Ionization and Dissociation of C_4H_8 Isomers

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Abstract: Appearance potentials of the parent, $C_3H_5^+$, and $C_2H_4^+$ ions from *cis*- and *trans*-butene-2, butene-1, methylpropene, methylcyclopropane, and cyclobutane have been determined using the Morrison Second Differential Ionization Efficiency Method. All isomers yield allyl ion with a heat of formation of 232 ± 3 kcal/mole near threshold, although methylcyclopropane shows a second, higher energy process as well which is consistent with the production of cyclopropyl ion with excess energy. The formation of ethylene ion from the cyclic structures appears to require excess energy. It is suggested that the isomers essentially lose identity before fragmentation and that the differences in the 70-eV spectra are a result of a shift in the internal energy distribution caused by the inequality of the heats of formation of the parent ions in their ground states.

The effect of molecular structure on the fragmentation of ions in the mass spectrometer is well known and has been studied extensively.[2] One of the first approaches to an understanding of ionic dissociation processes was based on the thermodynamics of ion formation.[3] The quasi-equilibrium theory of mass spectra also suggests a strong correlation between the energetics of possible processes and their abundance.[4] Since reliable appearance potentials necessary for this approach are frequently not readily available, most arguments advanced in organic mass spectrometry have derived rationalizations by inferring ion stabilities from considerations of resonance, induction, etc., familiar from organic mechanism;[5] however, the applicability of such arguments is not always clear.[6]

The six C_4H_8 molecules represent a simple and interesting system because they allow recognition of all isomerization and cyclization processes possible in olefins. The mass spectra of these compounds have been measured at 70 eV and differ from each other, except for those of the *cis*- and *trans*-butene-2 isomers.[7,8] Yet, the double bond is readily capable of migration in larger olefins,[2] and skeletal rearrangement appears to participate in the fragmentation of butene-1.[9] The differences may reflect the existence of structures for the precursors of fragmentation which are characteristic for each starting compound, or they may merely be the result of the difference in the ground state energetics of the molecular ions, so that all structures would be accessible to the excited molecular ion. For example, the $C_3H_5^+$ ion from methylcyclopropane may be derived from a cyclic ionic precurser; such a structure would require previous ring closure from the olefin ions. Conversely, the ring in methylcyclopropane ion may open before fragmentation.

While any arguments regarding the structure of such ions must be based at least in part on experiments using specifically labeled compounds, some possible processes can be eliminated if the thermodynamics of ion formation are known. Appearance potentials and heats of formation relevant to an understanding of the ionization and dissociation of C_4H_8 molecules are provided by this study.

Appearance Potential Determination

It is well known that it is difficult to assess the ionization and fragmentation thresholds of complex molecules,[10] particularly by electron impact.[11] Contributions of vibrational excitation[12-14] and the possible applicability of a nonlinear threshold law[15-17] combine to make the expectation that ion abundance is linear with excess electron energy unrealistic. Therefore, we have used the second differential ionization efficiency method of Morrison,[12] which circumvents these difficulties to some extent and gives a unique point identifiable with the appearance potential of the species in question, irrespective of the threshold law. The maximum in the second derivative can be assessed clearly and is not shifted more than 0.1 eV even if the threshold law applicable to the calibration ion is linear, and that of the ion of interest is proportional to the 1.8 power of the excess electron energy.[18] This method does not remove the difficulties associated with the formation of electronic or vibrationally excited levels; however such complications should be apparent through a considerable broadening of the distributions. While improved methods are now being developed, the data presented in this paper will be based on the assumption that contribution of excitation is not important as long as the ex-

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[1] R. A. Welch Foundation Predoctoral Fellow.

[2] Of the several fine reviews and books, a recent and comprehensive one is: H. Budzikiewitz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967.

[3] C. S. Cummings and W. Bleakney, *Phys. Rev.*, **58**, 787 (1940).

[4] For example, see H. M. Rosenstock in "Advances in Mass Spectrometry," E. Kendrick, Ed., Institute of Petroleum, London, 1968, p 523.

[5] (a) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Company, Inc., New York, N. Y., 1962; (b) F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, Inc., New York, N. Y., 1966.

[6] R. C. Dougherty, *J. Am. Chem. Soc.*, **90**, 5780 (1968).

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[8] Catalog of Mass Spectral Data, API Project 44, Texas A&M University, College Station, Texas, 1947–1961.

[9] G. G. Meisels, J. Y. Park, and B. G. Giessner, *J. Am. Chem. Soc.*, **91**, 1555 (1969).

[10] For example, consider the difficulties in establishing the adiabatic ionization potential of methane.

[11] A. J. C. Nicholson, *J. Chem. Phys.*, **29**, 1312 (1958).

[12] J. D. Morrison, *ibid.*, **14**, 1305 (1951).

[13] W. A. Chupka, *ibid.*, **30**, 191 (1959).

[14] E. Murad and M. G. Inghram, *ibid.*, **40**, 3263 (1964).

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[16] C. E. Brion and G. E. Thomas, *Int. J. Mass Spectrosc. Ion Phys.*, **1**, 25 (1968).

[17] P. Marchand, C. Paquet, and P. Marmet, *Phys. Rev.*, **180**, 123 (1969).

[18] B. G. Giessner and G. G. Meisels, 17th Annual Meeting on Mass Spectrometry, Dallas, Texas, May 1969, paper No. 62, to be published.

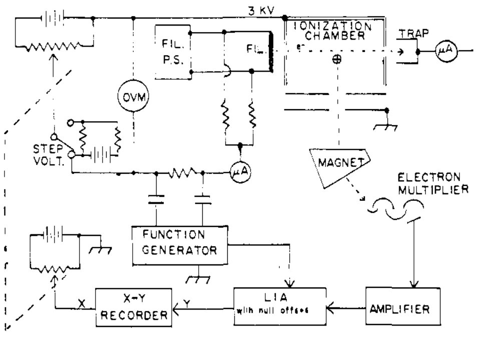

Figure 1. Schematic representation of circuits used for the determination of second differential ionization efficiency curves.

ponential "tails" of the second differential ionization efficiency curves are of the same shape as those of xenon.

Experimental Section

Materials. The butenes (Matheson & Company), methylcyclopropane (Chemical Procurement Laboratory), and cyclobutane (Frinton Laboratories) originally contained from 2 to 20% impurities and all were purified by preparative gas chromatography to at least 99.9% purity.

Instrumentation. All experiments were performed on a commercial 60°, 20-cm radius of curvature mass spectrometer (Atlas CH-4 with AN 4 ion source). It was modified by inserting a plastic junction box between the ion source and the power supply cable, and by isolating the filament power supply in the normal chassis of the instrument. Ionizing voltage was supplied from mercury batteries and a ten-turn 0.05% linear potentiometer, which was ganged with a second potentiometer of 0.05% linearity using plastic gearing; the output of this potentiometer was employed to drive the *x* axis of a Hewlett-Packard Model 2D3 *x-y* recorder. In early experiments the *x* deflection of the *x-y* recorder was calibrated for ionizing voltage using a Leeds and Northrup K-3 potentiometer, with the high voltage off. In later experiments, a Trimetrics model 4000-400M digital voltmeter with 0.01% accuracy, powered from an isolation transformer, permitted ionizing voltage measurements during each run. Dc potentials in precisely reproducible multiples of 0.07 V and the output from a Helwett-Packard Model 3300A function generator could be superimposed on the ionizing voltage (Figure 1). The peak to peak modulation voltages at the filament were calibrated, using a Tektronix Model 564 oscilloscope with 3A72 and 2B67 plug-in units, while the high voltage was off. The bypass capacitor (5μF) between filament and box (high voltage ground) reduced the 60-cycle noise to approximately 5-7 mV ptp. The modulation voltage between filament and box was independent of frequency between 40 and 400 Hz, dropping off by 10% at 10 Hz and 1.4 kHz, respectively. Modulation voltage in all experiments was 0.08 V peak to peak.

The filament shield was maintained at −0.6 V with respect to the filament, and the drawout potentials were equally set at −0.6 V each. The electron energy distribution was determined directly using a retarding potential on the electron collector and synchronous amplification of the modulated collector current (2 kHz) as described for ion current detection below. The width at half-height of the quasi-Maxwellian-shaped distribution function was 0.6 eV.[18]

The ion beam was defined by a 0.1-mm source slit and a 0.9-mm collector slit to obtain optimum peak flatness, a necessity since the ac resistance of the high voltage power supply is not negligible and a small amount of high voltage modulation is introduced.

The output of the electron multiplier went through one stage of amplification, and then to a Model 21 Princeton Applied Research Corporation lock-in amplifier. The reference ac signal for the synchronous amplifier was provided from the second output of the function generator.

First differential ionization efficiency curves were point-plotted directly. Second differential ionization efficiency curves were obtained by increasing the sensitivity of the lock-in amplifier by a factor of 10 and nulling the amplifier using zero offset. Ionizing voltage was then increased by 0.07 V, and the increase in the differential current recorded. The step switch was then returned to the original position, the voltage increased, and the procedure repeated. Alternatively, the first derivative could be recorded and the second derivative obtained by numerical techniques, using an IBM 7094 computer, with the same results.

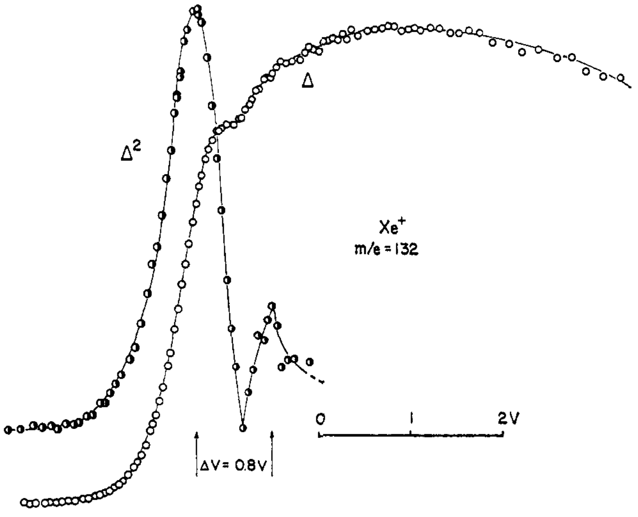

Figure 2. First and second differential ionization efficiency curves of xenon.

Results

The first and second differential ionization efficiency (SDIE) curves of xenon are shown in Figure 2. The maximum, corresponding to the first onset, is clearly defined and can be ascertained within ±0.05 eV. The width at half-height is 0.68 eV; it is reproducible to within 5% in repetitive determinations and reflects primarily the electron energy distribution as expected. The energy span between the 25% height and the maximum height is 0.55 eV. A second peak is 0.8 ± 0.05 eV above the lowest one. This separation is considerably less than the 1.31 eV difference between the ground state and the first excited state. It has been observed previously using second differential ionization,[19] velocity selected beams,[20] and the RPD technique,[21] but was not observed by the energy distribution difference technique[22] nor in a number of other investigations. It is a result of oscillation of the second derivative curve due to the autoionizing 6d state 0.3 eV above threshold.[18, 23]

The ability to assess ionization potentials accurately was checked by obtaining the SDIE curve for krypton, which yielded a maximum at 14.05 ± 0.10 eV when xenon was used as the calibrating gas. This value is in good agreement with the spectroscopic ionization potential of 13.996 eV.

Representative SDIE curves for the parent ions of cyclobutane and *cis*-butene-2 and for fragment ions from butene-1 and methylcyclopropane are shown in Figures 3–6. The positions of the maxima or the onsets of plateaus are also summarized in Table I.

The following comments on the behavior of individual ions need to be added. Parent and fragment ions ($C_4H_8^+$, $C_3H_5^+$, and $C_2H_4^+$) of the 2-butenes did not show clear, well-defined "normal" maxima (Figure 3). Instead, relatively broad "plateaus" were observed.

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

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(23) J. D. Morrison, *ibid.*, **40**, 2488 (1964).

Table I. Appearance Potentials of Some Major Ions from C_4H_8 Isomers, eV

Isomer	$C_4H_8^+$ This investigation	$C_4H_8^+$ Lit.	$C_3H_5^+$ This investigation	$C_3H_5^+$ Lit.	$C_2H_4^+$ This investigation	$C_2H_4^+$ Lit.
Cyclobutane	10.6 ± 0.1	10.6[a]	11.2 ± 0.2		11.0 ± 0.15	
Methylcyclopropane	10.1 ± 0.2	9.9[b]	11.2 ± 0.2		12.5 ± 0.2	
Butene-1	9.6 ± 0.1	9.6[c]	11.4 ± 0.1	11.5[d,e]	11.7 ± 0.2	12.4[e]
Methylpropene	9.2 ± 0.08	9.23[c]	11.8 ± 0.2	11.4[f]	12.0 ± 0.2	12.2[f]
cis-Butene-2	9.0 ± 0.15	9.13[c]	11.6 ± 0.15	11.6[e]	11.7 ± 0.25	12.2[e]
trans-Butene-2	9.1 ± 0.15	9.13[c]	11.7 ± 0.15	11.8[f]	11.8 ± 0.25	

[a] R. F. Pottie, A. G. Harrison, and F. P. Lossing, *J. Am. Chem. Soc.*, **83**, 3204 (1961). [b] F. H. Field, footnote in J. L. Franklin, *J. Chem. Phys.*, **22**, 1304 (1954). [c] K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectros. Radiative Transfer*, **2**, 369 (1962). [d] From ref 24. [e] I. Omura, *Bull. Chem. Soc. Jap.*, **35**, 1845 (1962). [f] From ref 26.

Such plateaus were also encountered for the $C_2H_4^+$ ions from all other isomers except that from cyclobutane, which showed fine structure with discernible peaks at 11.9 ± 0.15, 12.6 ± 0.1, and 13.0 ± 0.2 eV. "Normal" maxima were observed for all other parent ion peaks although cyclobutane showed a pronounced second maximum at 13.3 ± 0.2 eV (Figure 4). $C_3H_5^+$ ions were "normal" (Figure 5) except that from methylcyclopropane (Figure 6), whose structure has a probable maximum at 11.2 ± 0.2 eV and an unmistakable one at 12.1 ± 0.1 eV. $C_3H_5^+$ from methylpropene has an uncertain second maximum at 12.5 ± 0.2 eV. Dorman[24] reported that $C_3H_5^+$ from butene-1 may show a broad plateau; however, the maximum indicated in Figure 4 was well reproducible under our conditions.

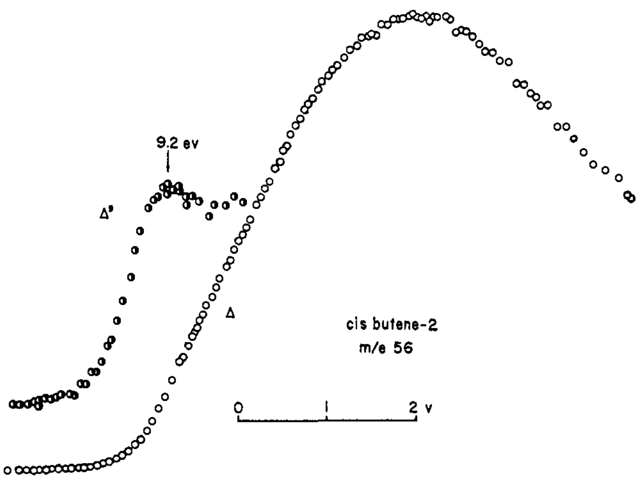

Figure 3. First and second differential ionization efficiency curves of parent ion formation from *cis*-butene-2.

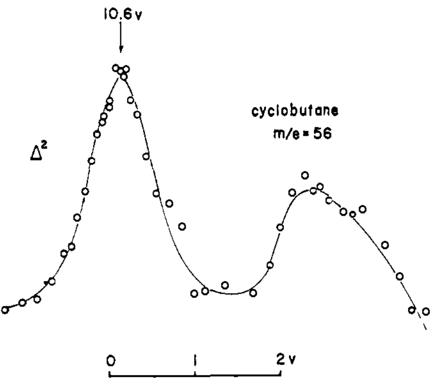

Figure 4. Second differential ionization efficiency curve of cyclobutane parent ion.

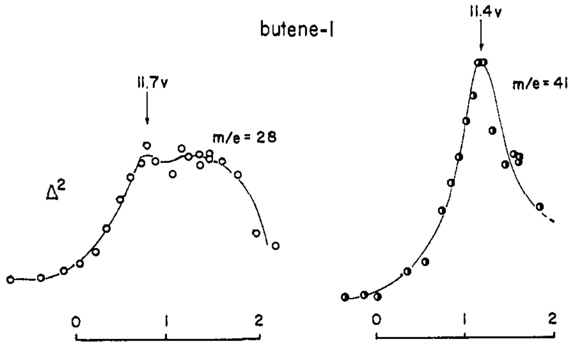

Figure 5. Second differential ionization efficiencies of $C_2H_4^+$ (*m/e* 28) and $C_3H_5^+$ (*m/e* 41) ions from butene-1.

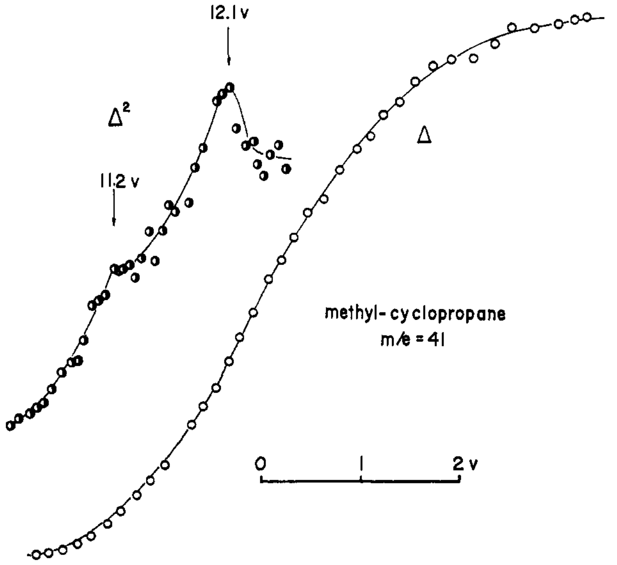

Figure 6. First and second differential ionization efficiency curves for $C_3H_5^+$ from methylcyclopropane.

Discussion

The maximum in the second differential ionization efficiency curves can often be ascertained easily, but many ions, such as the parent ions of the 2-butenes and essentially all $C_2H_4^+$ ions, show broad plateaus. Dorman[24] suggested that in such cases one could not meaningfully assess the ionization threshold. While uncer-

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(24) F. H. Dorman, *J. Chem. Phys.*, **43**, 3507 (1965).

Table II. Heats of Formation of $C_3H_5^+$ and $C_2H_4^+$ Fragments

Precursor neutral molecule	$\Delta H_f(C_3H_5^+)$, kcal/mole	$\Delta H_f(C_2H_4^+)$, kcal/mole
Cyclobutane	230 ± 5	267 ± 4
Methylcyclopropane	231 ± 5	280 ± 5
Butene-1	228 ± 2	257 ± 5
Methylpropene	234 ± 5	259 ± 5
cis-Butene-2	233 ± 3	257 ± 6
trans-Butene-2	235 ± 3	259 ± 6

Table III. Heats of Formation of Ions of Composition C_4H_8 and Some Fragments[a]

	ΔH_f, kcal/mole	$\Delta H_f - \Delta H_f$ (*trans*-$C_4H_8^+$-2), kcal/mole
Cyclo-$C_3H_5^+ + CH_3$	272	64
$C_2H_4^+ + C_2H_4$	266	58
Allyl-$C_3H_5^+ + CH_3$	262[b]	54
Cyclobutane$^+$	250	42
Methylcyclopropane$^+$	241[c]	33
Butene-1$^+$	221	13
Methylpropene$^+$	209	1
cis-Butene-2$^+$	209	1
trans-Butene-2$^+$	208	

[a] All values from ref 26 except as indicated. [b] Calculated from the heat of formation of allyl radical and its ionization potentials (ref 27 and 28). [c] Calculated from the estimated heat of formation (ref 26, p 261) and the ionization potential determined in this investigation.

Table IV. Some Major Peaks in the Mass Spectra of C_4H_8 Molecules at 70 eV (Nominal)

		Parent Compound					
m/e	ion	*trans*-Butene-2	*cis*-Butene-2	2-Methylpropene	Butene-1	Methylcyclopropane	Cyclobutane
56	$C_4H_8^+$	46.2	47.9	42.8	37	61.2	62.2
41	$C_3H_5^+$	100	100	100	100	100	89.3
39	$C_3H_3^+$	32.6	35.8	43.7	34.5	56.7	19.8
28	$C_2H_4^+$	32.1	31.7	21.5	29.5	37.7	100

tainty is introduced by such irregular behavior, some confidence in the association of the onset of the plateau with the minimum energy required to form an ion can be derived from the shape of the low energy tail. When the xenon curve scaled to the assigned maximum is overlaid, the tails superimpose. On the basis of this argument we shall therefore take the maximum or the plateau onset as the minimum energy required to form a given ion, and the values summarized in Table I correspond to this interpretation. The agreement with previous evaluations reported in the literature is excellent where such measurements are reliable.

The appearance potential data of Table I can be combined with the known heat of formation of ethylene[25] to obtain heats of formation of the $C_2H_4^+$ ion produced on fragmentation of the six isomers (Table II). ΔH_f $(C_2H_4^+)$ calculated from olefin ion fragmentation is 258 kcal/mole, only slightly higher than the established value of 253 kcal/mole.[26] Apparently there is little excess kinetic or electronic energy involved in the formation of this ion from the butenes. Considerably more energy is required, however, for the fragmentation of cyclobutane and methylcyclopropane ions to yield $C_2H_4^+$. This may indicate that a fast four-center dissociation is involved and that the ring opening does not precede the fragmentation of the cyclic molecule ion.

Similar calculations can be carried out for the formation of the $C_3H_5^+$ ion (Table II), yielding an average $\Delta H_f(C_3H_5^+) = 232 \pm 3$ kcal/mole. This is in excellent agreement with the value 229 ± 2 kcal/mole which can be calculated from the ionization potential of CH_2CHCH_2 (8.16 ± .05 eV)[27] and the best currently available heat of formation of allyl radical (41.4 ± 1.1 kcal/mole).[28] It suggests that the lower value of 216 kcal/mole, recommemded in a recent review,[26] which was based on an uncertain assignment of the appearance potential of $C_3H_5^+$ from propylene, is not correct. The cyclopropyl ion structure (heat of formation 239 kcal/mole)[26] is clearly excluded near the threshold. Since all six isomers yield allyl ion at the onset, the ring in cyclobutane and methylcyclopropane must open before or during dissociation. This is supported by an examination of metastable peaks.[29] It is of interest to note that reversible cyclization must occur from the linear structures if one is to account for the mass spectrum of 1 butene-4-C^{13}.[9] While the minimum energy configuration for such processes involves a methylcyclopropyl ion structure, the dissociation occurs *via* the lowest-energy path involving a linear structure.

There is a pronounced second maximum in the second derivative curve for $C_3H_5^+$ from methylcyclopropane (Figure 6), corresponding to a heat of formation of the ion of 252 kcal/mole. Similarly, there may be a barely discernible maximum when this ion is produced from 2-methylpropene, corresponding to $\Delta H_f(C_3H_5^+) = 250$ kcal/mole. While this may simply be a result of excited allyl ion formation, it is more attractive to accept these two maxima as evidence for a common precursor with a cyclopropyl ion structure. This ion may be electronically excited, since it is formed with more than 10 kcal excess energy. However, it is more probable that the rearrangement has an energy barrier, suggesting that these ions may be formed with excess vibrational and kinetic energies. The tertiary carbon structure required by such a mechanism may not be accessible to the linear alkenes and cyclobutane since no such structure in the $C_3H_5^+$ abundance curves is observed for these compounds.

The effect of ion thermodynamics on the important primary fragmentation processes can be summarized

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(25) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

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(28) D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969).

(29) P. Natalis, *Bull. Soc. Roy. Sci. Liege*, **29**, 94 (1960).

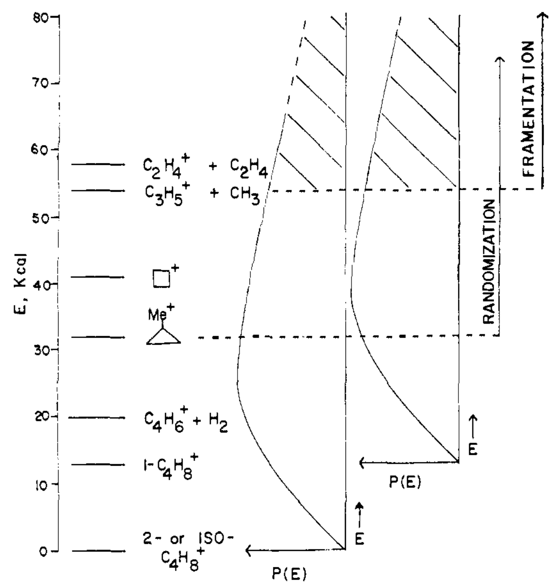

Figure 7. Schematic representation of relative energy contents of parent and fragment ions with total composition $C_4H_8^+$, with respect to the lowest energy form (butene-2 ion). Also shown are assumed energy deposition probability functions corresponding to ionization of butene-2 and butene-1 by 70-eV electrons. The shaded portion corresponds to the fraction of ions capable of yielding $C_3H_5^+$ fragments.

conveniently by considering the heats of the formations of all major species of total composition $C_4H_8^+$ (Table III). The last column lists the energy above that of the most stable structure (*trans*-2-butene ion) and reflects the minimum potential internal energy of the ion resulting from ionization of a given structure. All energy states are accessible to 70-eV electron impact, but the internal energy distribution above the ground state should vary depending on the ionization threshold. The second derivative of the total ionization efficiency curve by electron impact is thought to correspond approximately to the initial internal energy distribution of the ion,[30] and the general features of this curve do not vary greatly between similar compounds.[30,31] As a consequence cyclobutane ion will initially have a considerably higher internal energy content than the other isomers because the zero is considerably offset; it should therefore fragment considerably more. This is borne out by the 70-V mass spectra of these compounds (Table IV). The rationale is perhaps best demonstrated graphically by overlaying the estimated energy deposition distribution function of these molecules on the energy scheme, as demonstrated in Figure 7. The proportion of initial molecular ions capable of dissociation is much larger when the heat of formation of the parent ion is greater. The dissimilarities of the spectra of isobutylene and methylcyclopropane and those of the other isomers indicate that in the C_4H_8 system thermodynamic aspects dominate the fragmentation mechanism and the general features of the mass spectrum, and that the original structure enters primarily through its effect on the heat of formation of the analogous parent ion structure.

Acknowledgments. This investigation was supported in part by the United States Atomic Energy Commission and by the Robert A. Welch Foundation of Houston, Texas; we are deeply grateful for this assistance.

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Structural Effects on Electronic Relaxation Processes of Aliphatic Ketone Triplets at 77°K

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Abstract: The phosphorescence quantum yields and lifetimes of aliphatic ketones have been determined at 77°K in EPA. The results indicate that the α-CH stretching mode is a significant factor in radiationless decay, *i.e.*, $T_1 \rightsquigarrow S_0$. The phosphorescence quantum yields of the carbonyl compounds were observed to increase with alkyl substitution at the α carbon, and the phosphorescence wavelength maxima remained constant at 450 ± 3 nm. The results show that the natural radiative lifetime for phosphorescence is constant, while radiationless deactivation of the triplet is slowed down by substitution. The phosphorescence yield of di-*t*-butyl ketone in EPA at 77°K was determined to be 0.89 ± 0.10, which is greater than that of acetone by a factor of 21. Deuterated acetone exhibits enhanced phosphorescence relative to ordinary acetone. A comparison of absorption and phosphorescence data illustrates that the natural radiative lifetime for singlet and triplet are constant for the nine aliphatic ketones studied.

The photochemistry of ketones has been the subject of many investigations.[1] The lowest excited singlet of aliphatic ketones is generally accepted to be n,π^* in character and to exhibit a high intersystem crossing yield to the triplet. Data on absorption spectra have emphasized the importance of both structural and solvent effects on the n,π^* transitions of the carbonyl group.[2-5] Fluorescence studies of carbonyl

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[1] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, Chapter 5.

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