Mass Spectrometric Studies of Structural Isomers.
I. Mono- and Bicyclic C_7H_{12} Molecules

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Abstract: The mass spectra, metastable transitions, and the appearance potentials of several ions have been obtained for four monocyclic and two bicyclic C_7H_{12} isomers. The molecular ionization potentials determined by the energy distribution difference (EDD) technique are: 8.67 ± 0.02, 8.94 ± 0.03, 8.92 ± 0.02, 9.04 ± 0.03, 9.93 ± 0.02, and 9.03 ± 0.02 eV for 1-methylcyclohexene, 3-methylcyclohexene, 4-methylcyclohexene, methylenecyclohexane, bicyclo[2.2.1]heptane, and bicyclo[4.1.0]heptane, respectively. It is shown that these ionization potentials are dependent upon structural features of the isomeric molecules, *e.g.*, double-bond substitution and ring strain. The differences between the calculated heats of formation for the gaseous parent molecule ions are discussed in terms of the structural differences between the original molecules. Heats of formation for fragment ions indicate that ionization–fragmentation usually produces the same ionic species independent of the original molecules.

The 70-eV mass spectra of many molecules, especially unsaturated and/or cyclic hydrocarbons with the same empirical formula, are very similar.[1] The same ions occur in all the spectra and differ only in their relative abundance. For this reason it is difficult to make correlations between structure and spectra. In such cases, determination of the structure of a complete unknown, where several isomers are possible, is practically impossible if additional information is not available. However, since the energy necessary for ionization and ionization–fragmentation of organic molecules is dependent upon structure,[2] it should be possible to use experimentally determined ionization and appearance potentials (IP and AP) as the necessary additional information for structural elucidation of isomeric systems. One of the major difficulties, however, is the accurate determination of these potentials.[3] Because of the relatively wide energy spread of electrons emitted from a hot filament, the ionizing electrons may have energies differing by as much as ±1 eV from the mean energy.[4] This causes tailing in the ionization efficiency (IE) curves and prevents the determination of accurate threshold energies. However, it has recently been shown[5] that the effect of the electron energy distribution can be greatly reduced by employing a new technique [the energy distribution difference (EDD) technique] for the treatment of ionization efficiency curve data. Curves obtained by this method can be interpreted as ionization resulting from nearly monoenergetic electrons, *i.e.*, sharp ionization onsets are obtained. Previous results[5] for monoatomic and diatomic gases show ionization potentials may be determined with an accuracy of ±0.03 eV by this technique. It should be possible, therefore, to detect small differences between ionization and appearance potentials for different molecules or ions and to relate these differences to structural features in the molecules. In this paper, we report results for six C_7H_{12} mono- and bicyclic isomers: 1-methylcyclohexene, 3-methylcyclohexene, 4-methylcyclohexene, methylenecyclohexane, bicyclo[2.2.1]heptane, and bicyclo[4.1.0]heptane.

Experimental Section

The appearance potentials, metastable transitions, and mass spectra were obtained using an Atlas CH-4 mass spectrometer. The experimental conditions have been described previously.[5] The only change was replacement of the 10-turn electron energy potentiometer with a 20-turn potentiometer in order to increase the ease with which the electron accelerating voltage could be set at 0.05-eV intervals. Krypton (IP = 14.00 eV[6]) was used to calibrate the energy scale. Sample pressures in the ionization region were maintained at less than 10^{-5} torr.

The ionization efficiency curves ($\Delta I(V)$ *vs.* V) were obtained from ion current *vs.* accelerating voltage data by applying the simple expression[5]

$$\Delta I(V) = I(V) - bI(V') = I(V) - 0.65I(V + 0.10\text{ eV}) \quad (1)$$

where $I(V)$ is the ion current at accelerating voltage V and $I(V')$ is the ion current at a slightly higher voltage $V' = V + 0.10$ eV. The constant b was previously determined to be 0.65 for the operating conditions of the mass spectrometer. For $V' = V + 0.10$ eV and $b = 0.65$, the half-width of the difference distribution has been estimated to be 0.14 eV.[5]

The 1-methylcyclohexene, 3-methylcyclohexene, 4-methylcyclohexene, methylenecyclohexane, and bicyclo[2.2.1]heptane samples were obtained from the Aldrich Chemical Company (99% or better purity). Bicyclo[4.1.0]heptane was prepared by the Simmons–Smith reaction of cyclohexene with methylene iodide.[7] The product was purified by gas chromatography.

Results and Discussion

General Features of the Mass Spectra. The 70-eV mass spectra of the six C_7H_{12} isomers are shown in Figure 1. The spectra of 1-methylcyclohexene, 4-methylcyclohexene, and bicyclo[2.2.1]heptane reported here agree well with those in the API tables.[8] In light

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[1] For discussions of this subject, see the following: (a) L. D'Or, J. Momigny, and P. Natalis in "Advances in Mass Spectrometry," Vol. 2, R. M. Elliott, Ed., Pergamon Press Inc., New York, N. Y., 1962, p 370; (b) H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, Chapter 10.

[2] F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957, Chapter IV.

[3] M. Krauss and V. H. Dibeler in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, Chapter 3; A. J. C. Nicholson, *J. Chem. Phys.*, **29**, 1312 (1958).

[4] R. E. Honig, *ibid.*, **16**, 105 (1948).

[5] R. E. Winters, J. H. Collins, and W. L. Courchene, *ibid.*, **45**, 1931 (1966).

[6] A. J. C. Nicholson, *ibid.*, **43**, 1171 (1965).

[7] H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, **81**, 4256 (1959).

[8] Catalog of Mass Spectral Data, API Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa., Serial No. 1174, 1491, and 1466.

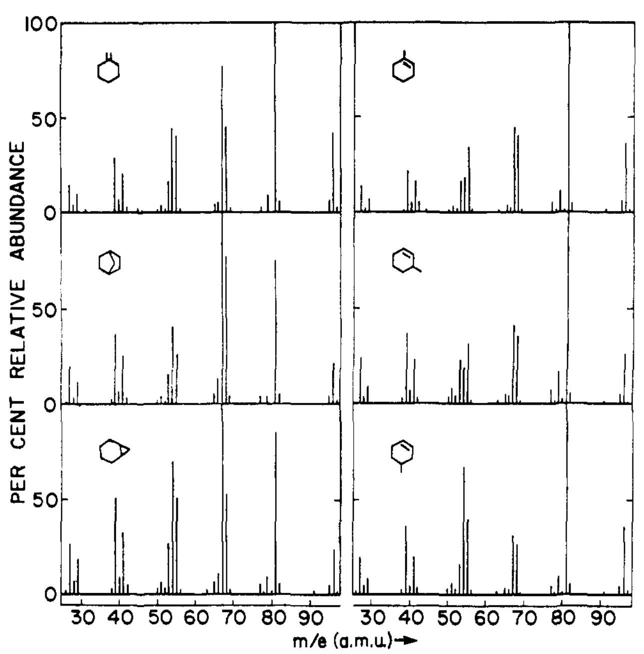

Figure 1. The 70-eV mass spectra for C_7H_{12} mono- and bicyclic isomers.

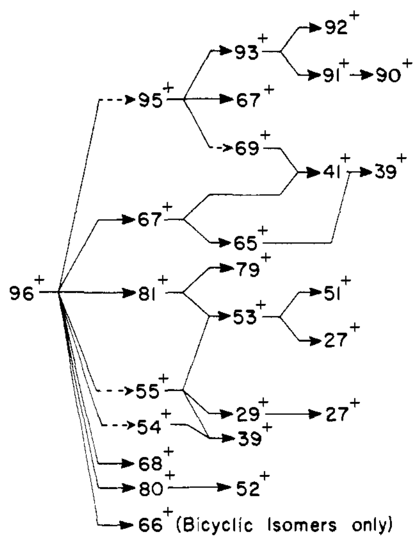

Figure 2. Proposed breakdown scheme for the mono- and bicyclic C_7H_{12} isomers. Metastable transitions observed are indicated by the solid lines.

of earlier work on isomeric systems,[1] the similarity between the spectra for these isomers is not surprising. Such similarity suggests that fragmentation in these molecules occurs by common pathways which involve common fragmentation intermediates. The metastable transitions shown in Figure 2 support this suggestion. Since metastable peaks are not observed for many decompositions, the general breakdown scheme of Figure 2 was derived by considering not only the metastable ions but also the principal fragment ions in the 70-eV mass spectra. For the monocyclic isomers, metastable peaks corresponding to the same series of competing and consecutive unimolecular decompositions were found. The bicyclic compounds also fragment by these pathways; however, an additional metastable peak corresponding to the loss of 30 amu (C_2H_6 or $C_2H_4 + H_2$) from the parent molecule ion was detected.

The strongest metastable peaks in the mass spectra of the C_7H_{12} compounds are those due to the transitions: $C_7H_{12}^+ \rightarrow C_6H_9^+ + CH_3$ and $C_6H_9^+ \rightarrow C_6H_7^+ + H_2$. The peak shape of the metastable peak due to the latter decomposition was found not to have the usual gaussian shape; instead, a "flat-topped" peak was observed. Previous studies[9] have attributed such a shape to the conversion of internal energy of the molecular ion into kinetic energy of the fragments.

Molecular Ionization Potentials. The ionization potentials for the six C_7H_{12} isomers are shown in Table I. Of these six cyclic molecules, photoionization ionization potential data have been reported only for 4-methylcyclohexene. Our value of 8.92 ± 0.02 eV is in agreement with the photoionization value of 8.91 eV.[10] Recently Pignataro, *et al.*,[11] reported electron impact ionization potentials for 3-methylcyclohexene and 4-methylcyclohexene (9.08 and 9.13 eV, respectively). These values are approximately 0.2 eV higher than our values and, in the case of 4-methylcyclohexene, approximately 0.2 eV higher than the photoionization value.[10] A possible reason for these discrepancies will be discussed later.

The electron removed upon ionization of the C_7H_{12} monocyclic isomers is undoubtedly one of the π electrons. Therefore the differences observed between the ionization potentials of these molecules can be attributed to substituent effects upon the double bond. As groups are attached to the double-bonded carbon atoms the ionization potential of the species is lowered. Thus the IP of 1-methylcyclohexene, which has three substituents on the double bond, is significantly lower than the ionization potentials of the isomers which have only two groups associated with the double bond. Also, whether the groups are bonded in the 1,1 or 1,2 positions of the double bond is important, *e.g.*, the IP of methylenecyclohexane (1,1 type) is approximately 0.1 eV higher than the IP of 3- or 4-methylcyclohexene (1,2 type). These are the same trends observed for methyl-substituted ethylenes.[12] The isomeric methylcyclohexenes with the methyl group in the 3 and 4 position have ionization potentials which are the same within experimental error and are very close to the ionization potential of cyclohexene (8.945 eV[12]). Therefore the substituent group effect is a relatively short-range effect which alters the ionization potential most when the group or groups are bonded directly to a carbon of the double bond.

The difference between the ionization potentials of the two saturated bicycloheptane isomers may be due to the strain energies in the molecules resulting from the bridging methylene group. Bicyclo[2.2.1]heptane (norbornane) is known to have little strain due to the CH_2 bridge.[13] Therefore, the ionization potential of this

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(9) J. H. Beynon, R. A. Saunders, and A. E. Williams, *Z. Naturforsch.*, **20a**, 823 (1965); T. W. Shannon, F. W. McLafferty, and C. R. McKinney, *Chem. Commun.*, 478 (1966).

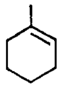
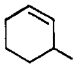
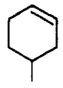
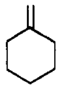
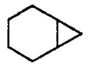
(10) K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectry. Radiative Transfer*, **2**, 369 (1962).

(11) S. Pignataro, A. Cassuto, and F. P. Lossing, *J. Amer. Chem. Soc.*, **89**, 3693 (1967).

(12) R. W. Kiser, "Tables of Ionization Potentials," U. S. Atomic Energy Commission, TID-6142, June 20, 1960; Additions and Corrections, June 20, 1962.

(13) C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press Inc., New York, N. Y., 1962, Chapter 2.

Table I. Appearance Potentials of the Principal Ions from the C_7H_{12} Mono- and Bicyclic Isomers

	Appearance potentials, eV					
Ion						
$C_7H_{12}^+$	8.67 ± 0.02	8.94 ± 0.03	8.92 ± 0.02	9.04 ± 0.03	9.93 ± 0.02	9.03 ± 0.02
$C_6H_9^+$	10.27 ± 0.09	9.98 ± 0.07	10.12 ± 0.10	10.27 ± 0.08	10.17 ± 0.06	9.30 ± 0.09
$C_5H_8^+$	10.56 ± 0.15	10.50 ± 0.04	10.39 ± 0.05	10.46 ± 0.08	10.30 ± 0.07	9.37 ± 0.07
$C_5H_7^+$	10.47 ± 0.07	10.43 ± 0.05	10.43 ± 0.10	10.45 ± 0.11	10.60 ± 0.10	9.53 ± 0.07
$C_4H_7^+$	11.48 ± 0.05	11.22 ± 0.05	11.24 ± 0.04	11.34 ± 0.04	11.45 ± 0.05	10.27 ± 0.08
$C_4H_6^+$	11.02 ± 0.08	10.94 ± 0.04	10.82 ± 0.12	10.94 ± 0.05	11.12 ± 0.03	10.10 ± 0.09
$C_4H_5^+$	13.22 ± 0.10	13.42 ± 0.07	13.43 ± 0.13	13.10 ± 0.10	13.44 ± 0.11	12.42 ± 0.10
$C_3H_5^+$	13.46 ± 0.09	13.29 ± 0.11	13.38 ± 0.11	13.25 ± 0.11	13.22 ± 0.12	11.90 ± 0.10
$C_3H_3^+$	14.06 ± 0.13	13.85 ± 0.08	14.02 ± 0.15	13.90 ± 0.13	14.03 ± 0.09	12.53 ± 0.12

bicyclic hydrocarbon should not, and certainly does not, differ greatly from the ionization potential of cyclohexane (9.88 eV[12]). However, the bicyclo[4.1.0]heptane molecule, with the bridge across adjacent carbon atoms resulting in a fused cyclopropane and cyclohexane bicyclic ring system, is quite strained.[13] The ionization potential of this molecule is 0.90 eV below that of the [2.2.1] isomer and is only slightly higher than cyclohexene (8.945 eV[12]).

Ionization efficiency (IE) curves for the six parent molecule ions are shown in Figure 3. The ionization onsets have been set at 0 eV to facilitate comparison. In each case there are two breaks in the region between onset and 0.7 eV above onset. Melton and Hamill[14] have discussed possible reasons for the occurrence of these breaks in IE curves of polyatomic molecules. Upon the basis of limited experimental evidence from measurements using monoenergetic electrons, we will not attempt to assign processes to the structure observed in these curves. It is possible, however, to make some general conclusions from the energy at which breaks occur in the curves for the $C_7H_{12}^+$ ions. Previous studies[14,15] have shown that for structurally analogous fragment ions, derived from various precursors, common breaks appear in their IE curves. This should be true for parent molecule ions with identical structure. Therefore, the variation in the energy at which breaks occur in the IE curves for the isomeric $C_7H_{12}^+$ ions (Figure 3) can be interpreted as evidence that the ions have different structures. It is of interest to note that even in the case of the positional isomers, 3- and 4-methylcyclohexene, differences are observed between their ionization efficiency curves.

It was previously noted that the ionization potentials of 3- and 4-methylcyclohexene are approximately 0.2 eV higher when determined by low-energy resolution[11] than when determined by the EDD technique or by photoionization. A possible explanation for this disagreement is that the transition of lowest energy for the $C_7H_{12}^+$ ions cannot be detected with low-energy resolution when the conventional methods[2] for onset detection are employed. Indeed, the IE curves for the $C_7H_{12}^+$ ions show a low relative cross section for the first energy transition and a sharp increase in ionization cross section approximately 0.2 eV above onset.

Thermochemical Considerations. The similarity of the mass spectra and of the metastable transitions for the isomeric compounds is consistent with, but does not prove, the suggestion that fragmentation forms ions of the same structure. Further support for this suggestion can be obtained from an examination of the heats of formation of the principal fragment ions from these compounds, since ionic heats of formation are independent of the source of the ions and the mechanism by which the ions are formed but do depend upon the structure of the ions. The results of the heat of formation calculations for the principal ions from the six isomers are listed in Table II. Thermochemical data that were used in the calculations are shown in Table III. Probable neutral product(s) formed with the ions in column one are shown in column two. Where possible the processes for the formation of the ions were made consistent with the metastable transitions (see Figure 2) observed in the 70-eV mass spectra; however, it should be noted that these processes are threshold processes and do not necessarily correspond to the major fragmentation paths at 70 eV.

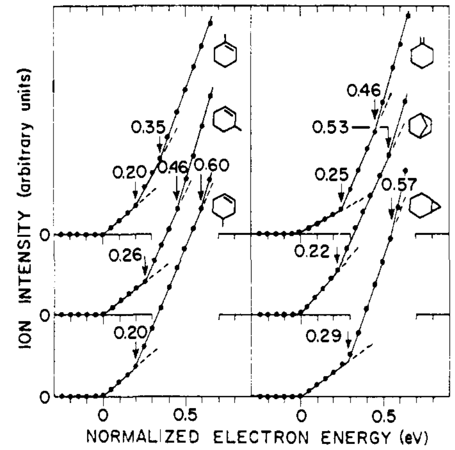


Figure 3. Ionization efficiency curves for $C_7H_{12}^+$ ions.

Variations in heats of formation of the parent molecule ions (Table II) are due to the fact that the molecule ions are structurally different. The thermodynamic stability is greater (lowest ΔH_f) for the 1-methylcyclohexene molecule ion and lowest for the ionized bicycloheptane isomers. This stability is consistent with the 70-eV mass spectra (Figure 1) since the fractional abundances of the parent molecule ions from the bicyclic isomers are much smaller than the fractional

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(14) C. E. Melton and W. H. Hamill, *J. Chem. Phys.*, **41**, 546 (1964).

(15) S. Tsuda and W. H. Hamill, *ibid.*, **41**, 2713 (1964); B. Steiner, C. F. Giese, and M. G. Inghram, *ibid.*, **34**, 189 (1961).

Table II. Heats of Formation of the Principal Ions of C_7H_{12} Isomers

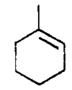
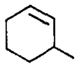
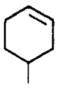
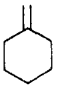
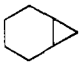
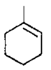
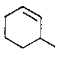
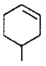
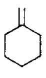
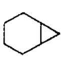
Ion	Probable neutral product(s) in addition to ion	ΔH_f(ion), kcal/mol 					
$C_7H_{12}^+$		190	198	198	202	218	216
$C_6H_9^+$	CH_3	192	188	192	197	190	189
$C_5H_8^+$	C_2H_4	221	222	219	223	214	212
$C_5H_7^+$	C_2H_5	205	207	207	209	208	202
$C_4H_7^+$	C_3H_5	216	213	213	217	215	207
$C_4H_6^+$	C_3H_6	239	239	237	241	241	236
$C_4H_5^+$	n-C_3H_7	274	281	281	275	278	273
	i-C_3H_7	277	284	284	278	281	277
$C_3H_5^+$	$C_2H_2 + C_2H_5$	220	219	221	220	214	203
	C_4H_7						(238)
$C_3H_3^+$	$CH_3 + C_3H_6$	275	273	276	275	274	258
	n-C_4H_9						(280)

Table III. Heats of Formation Employed in Thermochemical Calculations

Species	ΔH_f, kcal/mol	Ref	Species	ΔH_f, kcal/mol	Ref
	−10.4	*a*	C_2H_4	12.5	*e*
	−7.9	*b*	C_2H_5	25.7	*d*
	−7.9	*b*	C_3H_5	38	*d*
	−6.2	*b*	C_3H_6	5.0	*e*
			n-C_3H_7	21	*d*
	−11.0	*c*	i-C_3H_7	17.6	*d*
	8.0	*b*	C_4H_7 ($CH_3CH{=}CHCH_2$)	26	*f*
			n-C_4H_9	17	*d*
CH_3	34	*d*			
C_2H_2	54.2	*e*			

[a] Calculated from reported heat of combustion data [A. Labbauf and F. D. Rossini, *J. Phys. Chem.*, **65**, 476 (1961)] and heat of vaporization data [R. R. Dreisbach, "Physical Properties of Chemical Compounds," Advances in Chemistry Series, No. 15, American Chemical Society, Washington, D. C., 1955, p 490]. [b] Calculated by the group equivalent method [J. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949), and H. Lehmann and E. Ruschitzky, *Chem. Tech.* (Berlin), **16**, 18 (1964)]. [c] Reference 11, p 44. [d] J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966). [e] F. D. Rossini, *ibid.*, **27**, 1 (1940). [f] See ref 18.

abundances of the molecule ions from the monocyclic compounds.

The energy necessary to remove a methyl group from the parent molecule ion is approximately 1 eV greater for the monocyclic compounds than for the bicyclics. However, the $C_6H_9^+$ ions formed when a methyl group is lost may have the same structure. The average heat of formation for the six $C_6H_9^+$ ions is 191 ± 3 kcal/mol. No definite postulate can be made as to whether the ion is cyclic or acyclic.

The loss of two carbon atoms as C_2H_4 and C_2H_5 proceeds by primary competing processes (see metastable transitions in Figure 2). The ΔH_f values for the $C_5H_8^+$ ions are larger for the monocyclic isomers (221 ± 1 kcal/mol) than for the bicyclic isomers (213 ± 1 kcal/mol). The former value is in good agreement with 222 kcal/mol[16] for the ΔH_f of acyclic $C_5H_8^+$ from 2-methyl-1,3-butadiene, whereas the latter value is only slightly higher than the ΔH_f of cyclic $C_5H_8^+$ from cyclopentane.[17] The agreement between $C_5H_7^+$ ΔH_f values for the six C_7H_{12} compounds is quite good. Also, the ΔH_f(206 ± 2 kcal/mol) is only slightly lower than the 211 kcal/mol recently reported by Pignataro, *et al.*,[11] for this ion. These workers concluded that the $C_5H_7^+$ ion is cyclic since the heat of formation is too low to correspond to the formation of an acyclic $C_5H_7^+$ ion.

The C_4 fragments indicate the loss of C_3H_5, C_3H_6, and C_3H_7 from the parent molecules. The heats of formation for $C_4H_7^+$, $C_4H_6^+$, and $C_4H_5^+$ ions indicate structural similarity for each ion independent of the structure of the C_7H_{12} molecule from which it originates. The average value (214 ± 4 kcal/mol) for the heat of formation of $C_4H_7^+$ ions from the C_7H_{12} isomers is slightly higher than the values obtained for $C_4H_7^+$ ions from unsaturated straight- and branched-chain systems.[16,18] The agreement is good between the ΔH_f values for $C_4H_6^+$ from the C_7H_{12} compounds (239 ± 2 kcal/mol), from 1,3-butadiene (239 kcal/mol[16]), and from cyclohexane (243 kcal/mol[16]). The heat of formation of $C_4H_5^+$ is 280 ± 3 kcal/mol if the neutral fragment is isopropyl and 277 ± 3 kcal/mol if the accompanying neutral fragment is n-propyl. Both values are slightly lower than 285 kcal/mol for the ΔH_f reported for $C_4H_5^+$ from cyclopentene.[16]

The processes and the results of the heat of formation calculations for the C_3 fragments are summarized in Table II. The $C_3H_5^+$ and $C_3H_3^+$ ions are thought to be formed by the same processes in all the C_7H_{12} isomers except bicyclo[4.1.0]heptane. For the loss of C_2H_2 + C_2H_5 from the monocyclic isomers and bicyclo[2.2.1]heptane, the average value of $\Delta H_f(C_3H_5^+)$ is 219 ± 3 kcal/mol, in excellent agreement with 220 ± 6 kcal/mol previously reported[18] for the allyl ion. In the case of bicyclo[4.1.0]heptane, the ΔH_f calculated for $C_3H_5^+$

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(16) See ref 2, appendix.

(17) ΔH_f of $C_5H_8^+$ calculated from cyclopentene's ionization potential (9.01 ± 0.01 eV)[12] and heat of formation (1.16 kcal/mol) [M. B. Epstein, K. S. Pitzer, and F. D. Rossini, *J. Res. Nat. Bur. Stand.*, **42**, 379 (1949)].

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formed by the loss of $C_2H_2 + C_2H_5$ is 203 kcal/mol, much lower than expected for the allyl or the cyclopropyl ion.[18] If, however, C_4H_7 is lost, the $\Delta H_f(C_3H_5^+)$ is 238 kcal/mol which agrees well with 239 kcal/mol[19] and 240 kcal/mol[20] for the heat of formation of $C_3H_5^+$ from cyclopropane. The average value for the heat of formation of $C_3H_3^+$ is 276 ± 3 kcal/mol which is only slightly lower than Field and Franklin's "best value" of 283 kcal/mol[16] for the ΔH_f of $CH_2{=}C{=}CH^+$. The processes chosen for the formation of the $C_3H_3^+$ ions are shown in Table II. The loss of $CH_3 + C_3H_6$ is proposed for all the compounds except bicyclo[4.1.0]heptane for which loss of n-C_4H_9 best satisfies the energetics.

Conclusions

The study of six mono- and bicyclic C_7H_{12} isomers shows that minor structural differences in the molecules can be detected by ionization and appearance potential measurements. The ionization and appearance potentials can distinguish between all the isomers except 3- and 4-methylcyclohexenes.

The heat of formation data indicate that the parent molecule ions have different structures. The thermodynamic stability of the $C_7H_{12}^+$ ions is greater for the monocyclic isomers than for the bicyclic isomers. 1-Methylcyclohexene forms the most stable parent molecule ion. In most cases, ionization–fragmentation is thought to produce ions of the same structure independent of the structure of the original molecules. In the case of larger ions formed from more complex molecules, it is anticipated that more structurally dissimilar fragment ions will be formed.

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The Electronic Structure of Carbonium Ions. Alkyl Cations and Protonated Hydrocarbons

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Abstract: The electronic structure of alkyl cations and some protonated hydrocarbons has been studied by a semiempirical SCF MO treatment for valence electron systems. It is found that the inclusion of electron repulsion and core repulsion terms is essential for the successful investigation of charged species. Good agreements of calculated ionization potentials of alkyl radicals with experiments are obtained. The electronic excitation energies and oscillator strengths of some alkyl cations are presented; the energy changes in some ionic reactions are calculated, and the results compare satisfactorily with experiment. The change of σ and π electron populations with structural change in alkyl cations is investigated, and the comparison of the electronic structure of CH_5^+ and CH_5^- is carried out. The stable configurations of $C_2H_5^+$ and $C_2H_3^+$ are also examined.

The chemistry of carbonium ions has been developed extensively in recent years. Until recently, one of the most general features of carbonium ions was their transient character. But recently, it has been possible to capture carbonium ions in the form of stable salts with very strong acids.[1]

Theoretical studies of carbonium ions have been largely limited to conjugated cations and thereby the behavior of σ electrons, perhaps essential for the study of positively charged species, was left unsolved.

Recently, Hoffmann developed the extended Hückel theory[2] and applied it to some carbonium ions.[3] This was the first attempt to treat carbonium ions extensively, considering all valence electrons of the constituent atoms, and was very instructive. But one of the shortcomings of this treatment was that the electron interaction and nuclear repulsion terms were not taken into account explicitly.

In the present work, the electronic structures of some carbonium ions have been studied with our newly developed semiempirical ASMO SCF method for valence electron systems.[4] The carbonium ions investigated are some alkyl cations, such as methyl, ethyl, n-propyl, isopropyl, isobutyl, and t-butyl cations, and some protonated hydrocarbons, such as protonated methane, protonated ethylene, and protonated acethylene. We also examined the electronic structures of some alkyl anions and CH_5^- as a reference.

One of the main purposes of this study is to examine the effects of the electron repulsion term in charged species. It has been found that the inclusion of electron

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