High-Kinetic Energy Fragment Ions from Aliphatic Hydrocarbons under Electron Impact. I. Measurement and High-Kinetic Energy Methyl Ions from 1,3-Butadiene

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It has long been known that fragment ions from diatomic and polyatomic molecules by electron impact often have appreciable kinetic energies. The distribution of kinetic energies among the fragment ions formed from the diatomic molecules of a given species can now be explained satisfactorily on the basis of potential energy diagrams of the normal state and of the various ionized states using the Franck-Condon principle¹⁾.

Fragment ions from polyatomic molecules have not been so thoroughly studied as those from diatomic molecules. Hustrulid et al.²⁾, in a study of the mass spectrum of benzene, showed that the satellite peak on the high mass side of each of the peaks of the masses *m/e* 15, 26, 27, 14, 13 and 12, is caused by ions to which the dissociation process has imparted a large kinetic energy lying within a narrow range. It was suggested that the high energy ion came from the dissociation of doubly charged molecules into two singly charged fragments. The appearance potential of the satellite peaks was found to be much higher than the main peaks, a finding consistent with this explanation.

Hipple et al.³⁾ gave the collector of their mass spectrometer a positive potential, relative to the analyzer, sufficient to stop all ions of a zero initial velocity, and so was able to record the satellite peak alone. This experimental result shows that the satellite peak came from ions with a high initial velocity, too. Mohler et al.⁴⁾ measured the kinetic energies and intensities of satellites which accompany the *m/e* 15 spectra of 15 hydrocarbons; they also discussed the reaction mechanism by which the high kinetic energy ions are produced. Their mass spectrometer was provided with a metastable ion suppressor slit between the exit slit of the analyzer and the ion collector. The slit could be set at an adjustable positive potential to stop any ions which have lost kinetic energy while traversing the analyzer tube. The slit had a focusing action for ions and increased the resolving power of the instrument. They observed satellites on *m/e* 15 by applying the appropriatepoten tial to the suppressor slit and by using very low ion-accelerating voltages ranging from 500 to 145 V.

Berry⁵⁾, in a study of discrimination effect, has measured the velocity distribution of methyl ions from *n*-butane, and of various other ions, by deflecting the ion beam parallel to the magnetic field by an electric field. He confirmed that there are two groups of ions, one with a thermal distribution and the other with a high kinetic energy.

In this paper a method for measuring high energy ions with a conventional analytical mass spectrometer without any such equipment as an additional deflecting electrode or a metastable ion suppressor slit, and some results are described.

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1) H. D. Hagstrum, *Rev. Modern Phys.*, 23, 185 (1951).
2) A. Hustrulid, P. Kusch and J. T. Tate, *Phys. Rev.*, 54, 1037 (1938).
3) J. A. Hipple, R. E. Fox and E. U. Condon, ibid., 69, 347 (1946).
4) F. L. Mohler, V. H. Dibeler and R. M. Reese, *J. Chem. Phys.*, 22, 394 (1954).
5) C. E. Berry, *Phys. Rev.*, 78, 597 (1950).

Experimental

A Consolidated Model 21-103C analytical mass spectrometer with a dual collector slit was used in this research. This instrument has a mass-resolving power of about 600 when a 7 mil (ca. 0.2 mm.) slit is used. With the slit, if the magnetic field is reduced and the *m/e* 15 ion of propane is focused at about 500 V. or less, the satellite peak described by Mohler et al. appears. Figure 1 illustrates the mass spectrum of propane, *m/e* 15 and 14 under these conditions. The *m/e* 15 satellite originates from ions having excess kinetic energies* as has been well established[4]. However, if a satellite peak is observed in the mass spectrum of a new substance, the satellite may be a KE peak, or a peak which originates from metastable ions or from ordinary TE ions having an *m/e* value slightly different from the *m/e* value of the "mother" peak. We must, therefore, distinguish KE peaks from those peaks mentioned above. In the experiments made by Mohler et al. metastable ions, if desired, could be eliminated by the use of a metastable ion-suppressor slit.

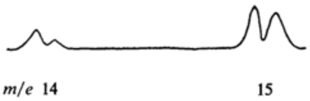

Fig. 1. Doublets at *m/e* 14 and *m/e* 15 in the spectra of propane.
Electron current; 19.5 μA, $V_i \fallingdotseq 500$ V., $V_r = 0$ V.

In order to study KE ions by means of a conventional mass spectrometer, we shall consider, for a moment, how to distinguish KE peaks from the other peaks in the spectrum. For this purpose, we shall now study the properties of the following doublets and peaks by varying the ion-accelerating and ion-repeler voltages: (1) *m/e* 15 doublets in the spectrum of *n*-butane and propane, (2) the *m/e* 31.9 peak of *n*-butane, and (3) the *m/e* 44 peaks of propane and carbon dioxide. The higher mass side peak of the *m/e* 15 doublet is the KE peak; the *m/e* 31.9 peak is a metastable peak, and the *m/e* 44 peaks are TE peaks.

Distinction between KE and Other Peaks.—*Influence of V_i.*—Figure 2 shows the effect of varying the ion-accelerating voltage, V_i, on various peaks. The spectra were taken by voltage scanning in appropriate magnetic fields. Curve 1 in this figure represents the *m/e* 15 peak ratio, I_k/I_t, for propane. The ion-repeler voltage, V_r, was about 5 V. Curve 2 is the peak ratio (*m/e* 31.9)/(*m/e* 30) for *n*-butane. V_r's were set at optimum positions for *m/e* 31.9 peak focusing. Curve 3 is the *m/e* 44 peak ratio of propane to the carbon dioxide in a mixture of these compounds. V_r's were about 0.5 V.

Curve 1 in Fig. 2, which gives the *m/e* 15 intensity ratio, I_k/I_t, for propane, has a large positive gradient, and can easily be distinguished from curves 2 and 3 in the same figure. According to Berry[5], the larger the initial kinetic energies of the ions, the larger the absolute value of the tangent of the ion intensity versus V_i curve. The behavior of curve 1 can be well explained by assuming that the ions on the higher mass side peak have greater kinetic energies.

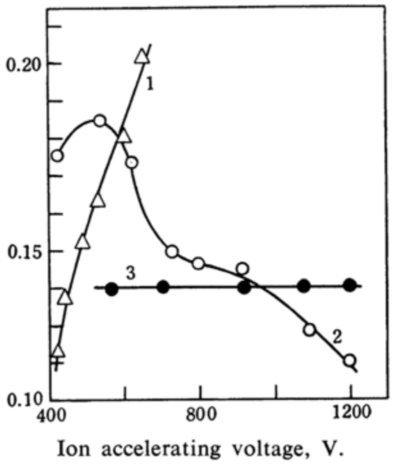

Fig. 2. Peak ratios γ versus ion accelerating voltage, V_i.
Curve 1: *m/e* 15 peak height ratio of propane, (Higher mass side peak)/(Lower mass side peak).
Curve 2: Peak height ratio of *n*-butane, (*m/e* 31.9)/(*m/e* 30).
Curve 3: *m/e* 44 peak height ratio, $(C_3H_8)/10\times(CO_2)$.

Metastable peaks result from the spontaneous dissociation of an ion after the ion has been accelerated but before it has passed very far into the analyzing magnetic field. The peaks do not follow the equation

$$m/e \propto H^2/V_i$$

where H is the magnetic field. The point where the dissociation takes place depends on the speed of the mother ion and is a function of V_i. Curve 2 in Fig. 2, which gives the peak intensity ratio (*m/e* 31.9)/(*m/e* 30) of *n*-butane, shows that the metastable peak intensity, I_m, tends to decrease relative to the normal ion intensity, I_t, as V_i is reduced in the range of V_i larger than about 500 V. This may be explained as follows. The smaller the V_i value is, the nearer to the point of formation of ordinary ions is the point of dissociation of the mother ion, and consequently, the more efficiently focused is the beam of the dissociated product ions. The details of curve 2 may be explained by the potential distribution in the various parts of the ion source. This explanation is a tentative one, and, moreover, the experiment concerns only the *m/e* 31.9 ion of *n*-butane. Therefore, to establish that the behavior of the metastable ion is proper to all metastable ions, further investigations on various ions are, of course, necessary. However, if a doublet is observed and if the ratio of the peak intensities

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* For convenience, ions having excess kinetic energies will hereafter be called KE ions, and the peaks due to KE ions will be called KE peaks. Similarly, ions having thermal energies corresponding to the temperature of the ion-source will be called TE ions, and the peaks due to TE ions will be called TE peaks. The intensities of the KE and TE peaks will be indicated by I_k and I_t respectively.

for the components behaves in the way shown by curve 2 in Fig. 2, the peaks invariably do not come from KE ions. The distinction between curves 1 and 2 is outstanding, as may be seen from a comparison of curves in Fig. 2.

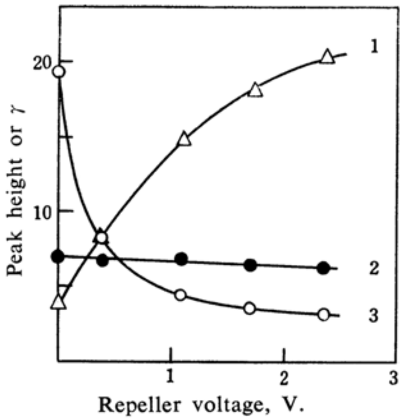

Fig. 3. KE peak height, I_k, TE peak height, I_t, and the ratio I_k/I_t versus ion repeller voltage, V_r.
n-Butane. $V_i \fallingdotseq 500$ V., electron current: 19.5 μA. Peak height is represented by an arbitrary scale.
Curve 1: I_t, m/e 15 lower mass side peak height.
Curve 2: I_k, m/e 15 higher mass side peak height.
Curve 3: $10\times(I_k/I_t)$.

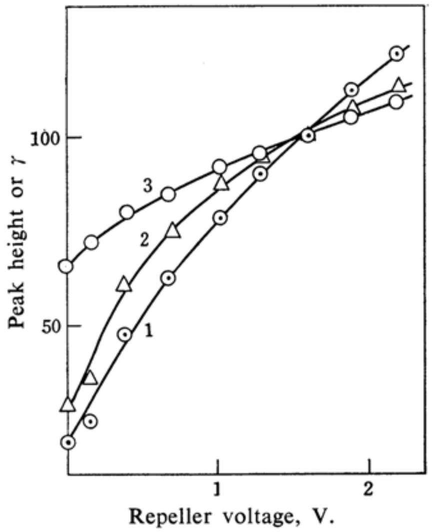

Fig. 4. Metastable ion peak height, I_m, TE peak height, I_t, and the ratio, I_m/I_t versus ion repeller voltage, V_r.
n-Butane. $V_i \fallingdotseq 500$ V., electron current: 19.5 μA. Peak height is represented by an arbitrary scale.
Curve 1: I_m, (m/e 31.9)$\times 10$
Curve 2: I_t, (m/e 30)
Curve 3: γ, $(I_m/I_t)\times 10^3$

Curve 3 in Fig. 2, which gives the m/e 44 peak ratio of propane to carbon dioxide, concerns two spepcies of ions which are produced at a normal position in the ionization chamber and which have close m/e values. These ions have only a kinetic energy corresponding to the temperature of the ionization chamber. The curve shows that the influences of V_i on these ions are nearly the same.

Influences of V_r.—Figures 3 and 4 show the influences of the ion-repeller voltage, V_r, on various peaks. The data in Fig. 3 were obtained by measurements of the doublet at m/e 15 of *n*-butane, with the V_i being fixed at about 500 V. In Fig. 3, curve 1 shows the I_t, i. e., the lower mass side peak height of the doublet, while curve 2 shows the I_k, the higher mass side peak height of the doublet, and curve 3 shows the ratio I_k/I_t. In Fig. 4, the height, I_m, of the m/e 31.9 metastable peak (curve 1), the height, I_t, of the m/e 30 peak (curve 2), and the ratio, I_m/I_t, (curve 3) are given as functions of V_r.

The m/e 44 peak versus the V_r curves for both propane and carbon dioxide showed much the same tendency as curve 1 in Fig. 3, and the ratio of the two peaks was almost constant over the range of V_r used.

The influence of the ion-repeller voltage, V_r, on metastable ion peaks was investigated by Hipple et al.[3] They showed that an increase in V_r increases both normal TE ion peaks and metastable ion peaks, and that the effect is more pronounced in the case of metastable peaks. They also pointed out that KE ions are less affected by V_r than TE ions. Curve 3 in Fig. 4, which represents the ratio of the metastable peak to the TE peak, has a positive tangent, as they demonstrated. Curve 3 in Fig. 3, which represents the ratio of the KE peak to the TE peak, has a negative tangent.

The ions produced in the ionization chamber are pushed out through the ionization chamber slit into the ion accelerating system by the action of the repeller voltage, V_r. When a small voltage V_r is applied to the repeler, I_t is increased by this action, as may be seen from curve 1 in Fig. 3. If ions with an initial kinetic energy are produced in the ionization chamber and have a velocity component perpendicular to the plane of the exit slit of the chamber, the ions are expected to pass through the slit irrespective of V_r values above zero. This expectation is shown to be true by curve 2 in Fig. 3, which, as Hipple et al. pointed out qualitatively, shows that the V_r values have only a slight effect on these ions, which are considered to have appreciable kinetic energies.

The finding that the ratio of the m/e 44 peaks of propane to carbon dioxide was practically independent of V_r shows that the influences of V_r on TE peaks are the same.

Measurement. — The KE peak, TE peak, metastable peak, and their ratios have been investigated as functions of V_r and V_i, by taking the peaks of *n*-butane and propane as examples. As is clear from a consideration of the results, the properties shown in Figs. 2, 3 and 4, except for the $I_m \sim V_i$ relation, are not specific to the substances taken as examples, but are specific to each species of ions.

To distinguish between the TE, KE, and metastable peaks, we may vary V_i or V_r and examine the resulting influences on the intensity, I, of the peak under consideration or on the intensity ratio of I to a peak which is known to be a TE peak.

All the KE ions observed so far have accompanied TE ions and have appeared as doublets. When a doublet spectra appeared in the mass spectrum of a compound, the high mass side peak was examined by the procedure mentioned above to determine whether or not it was KE peak. After a peak was identified as a KE peak, the kinetic energy, E, the ion-accelerating voltage difference of the doublet⁴⁾, was measured by one or both of the following procedures: (a) The ion accelerating voltages of the doublet are measured by setting the voltage manually on each peak, with the potentiometer supplied with the instrument to calibrate the mass scale. E is obtained as the difference of the voltages. (b) The ion-accelerating voltages of the two peaks just before and after a doublet are measured. From these values and the distances, recorded on the chart, between the two peaks and between the peaks of the doublet, the ion-accelerating voltage difference corresponding to the doublet is calculated by interpolation.

When the resolution and intensity are favorable, the reproducibility of the measurements was within ±0.2 eV.

The influences of the ion-accelerating voltage, V_i, and the ion-repeller voltage, V_r, on the measured kinetic energy values were checked by varying V_i and V_r values in the ranges 400∼600 and 0∼10 V. respectively. The results showed that the variation in these voltages has no influence on the measured kinetic energies.

Because of the overlapping of the tails of the major and minor peaks of a doublet, an error in locating the maximum point of the minor peak may result from a marked unbalance of the peak heights of a doublet. To minimize the effect of the overlapping of peak tails on the measured E value, all E values were measured with a repeller voltage of $V_r=0$.

Results and Discussion

Table I summarizes the results of the measurements of the kinetic energy peaks for methyl ion in ethane, propane, *n*-butane, isobutane, propylene, and 1, 3-butadiene. Since the first four substances were investigated by Mohler et al.⁴⁾, their results are also listed in the table as a check.

The second column gives the kinetic energy value found in the present work, and the fifth column, the value reported by Mohler et al. Taking the accuracies of measurements into account, the coincidence of data is reasonable.

The third column gives the intensity, found by the present measurements, of the satellite peak relative to the thermal energy peak, and the sixth column, the intensity found by Mohler et al. A comparison of the data shows that the values of the present work are about 10 times larger than those of Mohler et al. As can be seen from curve 1 in Fig. 2 and curve 3 in Fig. 3, these ratios depend markedly on the ion-accelerating voltage, V_i, and the ion-repeler voltage, V_r. The values of V_i and V_r used in this work were, respectively, about 500 and 0 V. On the other hand, the value of V_i used by Mohler et al. was 140 V.; their V_r value was not indicated. The discrepancies in the intensity ratios may be due to the differences in these experimental conditions.

In the present experiment, the *m/e* 15 KE ion of an appreciable intensity was found in the spectrum of 1, 3-butadiene. KE ions of *m/e* 14 were detected by Hipple et al.³⁾ in the spectrum of this compound. The *m/e* 15 peaks of 1, 3-butadiene are rearrangement peaks, and are unique in that the intensity of the KE peak is about four times higher than that of the TE peak. This phenomenon may be explained as follows: The first and fourth carbon atoms of the compound are more reactive than the second and third atoms. In an excited state, proposed by Eyring et al.⁶⁾, of the compound under electron impact, the more reactive first or fourth carbon atom takes the hydrogen atom from the adjacent second or third carbon atom and forms a methyl group. During this transfer, the equilibrium C=C distance is assumed to remain approximately the same. Since the equilibrium distance of CH_3-C is longer than that of CH_2=C, the Franck-Condon region corresponding to the CH_2=C bond of the mother compound crosses the CH_3-C potential energy curve for an upper state at a region higher than the dissociation asymptote of the curve; thus, the methyl ion, formed by rearrangement, dissociates with a high kinetic energy.

Hustrulid et al.²⁾ suggested that these ions of a high kinetic energy result from the dissociation of doubly-charged ions formed by electron impact. Mohler et al.⁴⁾ computed the repulsive energies of various compounds on this assumption. The "Coulomb energy" calculated by them, i. e., the calculated repulsive energy, is cited in the last column of Table I. When a molecular ion dissociates into two fragments, these fragments have equal momenta. By assuming that doubly-charged ions dissociate into two fragments, one of the two being methyl ion, and that the law of conservation of momenta holds, the total kinetic energy of both fragments has been computed from the value in column 2; this is listed in the fourth column of Table I. In the seventh column the total energy calculated by Mohler et al. is

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6) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig and H. Eyring, *Proc. Natl. Acad. Sci. U. S.*, **38**, 667 (1952).

TABLE I. CH_3^+ IONS OF HIGH KINETIC ENERGY IN MASS SPECTRA OF HYDROCARBONS

	Present experiment			Result of Mohler et al.*			
Compound	KE of satellite	Relative intensity	Total KE	KE of satellite	Relative intensity	Total KE	Coulomb energy
Ethane	2.5	0.54	5.0	2.3	0.03	4.6	5.6
Propane	2.4	0.89	3.6	2.2	0.076	3.3	3.7
Propylene	2.6	0.52	4.0	—	—	—	—
n-Butane	2.3	1.41	3.1	2.2	0.137	3.0	2.9
Isobutane	2.5	1.16	3.4	2.6	0.11	3.5	3.7
1, 3-Butadiene	2.5	4.15	3.3	—	—	—	—

Energy unit is eV.

* F. L. Mohler, V. H. Dibeler and R. M. Reese, *J. Chem. Phys.*, **22**, 394 (1954).

given for purposes of comparison. In the cases of ethane and propane, the total energies found in this work are nearer to the "Coulomb energy" than those found by Mohler et al. The total energies of other substances are nearly the same in both cases.

If the mechanism proposed by Hustrulid-Mohler* is valid, the total energy is approximately inversely proportional to the distance between the carbon atoms at both ends of the molecular chain(4). In the cases of two series of substances, ethane, propane, and *n*-butane, and propylene and propane, this expectation is realized qualitatively, as may be seen from the fourth column, Table I; the assumption of H-M appears to be true from this consideration. However, if a doubly-charged ion actually dissociates into two fragment ions, two species of ions with the same momentum must be observed. To clarify the origin of high kinetic energy ions from this point of view, it is desirable to study the kinetic energies of all the fragment ions of a compound.

Taking ethylene as an example, all peaks were examined, and kinetic energy satellites were found at *m/e* 13 and 14. Table II summarizes the results of these measurements. The first column gives the *m/e* values at which kinetic energy satellites were found; the second and third columns give, respectively, the kinetic energy value and the intensity of the satellite peak. The conditions of measurements were much the same as those for the measurements in Table I.

The following reactions were studied for the fragmentation of ethylene, according to the H-M mechanism:

$$C_2H_4 \rightarrow C_2H_4{}^{2+} \rightarrow \begin{cases} 2CH_2{}^+ & (1) \\ CH_2{}^+ + CH^+ + H & (2) \end{cases}$$

From Table II, the measured total energy for reaction 1 is 4.4 eV., if it is assumed that the fragments have only translational kinetic energies. If the H-M assumption were valid, the total energy for the fragmentation of KE ions of ethane would be smaller than that for reaction 1. However, since the value for ethane is 5.6 eV. according to the computation by Mohler et al.(4), is 5.0 eV. according to the computation made in the present work (Table I), the H-M mechanism of fragmentation does not hold for reaction 1.

TABLE II. IONS OF HIGH KINETIC ENERGY IN MASS SPECTRA OF C_2H_4

m/e	KE of satellite	Intensity (arbitrary unit)
13	2.1 eV.	2.4
14	2.2 eV.	6.6

If it is assumed that the H-M mechanism holds and that the hydrogen atom produced carries away a large amount of kinetic energy, the reaction represented by Eq. 2 can take place. However, according to the relation between the ion intensities of methylene ion and methylidyne ion in Table II, it is considered that all the methylene ions are not formed by the reaction. It follows that, from the standpoint of the H-M mechanism, a fraction of methylene KE ions is produced, together with neutral fragments.

Summary

With a conventional analytical mass spectrometer and without any additional electrodes, fragment ions produced with excess kinetic energies by electron impact can be detected and studied quantitatively. Mainly methyl KE ions in the spectra of seven hydrocarbons have been measured. A comparison of the results on methyl ions in four hydrocarbons with reported values showed a satisfactory consistency.

An appreciable part of the *m/e* 15 rearrangement ions of 1, 3-butadiene had excess kinetic energies. The mechanism of the formation of the ions has been proposed which assumes a transfer of the hydrogen atom from a second

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* Abbreviated as H-M.

carbon atom of the molecule to the first carbon atom followed by the recoil of the resulting two groups of atoms. The study of the KE ions in the spectra of the ethylene molecule from the standpoint of the H-M assumption shows that the mechanism of the formation of various KE ions is complicated and deserves more detailed study.

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