylene ion cannot be ruled out.

$C_8H_6^+$ Ion. This ion is formed in relatively large intensity from styrene and in modest (7–8%) intensity from the other compounds studied. $C_8H_6^+$ could be formed in each case by the loss of either H_2 or 2H. The heats of formation calculated in Tables I through VII have assumed the loss of a hydrogen molecule. These results would be lowered by 104 kcal/mole if the parent ion lost 2H instead of H_2. The heat of formation of the phenylacetylene ion which equals 279 kcal/mole[21] is assumed to be the most stable ion possible of this composition. Heats of formation 104 kcal/mole lower are unlikely.

With the exception of cubane (Table III) and benzocyclobutene (Table V), the heat of formation values are closely grouped around an average value of about 336 kcal/mole. The $C_8H_6^+$ ion from cubane has a heat of formation of 354 kcal/mole and from benzocyclobutene, 315 kcal/mole.

The $C_8H_6^+$ ion from biphenyl is 349 kcal/mole[5] and is calculated on the assumption of the loss of $2C_2H_2$ from the parent compound. An estimation of the heat of formation of the 3,5-octadiene-1,7-diyne ion, using Franklin's group equivalent method for the calculation of the heat of formation of the neutral parent molecule and his group orbital method for estimating its ionization potential, gives a heat of formation of approximately 345 kcal mole[5] for an acyclic ion of mass 102. This estimation should be accurate to within 20 kcal/mole of the correct value which coupled with the biphenyl value indicates that the P − 2 ions are probably linear. However, conclusions based upon such estimates are tentative so the possibility still exists that these ions, with the exception of the P − 2 from cubane, are excited phenylacetylene ions.

$C_6H_6^+$ Ion. There is little uncertainty as to the structure of this ion. Except for cubane, the $C_6H_6^+$ ion from all of the compounds studied in this series of isomers is an excited benzene ion. The ground-state heat of formation of the benzene ion is 233 kcal/mole.[22–24] The 78 ion from cyclooctatetraene is 239 kcal/mole while styrene, barrelene, benzocyclobutene, and *syn*- and *anti*-tricyclooctadiene yield values between 247 and 262 kcal/mole. If we are to assign a benzene structure to this ion from these compounds, we must assume it is excited by 20–30 kcal/mole. The heat of formation for a linear $C_6H_6^+$ ion has been determined experimentally by Momigny.[25] He measured the heat of formation of the parent ion from 2,4-, 1,3-, and 1,5-hexadiynes and found them all to be approximately 300 kcal/mole. This heat of formation has also been estimated for a linear $C_6H_6^+$ ion by the combined group equivalent and group orbital methods to be about 290 kcal/mole. Thus our heats of formation are either 30–40 kcal/mole

---

(19) B. D. Kybett, S. Carroll, P. Natalis, D. W. Bonnell, J. L. Margrave, and J. L. Franklin, *J. Am. Chem. Soc.*, 88, 626 (1966).

(20) J. L. Franklin, *Ind. Eng. Chem.*, 41, 1070 (1949).

(21) K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectry. Radiative Transfer*, 2, 369 (1962).

(22) F. M. Matsunaga, Air Force Cambridge Research Center, Contribution No. Scientific Report No. 3, Contract No. AF19 (604)-4576, 1961.

(23) F. I. Vilesov, *Russ. J. Phys. Chem.*, 35, 986 (1961).

(24) K. Watanabe, *J. Chem. Phys.*, 26, 542 (1957).

(25) J. Momigny, L. Brakier, and L. D'Or, *Bull. Classe Sci., Acad. Roy. Belg.*, 48, 1002 (1962).

low (assuming a linear structure) or 30 kcal/mole high (assuming a benzene ion structure). Since the tendency in electron impact values is to be high, the ions are assumed to correspond to an excited benzene ion.

There is little doubt that at the appearance potential the $C_6H_6^+$ ion from cubane is linear. In order for the $C_6H_6^+$ ion from cubane to be a benzene ion, it would have to be excited by some 55–70 kcal/mole. Since several linear $C_6H_6^+$ ions have heats of formation near 300 kcal/mole (Table X), it is concluded that $C_6H_6^+$ from cubane is probably linear.

Table X. Ionic Heats of Formation

Ion	m/e	Compound	ΔH_f, kcal/mole
$C_8H_7^+$	102	Biphenyl	349[5]
		Phenylacetylene	279[21]
$C_6H_6^+$	78	Benzene	233[22–24]
		2,4-Hexadiyne	301[25]
		1,3-Hexadiyne	307[25]
		1,4-Hexadiyne	319[25]
		1,5-Hexadiyne	338[25]
		Butadienylacetylene	304[25]
$C_6H_5^+$	77	Phenyl radical	282[26]
		Benzene	286[28]
		Benzene	298[29]
		2,4-Hexadiyne	293[25]
		1,3-Hexadiyne	304[25]
		1,4-Hexadiyne	309[25]
		1,5-Hexadiyne	312[25]
$C_5H_3^+$	63	Benzene	375[a,b]
		2,4-Hexadiyne	366[25]
$C_4H_4^+$	52	Vinylacetylene	294[29,30]
		Benzene	311[5]
		1-Butyne	291[31]
		2,4-Hexadiyne	314[25]
		1,3-Hexadiyne	313[25]
		1,4-Hexadiyne	314[25]
		1,5-Hexadiyne	308[25]
$C_4H_3^+$	51	Vinylacetylene	303[16]
		Benzene	337[a,c]
		1-Butyne	324[31]
$C_4H_2^+$	50	1,3-Butadiyne	338[31]
		1,3-Hexadiyne	361[25]
		1,4-Hexadiyne	387[25]
		1,5-Hexadiyne	391[25]
		Benzene	335[b,d]
		Benzene	396[b,e]
		1,3-Butadiene	415[4]
$C_3H_3^+$	39	1-Propyne	316[31]
		2,4-Hexadiyne	373[25]
		1,3-Hexadiyne	388[25]
		1,4-Hexadiyne	386[25]
		1,5-Hexadiyne	396[25]

[a] Photoionization. [b] V. H. Dibeler, R. M. Reese, and F. L. Mohler, *J. Chem. Phys.*, **26**, 304 (1957). [c] A. Hustrulid, P. Kusch, and J. T. Tate, *Phys. Rev.*, **54**, 1037 (1938). [d] Assumes neutrals of $C_2H_3 + H$. [e] Assumes neutrals of $C_2H_2 + H_2$.

$C_6H_5^+$ Ion. Since this ion is a significant contributor to the spectra of nearly all aromatic and related compounds, there have been many attempts to establish firmly its structure by determining its heat of formation from both cyclic and acyclic compounds. The conclusions seem to oscillate between the ions always being acyclic to always having a phenyl ion structure. Much early work was done by Grubb and Meyerson[1] who studied the heats of formation of the $C_6H_5^+$ ions from the 2-methyl-2-phenylalkanes, phenyl alkyl ketones, α-chloroethylbenzene, ethylbenzene, *p*-xylene, toluene, and benzene. They concluded that, with the exception of the first two mentioned compounds, the $C_6H_5^+$ ion was probably not a phenyl ion. Even in the case of the two exceptions they stated that the ion could be a phenyl ion but was not necessarily so. They also concluded that the $C_6H_5^+$ ion from benzene was probably not the phenyl ion. This argument was given further support when Lossing, *et al.*,[26] succeeded in measuring the ionization potential of the phenyl radical and determined the heat of formation of the phenyl ion as 282 kcal/mole. The heat of formation of the $C_6H_5^+$ ion from benzene as determined by numerous workers is approximately 300 kcal/mole.[5,27] Momigny[25] determined the heat of formation of the $C_6H_5^+$ ion from several linear C_6H_6 isomers, and his data indicated that the heat of formation of a $C_6H_5^+$ ion from linear compounds is also about 300 kcal/mole. Until recently the difference between the 282 kcal/mole for the phenyl ion and the approximately 300 kcal/mole of the ion from aromatic and acyclic compounds was assumed to indicate that the $C_6H_5^+$ ion from these compounds was not the phenyl ion. However, recently Brehm[28] has determined the appearance potential of this ion from benzene by photoionization and obtained a heat of formation of 286 kcal/mole. This indicates that the $C_6H_5^+$ ion from benzene and the phenyl radical have very nearly the same heat of formation and, hence, probably the same structure, at least at the onset for ionization. These previous measurements of the appearance potential of the $C_6H_5^+$ ion from aromatic compounds could merely have involved excess energy which may or may not have resulted in ring opening. Similarly, more careful measurements of the appearance potential of the $C_6H_5^+$ ion from linear molecules will be required before it will be possible to determine whether the $C_6H_5^+$ ions from linear sources remain linear or cyclize. Estimation of the heat of formation of some linear $C_6H_5^+$ ions yield values in the 280–300-kcal/mole range. The result is that it may not be possible to distinguish between a linear and cyclic $C_6H_5^+$ ion on an energy basis and, if this is true, both structures will probably be present in all cases.

$C_5H_3^+$ Ion. Each of these isomers has a small but significant $C_5H_3^+$ ion in its spectrum. It is assumed to be produced by the successive loss of CH_3 and acetylene from the parent ion. This scheme is at least partially confirmed by the observation of a metastable transition corresponding to the $C_7H_5^+$ to $C_5H_3^+$ decomposition. Since anything other than a linear structure seems implausible and since the estimated heats of formation of a linear $C_5H_3^+$ ion is 290 kcal/mole, it seems very likely that the $C_5H_3^+$ ion from these compounds is an excited linear ion.

$C_4H_4^+$ Ion. With the exception of styrene and cubane, the $C_4H_4^+$ ions have heats of formation between 298 and 316 kcal/mole. These values probably correspond to an excited vinylacetylene ion, since its heat of formation determined by direct ionization of the neutral molecule is 294 kcal/mole.[29,30] This is apparently

---

(26) I. P. Fisher, T. F. Palmer, and F. P. Lossing, *J. Am. Chem. Soc.*, 86, 2741 (1964).

(27) J. R. Majer and C. R. Patrick, *Trans. Faraday Soc.*, **58**, 17 (1962).

(28) B. Brehm, *Z. Naturforsch.*, **21a**, 196 (1966).

(29) J. L. Franklin and F. H. Field, *J. Am. Chem. Soc.*, 76, 1994 (1954).

(30) C. J. Varsel, F. A. Morrell, F. E. Resnik, and W. A. Powell, *Anal. Chem.*, 32, 182 (1960).

Table XI. Sum of Appearance Potential and Heat of Formation of Parent Molecule (kcal/mole)[a]

	Styrene	COT	BCB	B	Cubane	S	A	Av
C_8H_7	323	321	317	307	355	318	318	317
C_8H_6	331	341	315	337	354	339	335	336
C_6H_6	320	294	308	303	356	317	315	310
C_6H_5	397	405	402	396	401	394	397	399
C_5H_3	446	449	441	433	462?	432	439	440
C_4H_4	434	419	410	415	445	428	429	426
C_4H_3	489	490	473	478	493	476	477	482
C_4H_2	494	466	460	459	480	473	495	
C_3H_3	380	380	369	376	380	382	384	379

[a] COT = cyclooctatetraene, BCB = benzocyclobutene, B = barrelene, S = *syn*-tricyclooctadiene, and A = *anti*-tricyclooctadiene.

the lowest heat of formation possible for a linear $C_4H_4^+$ ion as the heat of formation values for the $C_4H_4^+$ ion from a variety of other compounds are approximately 310 kcal/mole (benzene, 2,4-, 1,3-, 1,4-, and 1,5-hexadiyne). The only compound with a heat of formation for the $C_4H_4^+$ ion lower than the 294 kcal/mole for vinylacetylene is 1-butyne,[31] and we suspect that the quoted value of 291 kcal/mole is probably slightly in error.

$C_4H_3^+$, $C_4H_2^+$, and $C_3H_3^+$ Ions. The heat of formation of the P − 1 ion from vinylacetylene is 303 kcal/mole,[18] and, for additional comparison, the heats of formation of this ion from benzene and 1-butyne are 337 and 324 kcal/mole, respectively. The heat of formation of this ion is calculated assuming the loss of H + $2C_2H_2$. There is no doubt that this is the path of decomposition, as the metastable transitions of $C_8H_7^+$ to $C_6H_5^+$ to $C_4H_3^+$ were observed in all the compounds on which the metastables were determined. There again seems to be little doubt as to the structure of this ion.

The heat of formation of the $C_4H_2^+$ ion is extremely difficult to determine from these compounds. Both our experimental values and those determined by other investigators show a considerable amount of scatter. Values from the C_8H_8 isomers range from 340 to 384 kcal/mole. The literature values are similar: benzene, 335; 1,3-butadiyne, 338; 1,3-hexadiyne, 361; 1,4-hexadiyne, 387; 1,5-hexadiyne, 391; and 1,3-butadiene, 415. One possible explanation for this unusual amount of scatter is that there is simply no common ion and that two or three structures are involved. We feel that the primary reason for the scatter involved in these values is the uncertainty involved in assigning the paths producing the ions and by the varying amount of excess energy involved in their production. The $C_4H_2^+$ ion is produced by two known paths. When there is this much uncertainty involved in the path producing the ion, then the value selected becomes somewhat meaningless. Regardless of the uncertainty involved, it is difficult to postulate any structure for this ion other than a linear one.

Little can be said about the structure of the $C_3H_3^+$ ion and the results are listed only in the hope that future determinations will find the energetic data useful. There are no observed metastable transitions in these compounds for the production of this ion.

Discussion

A convenient way of comparing energy properties of a certain ionic species from several isomers is to compare the sum of the appearance potential of the ion plus the heat of formation of the parent molecule for the various isomers.[1] This comparison for all of the fragment ions in this study is given in Table XI. This comparison is not valid for the parent ion and these have not been included in the table. For each of the ions formed by fragmentation it is evident from the table that the values are approximately the same from all compounds, with a few exceptions. The most obvious exceptions are the $C_8H_7^+$, $C_8H_6^+$, and $C_6H_6^+$ ions from cubane, all of which are significantly higher than the average value for each species from the other compounds. It will be noted from Table III that the appearance potentials of all of these ions fall quite close to that of the parent ion. This behavior suggests that the ground-state appearance potentials of these three ions ($C_8H_7^+$, $C_8H_6^+$, and $C_6H_6^+$) should all be considerably less than the ionization potential, and approximate calculations bear this out. However, ionization necessarily precedes fragmentation and, hence, the appearance potentials of these ions are unavoidably high by some 1.5–2.5 eV. Since this is the case, these ions would not be expected to conform to the behavior observed for the corresponding ions from the other compounds. The remaining ions from cubane have appearance potentials that are 2 V or more greater than the ionization potential so the above argument does not apply to them. Some of these ions also appear to be formed with excess energy whereas others do not. However, the excess energy is in most instances considerably less than that observed with $C_8H_7^+$ and $C_8H_6^+$.

From the approximate agreement of the sum of the appearance potential plus heat of formation of the parent molecule as shown in Table XI, one concludes that at least in most instances ions of the same composition from all of these isomers must pass through a common intermediate and probably are formed with the same structure and heat of formation. This observation is in agreement with observations of Meyerson[1] and of Von Brunt and Wacks.[2]

Acknowledgments. The authors wish to express their gratitude to The Robert A. Welch Foundation for support of this research. We are also deeply grateful to Professor Rowland Pettit, Professor H. E. Zimmerman, Professor R. B. Turner, and Professor P. E. Eaton for supplying most of the compounds used in this study. We also acknowledge the assistance of Dr. Thomas Aczel of the Humble Oil and Refining Co. for determining the metastable transitions used in this study.

(31) F. H. Coats and R. G. Anderson, *J. Am. Chem. Soc.*, **79**, 1340 (1957).