Effect of Molecular Structure on Ionic Decomposition. II. An Electron-Impact Study of 1,3- and 1,4-Cyclohexadiene and 1,3,5-Hexatriene

J. L. Franklin and S. R. Carroll

Contribution from the Department of Chemistry, Rice University, Houston, Texas 77001. *Received May 8, 1969*

Abstract: Ionization and fragmentation schemes were constructed for 1,3- and 1,4-cyclohexadiene and 1,3,5-hexatriene through the use of energetic and metastable data. A value of 165 kcal/mole was obtained for the proton affinity of benzene from the heat of formation of the $C_6H_7^+$ ion from the three C_6H_8 isomers. It was found that the greater part of the M − 1 and M − 2 ions from 1,3,5-hexatriene were of cyclic structure although a small portion of these may be acyclic. The $C_4H_4^+$ ion from 1,4-cyclohexadiene and 1,3,5-hexatriene had a distinctly lower heat of formation than could be correlated to a linear ion and is suspected of being the cyclobutadiene ion.

The literature contains little information about the ions from the isomeric cyclohexadienes and 1,3,5-hexatriene. These three isomers are particularly interesting in that they illustrate the extent to which ring openings and closures take place in ionic decompositions of isomers. Also, these isomers provide a convenient means of obtaining the heat of formation of the benzenium ion ($C_6H_7^+$), an important intermediate in electrophilic aromatic substitution reactions, and the proton affinity of benzene.

Experimental Section

The mass spectra and appearance potential data were obtained primarily by means of a Consolidated Electrodynamics Corp. mass spectrometer, Type 21-701. This instrument has been discussed in the literature[1] as has its application to other problems of this type.[2] The Bendix TOF mass spectrometer which was used to determine some RPD appearance potentials has also been previously discussed.[2]

Carbon dioxide was used as a reference gas for calibration of the electron energy scale in the appearance potential determinations. The appearance potential data reported were evaluated by the EVD method of Warren.[3] 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 the reproducibility is 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 the ionization potentials and the ions produced by primary decompositions, the accuracy seems to be 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. The appearance potential values were corrected for the measured translational energy of the fragments by the method of Franklin and Haney which has previously been discussed.[2]

All three compounds studied in this work were reasonably volatile liquids which allowed the use of our normal liquid and gas inlet system. The background pressure was approximately 4×10^{-7} Torr, and a sample pressure of about 1×10^{-6} Torr was maintained on the source ionization gauge while measurements were being taken. Sample pressure in the ion source was controlled with a Granville–Phillips variable leak placed between the inlet's reservoirs and the source of the mass spectrometer. This leak provides a very fine, continuous control of the source pressure. All mass spectra were taken at a nominal voltage at 50 eV and a scan rate of approximately 20 min per 2500 V. The mass spectrum was scanned by varying the high voltage (accelerating potential) and holding the magnetic field constant. The mass discrimination of this CEC instrument has already been outlined.[2]

The CO_2 was obtained from Matheson, Inc., and the cyclohexadienes and the hexatriene were from K & K Laboratories, Inc.

Qualitative Features of Mass Spectra. The relative intensities of the major ions in the mass spectra are given in Tables I–III. Figure 1 is a breakdown pattern for the formation of all the principal ions; the modes of decomposition are confirmed through the use of metastable transitions and the energetics involved.

In the spectra of all three isomers, the loss of H, H_2, and C_2H_2 predominate. The rearrangement and resultant loss of CH_3 is also noted in all three of these C_6H_8 isomers. The P − 1 ion is the most intense peak with the parent ion being about 80% of the P − 1 ion in all three cases. The $C_6H_6^+$ ion is a very small peak in the spectrum of each isomer. In the mass spectra of these compounds, several doubly charged ions but no triply charged ions were observed.

Results

Ionization Potentials. Our experimental values are in fair agreement with previously determined ionization potentials for these compounds. Literature values for 1,3-cyclohexadiene are 8.54 eV[4] (electron impact) and 8.40 eV[5] (spectroscopic), which compare well with our values of 8.52 (EVD) and 8.30 eV for the RPD values. The 9.05-eV[4] ionization potential for 1,4-cyclohexadiene agrees less well with our values of 8.87 (EVD) and 8.65 eV (RPD). The only IP value we could find for 1,3,5-hexatriene in the literature was a theoretically calculated one by Streitwieser,[6] and it is 0.2 eV more than our experimental values of 8.44 (EVD) and 8.42 eV (RPD). We also compared our experimental ionization potentials to values calculated by Franklin's extension[7] of Hall's group orbital method.[8] We obtained calculated values of 8.5, 8.3, and 8.3 eV, respectively, for 1,3,5-hexatriene and 1,4- and 1,3-cyclohexadiene. The agreement of our experimental and calculated values is about 0.20 eV.

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(2) J. L. Franklin and S. R. Carroll, *J. Am. Chem. Soc.*, 91, 5940 (1969).
(3) J. W. Warren, *Nature*, 165, 810 (1950).
(4) S. Pignataro, A. Cassuto, and F. P. Lossing, *J. Am. Chem. Soc.*, 89, 3693 (1967).
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(7) J. L. Franklin, *J. Chem. Phys.*, 22, 1034 (1954).
(8) G. G. Hall, *Proc. Roy. Soc.* (London), 205a, 541 (1951); *Trans. Faraday Soc.*, 49, 113 (1953).

Table I. Appearance Potentials for 1,3,5-Hexatriene

Ion	m/e	Rel abundance	AP, eV	Total excess transl energy, eV	Neutrals[a]	ΔH_f, kcal/mole
$C_6H_8^+$	80+	55.9	8.42 ± 0.05[b]	...	...	234[c]
			8.44 ± 0.10			
$C_6H_7^+$	79+	100.0	9.96 ± 0.15	...	H	218
$C_6H_6^+$	78+	8.6	10.77 ± 0.10[b]	...	H_2	288[c]
			11.37 ± 0.15			
$C_6H_5^+$	77+	47.6	13.11 ± 0.10	...	H_2 + H	290
$C_5H_5^+$	65+	13.2	12.25 ± 0.10	0.06	CH_3	288
$C_5H_3^+$	63+	5.6	14.95 ± 0.15	0.18	H_2 + CH_3	347
$C_4H_6^+$	54+	7.1	12.25 ± 0.30	...	C_2H_2	268
$C_4H_5^+$	53+	21.4	13.60 ± 0.10	0.23	C_2H_2 + H	242
$C_4H_4^+$	52+	32.2	12.82 ± 0.10[b]	0.21	H_2 + C_2H_2	277[c]
$C_4H_3^+$	51+	43.8	16.54 ± 0.15[b]	0.21	H_2 + H + C_2H_2	310
$C_4H_2^+$	50+	29.5	16.46 ± 0.15[b]	0.31	$2H_2$ + C_2H_2	358[c]
$C_3H_3^+$	39+	82.3	14.65 ± 0.10	0.30	(CH_3 + C_2H_2)?	284

[a] Insufficient compound was available to permit measuring metastable transitions. [b] RPD. [c] Calculated using RPD value.

Appearance Potentials. The appearance potentials of the ions with relative intensity greater than 5–10% are given in Tables I–III. The metastable transitions leading to individual ions, the measured excess translational energy, and the neutrals assumed in calculating the ionic heats of formation are also indicated. The heats of formation of the neutrals used in the calculation of the ionic heats of formation are given in Table IV. The possible structures of the fragment ions from these isomers are discussed below with emphasis on rearrangements.

$C_6H_7^+$ Ion. The energy required to remove a hydrogen from these compounds is approximately the same as in cyclooctatetraene and barrelene.[2] This is especially surprising for 1,3,5-hexatriene as it would be expected that 2–3 eV more energy than this would be required if the process is the simple removal of a hydrogen from a double bond. In the cyclohexadienes there is also less energy required than is expected for removing a hydrogen from the double bond but is about what one would expect if the hydrogen is removed from a methylene group with the resulting opportunity for delocalization of the charge. These observations indicate that the resultant ion possesses an unusually stable structure. Further, the experimental heats of formation of the $C_6H_7^+$ ion from the cyclohexadienes and hexatriene are all very nearly the same (226, 223, 218 kcal/mole, respectively) which indicates that the P − 1 ions from all three of these compounds have the same structure. Since hexatriene is acyclic, a linear structure for the resulting ion is initially suggested. The heat of formation of a linear 79 ion can be estimated by a method developed by Franklin[9] for calculating the heats of formation of gaseous free radicals and ions. This method is essentially the group equivalent method with values assigned to individual ion and radical groups. Using it, we estimate a heat of formation of 245–250 kcal/mole for a linear $C_6H_7^+$ ion. A confirmation of this estimation is given by Harrison, *et al.*[10] They compared the heat of formation of the 79 ion from methyl-substituted cyclopentadienes to values previously obtained from a variety of other compounds. They found two distinct groupings of the heats of formation for this ion; one grouping was between 225 and 235 kcal/mole and the other between 250 and 260 kcal/mole. The higher values were assumed to correspond to a linear ion primarily because most of the compounds that gave results in this region were acyclic. Another indication that the heat of formation of a linear 79 ion is approximately 250 kcal/mole can be obtained by calculating the proton affinity of a linear C_6H_8 molecule. If one assumes that the 250 kcal/mole is the heat of a linear 79 ion, then a proton affinity of 205 kcal/mole is obtained. This value is in line with what one would expect by calculating the proton affinity of propadiene (193 kcal/mole) and 1,3-butadiene (186 kcal/mole) by the same method. This indicates that the 250–260 kcal/mole is a reasonable estimation of the heat of formation of a linear 79 ion. Harrison estimated the heat of formation of the methylcyclopentadienyl ion to be approximately 260 kcal/mole which means that the structure of the ions corresponding to the lower heats of formation does not resemble either a linear or cyclopentadienyl structure.

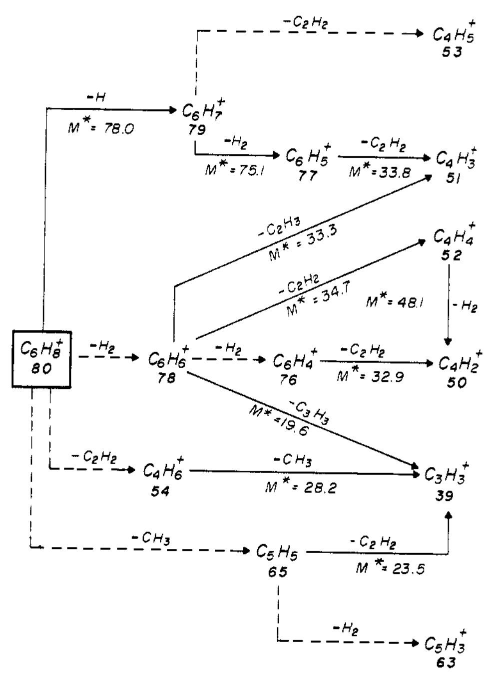

Figure 1. Fragmentation pattern.

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Table II. Appearance Potentials for 1,4-Cyclohexadiene

Ion	m/e	Rel abundance	AP, eV	Total excess transl energy, eV	Obsd metastable transitions $[m^*]$		Neutrals	ΔH_f, kcal/mole
$C_6H_8^+$	80^+	78.4	8.65 ± 0.05[a]	...	...	...	...	226[b]
			8.87 ± 0.10					
$C_6H_7^+$	79^+	100.0	10.94 ± 0.10	...	...	...	H	226
$C_6H_6^+$	78^+	14.2	9.86 ± 0.05[a]	...	...	...	H_2	254[b]
			9.61 ± 0.10					
$C_6H_5^+$	77^+	60.7	13.92 ± 0.10	...	...	...	$H_2 + H$	295
$C_5H_5^+$	65^+	9.6	13.41 ± 0.10	0.07	...	...	CH_3	301
$C_5H_3^+$	63^+	4.1	16.12 ± 0.10	0.20	...	...	$CH_3 + H_2$	360
$C_4H_6^+$	54^+	5.6	12.17 ± 0.10	...	...	...	C_2H_2	253
$C_4H_5^+$	53^+	13.3	14.48 ± 0.10	0.05	...	...	$C_2H_2 + H$	253
$C_4H_4^+$	52^+	26.8	13.55 ± 0.10	0.05	34.7	$78^+ = 52^+ + 26$	$C_2H_2 + H_2$	283
$C_4H_3^+$	51^+	39.2	17.08 ± 0.10	0.09	33.3	$78^+ = 51^+ + 27$	$H + H_2 + C_2H_2$	312
					33.8	$77^+ = 51^+ + 26$		
$C_4H_2^+$	50^+	22.8	17.82 ± 0.25	0.20	32.9	$76^+ = 50^+ + 26$	$2H_2 + C_2H_2$	378
					48.1	$52^+ = 50^+ + 2$		
$C_3H_4^+$	40^+	7.9	13.95 ± 0.10	...	...	...	...	...
$C_3H_3^+$	39^+	49.6	15.20 ± 0.10	(0.08)?	19.6	$78^+ = 39^+ + 39$	$CH_3 + C_2H_2$	288
					28.2	$54^+ = 39^+ + 15$		
$C_3H_2^+$	38^+	12.4	19.21 ± 0.15	...	...	...	...	...

[a] RPD. [b] Calculated using RPD value.

Table III. Appearance Potentials for 1,3-Cyclohexadiene

Ion	m/e	Rel abundance	AP, eV	Total excess transl energy, eV	Observed metastable transitions $[m^*]$		Neutrals	ΔH_f, kcal/mole
$C_6H_8^+$	80^+	49.3	8.28 ± 0.05[a]	...	...	...	...	217[b]
			8.52 ± 0.10					
$C_6H_7^+$	79^+	100.0	10.82 ± 0.10	...	78.0	$80^+ = 79^+ + 1$	H	223
$C_6H_6^+$	78^+	10.4	10.12 ± 0.10[a]	...	...	...	H_2	259[b]
			9.88 ± 0.10					
$C_6H_5^+$	77^+	46.3	13.92 ± 0.10	...	75.1	$79^+ = 77^+ + 2$	$H_2 + H$	295
$C_5H_5^+$	65^+	10.3	13.02 ± 0.10	0.13	...	...	CH_3	290
$C_5H_3^+$	63^+	4.0	15.44 ± 0.10	0.07	...	...	$CH_3 + H_2$	347
$C_4H_6^+$	54^+	7.6	12.60 ± 0.10	...	...	...	C_2H_2	262
$C_4H_5^+$	53^+	15.5	14.69 ± 0.10	0.04	...	...	$C_2H_2 + H$	258
$C_4H_4^+$	52^+	32.1	13.91 ± 0.20	0.10	34.7	$78^+ = 52^+ + 26$	$C_2H_2 + H_2$	290
$C_4H_3^+$	51^+	46.6	17.62 ± 0.10	0.13	33.8	$77^+ = 51^+ + 26$	$H_2 + H + C_2H_2$	323
$C_4H_2^+$	50^+	29.0	19.81 ± 0.10	0.10	32.9	$76^+ = 50^+ + 26$	$C_2H_2 + 2H_2$	429
					48.1	$52^+ = 50^+ + 2$		
$C_3H_4^+$	40^+	10.7	14.52 ± 0.10	...	...	...	...	...
					19.6	$78^+ = 39^+ + 39$		
$C_3H_3^+$	39^+	64.5	14.87 ± 0.10	(0.11)?	23.5	$65^+ = 39^+ + 26$	$(CH_3 + C_2H_2)$?	279
					28.2	$54^+ = 39^+ + 15$		
$C_3H_2^+$	38^+	12.3	23.51 ± 0.50	...	...	...	...	...

[a] RPD. [b] Calculated using RPD value.

Table IV. Neutral Heats of Formation

Neutral	ΔH_f, kcal/mole	Ref sources
1,3,5-Hexatriene	40[a]	*b*
1,4-Cyclohexadiene	26.3[a]	*c*
1,3-Cyclohexadiene	26.0[a]	*c*
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 Franklin's group equivalent method: J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949). [b] R. B. Turner, personal communication, Chemistry Department, Rice University. [c] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1941, p 275. [d] D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. 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.

The most plausible structure for the $C_6H_7^+$ ion might correspond to the low heat of formation observed in a benzenium ion.[10–12] This postulate requires the hexatriene to form a ring. The benzenium ion is especially interesting because it enables one to calculate the proton affinity of benzene to be 165 kcal/mole. This is in fair agreement with a previously determined value (150 kcal/mole) which used the heat of formation of the 79 ion from 1,3-cyclohexadiene and 5-methyl-1,3-cyclohexadiene.[13] The heat of formation of the benzenium ion can be estimated by the group equivalent method and is about 225 kcal/mole. This value agrees with the lower group of experimentally determined heat of for-

(11) H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, Inc., New York, N. Y., 1963, pp 453–527.
(12) P. Natalis and J. L. Franklin, *J. Phys. Chem.*, 69, 2935 (1965).
(13) J. L. Franklin, F. W. Lampe, and H. E. Lumpkin, *J. Am. Chem. Soc.*, 81, 3152 (1959).

mation values. The available data leave little doubt that a 79 ion with a heat of formation of about 220 kcal/mole is a benzenium ion.

$C_6H_6^+$ Ion. The heats of formation of this ion from 1,3- and 1,4-cyclohexadiene and 1,3,5-hexatriene are 259, 254, and 288 kcal/mole, respectively. Since the ground-state heat of formation of the benzene ion is 233 kcal/mole,[14-16] we must assume that $C_6H_6^+$ from the cyclohexadienes is excited by 20–25 kcal/mole. However, if we assume that it is an acyclic ion, we find our values are 30–40 kcal/mole low. The estimated heat of formation for a linear 78 ion using the group equivalent and the group orbital methods is approximately 290 kcal/mole and has been experimentally confirmed by Momigny.[2,17] Since it is unlikely that electron-impact values will be low, due to the Franck–Condon principle,[18,19] the ions are assumed to correspond to an excited benzene ion.

The heat of formation of $C_6H_6^+$ from hexatriene is sufficiently high to be in fair agreement with values obtained from several linear C_6H_6 molecules by Momigny, *et al.*[17] However, it is possible that this ion is the benzene ion formed by a process involving more excess energy than do the others discussed above. Thus, it is not possible to decide whether this ion is linear or cyclic, although we are inclined to think it is probably linear.

What is not clear, however, is why the 79 ion from hexatriene is cyclic and the 78 ion is apparently linear. If one attempts to calculate the energy required for hexatriene to form a benzene ion (assuming no excess energy) by the loss of H_2 or 2 H, he finds that the former process should require 8.4 eV and the latter 12.9 eV. There is no doubt that the first process is not occurring as the appearance potential of the hexatriene's 78 ion is 10.8 eV with no indication of a lower energy process being present. However, if hexatriene formed a benzene ion by the loss of H from the postulated benzenium ion, it would correspond to the second process, the loss of 2 H, and would have an appearance potential of 12.9 eV. There is a definite break in the RPD curve for the 78 ion from hexatriene, about 2.5 eV above onset or at 13.3 eV. It cannot be known with certainty whether this break corresponds to the formation of benzene ion from the benzenium ion or to an excited state of the linear ion, but the break is so distinct that we think it is the former. The break in the RPD curve indicates nothing as to why hexatriene does not form its 78 ion by the lowest available path (8.4 eV), but it does lend some indirect evidence to the existence of the postulated benzenium ion.

$C_6H_5^+$ Ion. The heats of formation of this ion are 290, 295, and 295 kcal/mole, respectively, for 1,3,5-hexatriene and the cyclohexadienes. The importance of this ion and the difficulties of the determination of its structure have been previously discussed in the literature,[2] and the heats of formation of the 77 ion from these compounds do nothing to clear up the difficulties outlined in the above reference. The heats of formation for the 77 ion from the C_6H_8 studied are between the postulated values for the cyclic and acyclic structures.

$C_5H_5^+$ and $C_5H_3^+$ Ions. The $C_5H_5^+$ ion is produced from the parent ion by the loss of a methyl radical with accompanying rearrangement. Harrison, *et al.*,[10] studied the 65 ion from a series of methyl-substituted cyclopentadienes and related compounds; he determined heats of formation from a number of cyclic and acyclic compounds to be between 280 and 310 kcal/mole. We obtained values of 301, 290, and 288 kcal/mole for the heat of formation of this ion from 1,4- and 1,3-cyclohexadiene and 1,3,5-hexatriene, respectively. Harrison determined the heat of formation of this ion from 1,4-cyclohexadiene to be 309 kcal/mole,[10] which confirms our experimental determination. His results from other C_6H_8 isomers give 65 ions of nearly identical energy (see Table V) and, hence, of similar structures. Harrison estimated the heat of formation of the cyclopentadienyl cation to be about 270 kcal/mole and concluded that he had insufficient information to assign the cyclopentadienyl structure to the $C_5H_5^+$ ion. Like Harrison, we are unable to assign a structure to this ion.

The structure of the $C_5H_3^+$ ion is probably linear as any other structure is improbable. That does not mean that the heat of formation is a certainty because there is no metastable transition confirming the mechanism of production of this ion; however, the total loss of 17 mass units from the parent ion probably corresponds to the loss of CH_3 and H_2. This is the mechanism used to calculate the heat of formation values given in Tables I–III. If the ion were formed with the loss of CH_4 and H or CH_3 and 2H, the heat of formation would be the same in the former case and lowered by 104 kcal/mole in the latter case. The loss of CH_3 and 2 H would result in much too low a heat of formation for the ion, and it is obvious that we cannot distinguish between the neutral combinations of $CH_3 + H_2$ and $CH_4 + H$. The estimated heat of formation of a linear 63 ion is 290 kcal/mole, and our experimental values range from 347 to 360 kcal/mole. It is unlikely that we can have a heat of formation 60–70 kcal/mole above that estimated for a linear ion and be anything but an excited linear ion.

$C_4H_6^+$ and $C_4H_5^+$ Ions. The experimental heats of formation of $C_4H_6^+$ from 1,4- and 1,3-cyclohexadiene and 1,3,5-hexatriene are 253, 262, and 268 kcal/mole, respectively. The heat of formation of this ion from 1- and 2-butyne,[20,21] 1,2- and 1,3-butadiene,[20,22,23] 1,3-*trans*-pentadiene,[23] and 2,4-hexadiene[23] are 275, 264, 260, 236, 227, and 229 kcal/mole, respectively. It is difficult to understand why the values from the cyclohexadienes, hexatriene, the butynes, and 1,2-butadiene are so much higher than those from 1,3-butadiene, 1,3-*trans*-pentadiene, and 2,4-hexadiene. It is evident that our values correspond fairly closely to the heat of formation of the butyne or 1,2-butadiene ion and not to the 1,3-butadiene ion. If one estimates the heat of formation of cyclobutene, he gets approximately 250–260

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(19) J. Franck, *Trans. Faraday Soc.*, **21**, 536 (1926).
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(21) K. Watanabe, T. Nakayama, and J. Mottlo, *J. Quant. Spectrosc. Radiative Transfer*, **2**, 369 (1962).
(22) B. Brehm, *Z. Naturforsch.*, **21a**, 196 (1966).
(23) J. L. Franklin and A. Mogenis, *J. Phys. Chem.*, **71**, 2820 (1967).

Table V. Ionic Heats of Formation

Ion	m/e	Compound	ΔH_f, kcal/mole[a]
$C_6H_7^+$	79	2,4-Hexadiene	274[23]
		2,5-Dimethyl-2,4-hexadiene	266[23]
		1,3-Cyclohexadiene	235[10]
		Benzyl alcohol	228[10]
		1,2-Dimethylcyclopentadiene	233[10]
		Isobutenylacetylene	249[10]
		Bicyclo[3.2.0]hept-6-ene	224[10]
		1,3-Cycloheptadiene	224[10]
		Butenylacetylene	252[10]
$C_6H_6^+$	78	Benzene	233[14-16]
		2,4-Hexadiyne	301[17]
		1,3-Hexadiyne	307[17]
		1,4-Hexadiyne	319[17]
		1,5-Hexadiyne	338[17]
		Butadienylacetylene	304[17]
$C_6H_5^+$	77	Phenyl radical	*282[b]
		Benzene	*286[22]
		Benzene	298[17]
		2,4-Hexadiyne	293[17]
		1,3-Hexadiyne	304[17]
		1,4-Hexadiyne	309[17]
		1,5-Hexadiyne	312[17]
$C_5H_5^+$	65	Bicyclo[3.2.0]heptadiene	299[10]
		Toluene	290[10]
		Methylcyclopentadiene	306[10]
		Cyclopentadiene	271[c]
		Cycloheptatriene	306[d]
		2,4-Hexadiyne	301[23]
		1,3-*trans*-Pentadiene	288[23]
		1,4-Cyclohexadiene	309[10]
		Butadienylacetylene	307[10]
$C_5H_3^+$	63	Benzene	375[e]
		2,4-Hexadiyne	366[17]
$C_4H_6^+$	54	1,3-Butadiene	*236[22,23]
		1,3-*trans*-Pentadiene	227[22]
		2,4-Hexadiene	229[22]
		1-Butyne	*275[20,21]
		2-Butyne	264[20]
		1,2-Butadiene	260[20]
$C_4H_5^+$	53	1,3-Butadiene	*237[22]
		1,3-Butadiene	255[23]
		1,3-*trans*-Pentadiene	275[23]
		2,4-Hexadiene	257[23]
		2,5-Dimethyl-2,4-hexadiene	255[23]
		1-Butyne	245[20]
		2-Butyne	262[20]
$C_4H_4^+$	52	Vinylacetylene	294[24,25]
		Benzene	311[12]
		1-Butyne	291[20]
		2,4-Hexadiyne	314[17]
		1,3-Hexadiyne	313[17]
		1,4-Hexadiyne	314[17]
		1,5-Hexadiyne	308[17]
$C_4H_3^+$	51	Vinylacetylene	303[26]
		Benzene	337[27]
		1-Butyne	324[20]
$C_4H_2^+$	50	1,3-Butadiyne	338[20]
		1,3-Hexadiyne	361[17]
		1,4-Hexadiyne	387[17]
		1,5-Hexadiyne	391[17]
		Benzene (assuming the loss of C_2H_3 + H)	335[e]
		Benzene (assuming the loss of C_2H_2 + H_2)	396[e]
		1,3-Butadiene	415[23]
$C_3H_3^+$	39	1-Propyne	316[20]
		2,4-Hexadiyne	373[17]
		1,3-Hexadiyne	388[17]
		1,4-Hexadiyne	386[17]
		1,5-Hexadiyne	396[17]

[a] Starred values denote photoionization. [b] I. P. Fisher, T. F. Palmer, and F. P. Lossing, *J. Am. Chem. Soc.*, **86**, 2741 (1964). [c] A. G. Harrison, L. R. Honne, J. J. Dauben, and F. P. Lossing, *ibid.*, **82**, 5593 (1960). [d] C. Lifshitz and S. H. Bauer, *J. Phys. Chem.*, **67**, 1629 (1963). [e] J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

kcal/mole, so our values might also correspond to a cyclobutene ion.

The heats of formation of $C_4H_5^+$ are calculated on the basis of the loss of C_2H_2 + H from the parent ion. The other choice for a neutral product, the loss of C_2H_3, would raise the heat of formation by 41 kcal/mole. This is considerably greater than the heat of formation of any reasonable structure. Our experimental heats of formation are between 240 and 260 kcal/mole as are most of the literature values.[20,22,23] An estimation of the heat of formation of a linear 53 ion is about 240 kcal/mole and, although we do not have sufficient information to be certain, we feel that we can reasonably conclude that the $C_4H_5^+$ ion has a linear structure.

$C_4H_4^+$ Ion. The heat of formation of $C_4H_4^+$ from 1,4- and 1,3-cyclohexadiene and 1,3,5-hexatriene has values of 283, 290, and 277 kcal/mole, respectively. Normally this ion is assumed to have the vinylacetylene ion structure. The heat of formation for the vinylacetylene ion is 294 kcal/mole.[24,25] The 290 kcal/mole for this ion from 1,3-cyclohexadiene is within experimental error of this value. Only one other compound has yielded a heat of formation for the 52 ion lower than the 294 kcal/mole for the vinylacetylene ion and that is the 291 kcal/mole from 1-butyne.[21] This value also agrees within experimental error, but the 283- and 277-kcal/mole values for 1,4-cyclohexadiene and 1,3,5-hexatriene are beyond experimental error, and another structure must be suspected. By using the group equivalent method to estimate the heat of formation of cyclobutadiene and by then estimating its ionization potential, an upper limit for the heat of formation of the cyclobutadiene ion is determined to be 270–280 kcal/mole. As was pointed out earlier, the tendency of electron-impact values is to be high so, if we can assume our estimation of the heat of formation is even a reasonable approximation to the actual heat of formation of the cyclobutadiene ion, then we can postulate that the 52 ion from the cyclohexadienes and hexatriene may well in fact be the cyclobutadiene ion. Obviously this inference is highly speculative.

$C_4H_3^+$ and $C_4H_2^+$ Ions. The heats of formation of $C_4H_3^+$ are listed in Tables I–III. The values obtained are fairly constant, ranging from 310 to 323 kcal/mole, and are consistent with previous determinations.[2,20,26,27] One possible explanation for this unusual amount of scatter is that there is simply no common ion and that two or three different structures are involved. The authors feel that the reason for the scatter in the values determined in this work is the uncertainty involved in assigning the paths producing the ions and by the varying amounts of excess energy involved in their production. This ion is produced by three known paths, and, when there is that much uncertainty involved in the path producing the ion, then the value selected for a heat of formation is somewhat meaningless. Regardless of the uncertainty involved, it is difficult to postulate any structure for this ion other than a linear one.

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$C_3H_4^+$, $C_3H_3^+$, and $C_3H_2^+$ Ions. Little can be said about the structure of these ions, and they are listed only in the hope that future determinations will find the energetic data useful. As with the $C_4H_2^+$ ion, the almost total uncertainty as to the origin of these ions makes a calculation of a heat of formation virtually impossible.

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Magnetic Resonance Studies of Some Phenoxy and Nitroxide Biradicals

Peter W. Kopf[1] and Robert W. Kreilick

Contribution from the Department of Chemistry, University of Rochester, Rochester, New York 14627. *Received April 22, 1969*

Abstract: We have taken the nmr and esr spectra of a series of phenoxy and nitroxide biradicals. The susceptibilities of these compounds were measured by monitoring the shifts of internal diamagnetic reference peaks as a function of radical concentration. The sign and magnitude of most of the electron-nuclei coupling constants could be determined from these data. In some instances we were able to measure singlet-triplet energy separations. Both the contact shifts and the susceptibilities were measured at a series of different temperatures.

In a series of earlier papers we have reported the nmr spectra of a number of organic monoradicals.[2] The liquid radical di-*t*-butyl nitroxide (DBNO) has been used as a solvent for a second solute radical. Rapid spin exchange between solute and solvent molecules averages the electron spin states, and one is able to observe relatively sharp nmr lines. The sign and magnitude of the electron-nuclei coupling constants can be determined from the shifts of the nmr lines.

The same general technique can be used to obtain the nuclear resonance spectra of biradicals. This type of study is of particular interest, as in many cases the dipolar interaction between the two electrons of the biradicals broadens the esr spectra and one is unable to determine coupling constants. The equation relating nmr shifts ($\Delta\nu$) to coupling constants (a_i) is given by

$$\left(\frac{\Delta\nu}{\nu}\right)_{\text{contact}} = -a_i\chi_m/Ng_N\beta_Ng\beta \qquad (1)$$

If the spin energy levels are defined by singlet and triplet functions, the molar susceptibility (χ_m) is given by[3]

$$\chi_m = \frac{S(S+1)g^2\beta^2N}{3kT}\left[\frac{1}{1+\exp(\Delta G/RT)}\right] \qquad (2)$$

ΔG is the energy separation between the singlet and triplet states and is defined: ΔG = G(triplet) − G(singlet). If one introduces eq 2 into 1, one obtains an equation for the shifts in terms of ΔG and a_i.

$$\left(\frac{\Delta\nu}{\nu}\right)_{\text{contact}} = \frac{-a_ig\beta S(S+1)}{3kT[1+\exp(\Delta G/RT)]} \qquad (3)$$

If independent measurements of contact shifts and susceptibilities are made, it is possible, in some instances, to obtain the values of both a_i and ΔG.

The volume susceptibilities of the biradicals can be determined from susceptibility shifts of diamagnetic solvent peaks.[4] The relation between the volume susceptibility and the shift given by

$$\left(\frac{\Delta\nu}{\nu}\right)_{\text{susceptibility}} = \frac{2}{3}\pi\Delta\chi \qquad (4)$$

If susceptibilities are determined by this technique one can calculate ΔG from eq 2 and determine coupling constants from the contact shifts.

The biradical's coupling constants should depend on the magnitude of the exchange integral for the two spins.[5] The spin-Hamiltonian which has been used to describe the hyperfine and exchange interactions can be written as

$$H = a(S_1\cdot I_1 + S_2\cdot I_2) + JS_1\cdot S_2 \qquad (5)$$

In this expression J represents the exchange integral, and I_1, I_2, S_1, and S_2 are the nuclear and electron spin operators. In cases in which $a \gg J$, the biradical acts as two separate monoradicals with each electron interacting with n_1 nuclei on a given side of the molecule. In this case one observes $2n_1I + 1$ lines in the esr spectra with a separation of a. When J is greater than a, both electrons interact with all of the nuclei (n_2) and one observes $2n_2I + 1$ lines separated by $(n_1/n_2)a$.

We have taken nmr and esr spectra of a series of phenoxy and nitroxide radicals shown in Figure 1. The nmr and esr spectra of the phenoxy monoradicals were also taken. Susceptibility measurements were made on all of the biradicals except compound III which was too unstable for this type of measurement. Both the contact shifts and the susceptibility shifts were mea-

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