

High-kinetic Energy Fragment Ions from Aliphatic Hydrocarbons under Electron Impact. III. Nine Hydrocarbons Ranging from C₂ to C₄

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In previous papers, we have described a method for measuring the kinetic energy of the fragment ions observed in the mass spectra of hydrocarbons¹⁾ and have reported some findings.²⁾ In the present work, we will measure the kinetic energies of the fragment ions of nine hydrocarbons by the method and will discuss the findings in an attempt to clarify the mechanism of the decomposition of molecules into various high-kinetic energy fragment ions.

The samples were standard one obtained from the Takachiho Chemicals Co.; their nominal purities were 99% or higher and

we found them to be pure by a mass spectrometer. The procedure of measurement has been described previously.¹⁾ The approximate values of the appearance potential of a few high-kinetic energy fragment ions were measured by the vanishing current method, using neon as the calibrating gas.

Results

The results of these measurements are given in Tables I—III. The previously-reported data, for ethylene, propane and methyl high-kinetic energy ions from 1,3-butadiene,¹⁾ are also included for the purpose of comparison. Table I summarizes the measurements of the kinetic energies of fragment ions. The measured peak height values are given in Table

1) T. Tsuchiya, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **35**, 1221 (1962).

2) T. Tsuchiya, *J. Chem. Phys.*, **36**, 568 (1962).

TABLE I. EXCESS KINETIC ENERGY OF FRAGMENT IONS (in eV.)

Compound	m/e									
	12	13	14	15	16	25	26	27	28	29
Ethylene		2.1	2.2							
Ethane		2.2	2.1	2.5	2.6					
Propylene		2.5	2.6	2.6			1.2	1.3		
Propane		2.5	2.4	2.4	2.6		1.3	1.2	1.1	
<i>n</i> -Butane		2.3	2.3	2.3	2.4		1.8	1.8	1.8	1.9
Isobutane		2.4	2.6	2.5	2.7			1.4	1.7	
1-Butene	2.3	2.3	2.4	2.4	2.4	1.8	1.8	1.9	1.9	
<i>cis</i> -2-Butene	2.2	2.3	2.4	2.5	2.6	1.7	1.8	1.9	1.9	
<i>trans</i> -2-Butene	2.3	2.3	2.4	2.4	2.5	1.7	1.8	1.9	1.9	
Isobutene	2.3	2.4	2.6	2.7	2.9		1.8	1.9	1.9	
1, 3-Butadiene	2.3	2.3	2.5	2.4		1.7	1.8	2.0		

TABLE II. INTENSITY OF IONS

The upper row for each compound is the intensity of the ions with excess kinetic energy, the lower one, that of the ions with thermal energy only (in arbitrary units)

Compound	m/e																	
	12	13	14	15	16	25	26	27	28	29	36	37	38	39	40	41	42	
Ethylene		1.7 11.2	4.7 16.7															
Ethane		0.9 6.3	3.5 11.5	8.9 16.5	0.4 0.4													
Propylene		1.0 3.3	4.7 10.6	5.9 11.2			4.6 26.1	6.9 68.8										
Propane		0.6 3.0	3.8 9.0	17.5 19.6	0.5 0.6		4.9 43.0	13.8 177	7.5 130									
<i>n</i> -Butane		0.6 1.2	2.5 4.0	24.0 17.0	0.4 0.5		4.7 37.6	12.4 203	3.3 119	2.1 175			+	+			+	
Isobutane	0.3 0.7	0.9 1.6	4.0 6.2	31.8 27.4	1.0 0.8		1.8 19.1	2.6 164					+	+	+	+	+	
1-Butene	0.5 1.4	1.0 2.5	4.4 6.6	17.6 15.8	0.3 0.4	1.3 4.9	6.6 50.1	8.8 145	1.8 101				+	+	+	+		
<i>cis</i> -2-Butene	0.5 1.2	0.7 1.7	2.8 3.5	17.3 11.3	0.1 0.1	1.3 6.1	8.8 51.8	10.5 140	2.6 96				+	+	+	+		
<i>trans</i> -2-Butene	0.2 1.1	0.6 1.3	2.7 3.3	16.5 9.4	0.2 0.4	0.9 5.9	8.5 49.2	10.2 130.5	3.4 91.2				+	+	+	+		
Isobutene	0.6 1.7	1.4 2.5	6.0 6.4	21.7 14.2	0.4 0.4		3 24	3 93	0.4 63	0.4 32	+	+	+	+	+	+		
1, 3-Butadiene	1.1 3.6	2.0 3.7	4.9 5.4	7.4 1.8		1.2 10.5	9.3 63.5	10.9 176					+	+	+	+		

TABLE III. APPEARANCE POTENTIAL OF HIGH KINETIC ENERGY IONS (in eV.)

Compound	m/e			
	14	15	26	27
Ethylene	35±4			
Ethane		30±3		
Propylene	30±3	29±3	38±3	30±3

II, where the upper row for each substance shows the values for the high-kinetic energy peaks,* or satellite peaks, and the lower one,

* For convenience, ions having excess kinetic energies will hereafter be called KE ions, while those having thermal energies corresponding to the temperature of the ion-source will be called TE ions.

the values for the thermal energy peaks. Table III gives the rough values of the estimated appearance potentials of some satellite peaks.

Discussion

Hustrulid³⁾ and Mohler⁴⁾ have discussed the mechanism of the formation of KE ions and have proposed that KE ions result from the dissociation of doubly-charged ions formed by electron impact. For convenience, this mecha-

3) A. Hustrulid, P. Kusch and J. T. Tate, *Phys. Rev.*, **54**, 1037 (1938).

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

TABLE IV. BOND ENERGY D , IONIZATION ENERGY I , AND APPEARANCE POTENTIAL A (eV.)

D		I		A	
$\text{CH}_3\text{-C}_2\text{H}_5$	3.9 ^a	C_2H_5	10.3 ^c	$\text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_3^+ + \text{H}$	14.0 ^b
$\text{CH}_3\text{-CH}_3$	3.7 ^a	CH_3	10.0 ^b	$\text{C}_2\text{H}_4 \rightarrow \text{CH}_2^+ + \text{CH}_2$	19.3 ^b
$\text{CH}_2\text{-H}$	3.5 ^b	CH_2	11.9 ^b	$\text{CH}_2 \rightarrow \text{C}^+ + 2\text{H}$	18.0 ^b
$\text{C}_2\text{H}_2^+ \text{-H}$	3.8 ^b	CH	11.1 ^b		
$\text{CH}_2^+ \text{-H}$	5.3 ^b	C	11.3 ^b		
$\text{CH}^+ \text{-H}$	3.5 ^b				

a J. S. Roberts and H. A. Skinner, *Trans. Faraday Soc.*, **45**, 339 (1949).

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

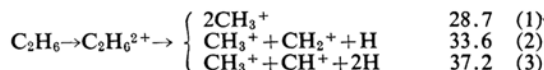
c M. B. Wallenstein, Thesis, Univ. Utah, 1951.

nism will hereafter, as in the previous report, be referred to as the H-M mechanism.

m/e 16.—In some cases weak doublets are observed at m/e 16, as Table II shows. One or more of the following ions can contribute to the peak at m/e 16: (a) rearrangement ions of the sample material, (b) isotope ions of the m/e 15 ion, (c) ions from impurities contained in samples such as the parent ion of methane and oxygen ions from oxygen or from water, and (d) the background peaks of oxygen ions from oxygen or from water. The contributions from (c) and (d) could be eliminated by scrutinizing the kinetic energy value of the satellites⁵⁾ and the sensitivity of the instrument and by referring to the m/e 32 and to the m/e 18 peaks. After the isotope contribution was subtracted, it was found that some of the m/e 16 satellites of ethane, propane, *n*-butane, isobutane, and isobutene are due to inherent high-kinetic energy ions. Presumably, these ions are methane ions, produced by rearrangement. Though the intensities of the satellites are small, the following trends, concerning the intensity of m/e 16 KE ions, can be seen from Table I. The longer the carbon chain of a molecule, the smaller the intensity of the KE ion. Whereas the iso-structure has a favorable effect on KE ion production, double bond has a negative influence.

Ethane.—In the following discussions, the numbers shown after each reaction equation indicate the energy of the formation of the KE ions, as computed from the values in Table IV and the measured KE values of the concerned ions in eV. These computed energies represent the lower limits of the true energies of formation, since the produced fragments may possibly be in the excited state.

The following reactions were investigated as reactions giving CH_3^+ KE ions according to the H-M mechanism:



For example, the energy of the formation of CH_3^+ KE ions, $F(\text{CH}_3^+)$, in reaction 2 was computed by the following cycle:

$$F(\text{CH}_3^+) = D(\text{CH}_3\text{-CH}_3) + 2I(\text{CH}_3) + D(\text{CH}_2^+ \text{-H}) + E(\text{CH}_3^+) + E(\text{CH}_2^+) + E(\text{H})$$

Where

$D(\text{X-Y})$: the dissociation energy of the X-Y bond,

$I(\text{X})$: the ionization potential of the radical X,

$E(\text{Y})$: the kinetic energy of the radical or ion Y.

From the experimental values in Table I and from the data in Table IV, $F(\text{CH}_3^+)$ is found to be:

$$F(\text{CH}_3^+) = 33.6 + E(\text{H})$$

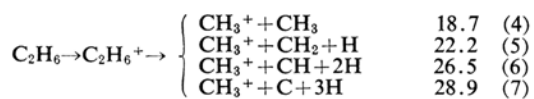
Other F values were computed in a similar way.

The appearance potential of the CH_3^+ ion, $A(\text{CH}_3^+)$, is 30 ± 3 eV. (Table III). The F value for reaction 1 is compatible with the experimental value, $A(\text{CH}_3^+)$. The experimental value for the total kinetic energy, which is the summation of the kinetic energies of the ions, 5.0 eV., differs from the value, 5.6 eV., calculated by Mohler et al.⁴⁾ Taking into consideration, however, the fact that the computation of Mohler et al. contains an assumption about the distance between charges, reaction 1 may also be valid.

Reactions 2 and 3 are both accompanied with neutral fragments. Comparing the F values with $A(\text{CH}_3^+)$, these reactions are considered to be improbable. If hydrogen is produced as a molecule instead of atoms, however, reaction 3 is not impossible.

Apart from the H-M mechanism, the following reactions were investigated:

5) J. D. Morrison and H. E. Stanton, *J. Chem. Phys.*, **28**, 9 (1958).



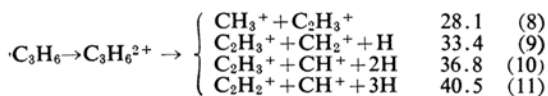
In computing the F values, the kinetic energies of the neutral fragments as a whole were assumed to be equal to that of the CH_3^+ ion, i. e., 2.5 eV. The energy of formation for reaction n , F_n , was computed as before. $D(\text{CH}-\text{H}) = 4.3$ eV., necessary to determine F_6 , was calculated from the equation:

$$D(\text{CH}-\text{H}) = I(\text{CH}_2) + D(\text{CH}^+-\text{H}) - I(\text{CH})$$

From a similar cycle, $D(\text{H}-\text{C}-\text{H})$ was found to be 6.7 eV. and was used to obtain F_7 .

Comparing the $A(\text{CH}_3^+)$ values with the F values, reactions 4 and 5 can be eliminated, provided the products are not in the excited state. Since we know very little about the energies of the neutral fragments in reactions 4 and 5, nothing can be inferred from their F values about these reactions. The summation of the intensities of ions other than the m/e 15 ion is about one-half of the intensity of the m/e 15 ion (Table II). Accordingly, only some m/e 15 ions are produced in pairs with other KE ions, since equal numbers of the two species of an ion pair are necessarily produced by a particular reaction and the sensitivities of those ion pairs in Eqs. 1–7 are reasonably assumed to be approximately equal.²⁾ Thus, the CH_3^+ KE ion seems to be produced from ethane by reaction 1 according to the M–H mechanism and by some of the reactions 4–7 with neutral fragments, if the produced fragments are excited appropriately.

C_3H_6 .—When a doubly-charged molecular ion dissociates, the two resulting fragments have equal momentum. As has been discussed previously,²⁾ pairs of ions were selected in this respect and the following reactions were investigated:



Mohler et al.¹⁴⁾ gave 3.7 eV. as their “Coulomb energy” for propane. Using an appropriate value⁶⁾ for the distance between end carbon atoms in propylene, instead of that in propane,⁷⁾ computation similar to Mohler gives 3.9 eV. as the “Coulomb energy” of propylene. The summation of the kinetic energies of the ion pair in reaction 8 is 3.9 eV. (Table I), which agrees with the computed value. $A(\text{C}_2\text{H}_3^+)$ in Table III is also compatible with the energy of the formation of 8.

While the energies of the formation of reactions 9 and 10 are incompatible with the appearance potentials (Table III), that of reaction 11 is compatible with $A(\text{C}_2\text{H}_2^+)$ in Table III, provided we assume that the hydrogen atoms produced have no kinetic energy. Thus 8 and 11 seem to be important reactions from the standpoint of the H–M mechanism.

Apart from the H–M assumption, the following reactions were investigated because their energies of formation are reasonable when compared with the measured appearance potentials of the corresponding ions. In deriving the energy of formation, the momentum of the KE ions and of the neutral fragments as a whole were assumed to be conserved.

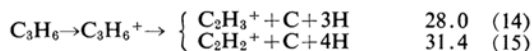
Among the reactions producing the CH_3^+ KE ion only, reaction 12 requires an energy of formation less than $A(\text{CH}_3^+)$:



Similarly, for CH_2^+ , we have reaction 13:



For C_2H_3^+ and C_2H_2^+ , we have:



As the neutral fragments produced may be excited, 12–15 are feasible reactions from the standpoint of the energy of formation.

The sum of the peak heights of high-energy ions in the C_1 group is about 11.6, while that of those in the C_2 group is 11.5 (Table II). As has already been reported for propane,²⁾ this suggests that the two groups of ions are produced simultaneously in pairs and that the contributions of 12–15 may be of little importance.

C_4 Compounds.—The KE values and the intensities of KE ions of a mass number higher than m/e 30 could not be measured because the resolving power of the present instrument was insufficient, although the presence of KE ions could be recognized clearly because of partly-overlapped satellites. The KE values in this m/e range were roughly estimated to be about 0.8 eV. The number of + marks in Table II indicates the approximate intensity of the KE ions.

Although the results of the present experiment on C_4 compounds are insufficient to describe the phenomena accurately, the following points are conceivable. The KE of each m/e 12–15 ion is larger than that of each m/e 25–29 ion, but the magnitude of momentum is in the reverse order. By the H–M mechanism, when a doubly-charged molecular ion dissociates, the two resulting fragments have equal momentum. Since the kinetic energies of the m/e 40 group ions are, roughly,

6) D. R. Lide, Jr., and E. E. Mann, *J. Chem. Phys.*, **27**, 868 (1957).

7) L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.*, **59**, 1223 (1937).

0.8 eV., their momentum is in the same range as that of m/e 12~15 group ions. The summation of the KE of the two groups is about 3 eV., a value which is nearly the same as the total KE value computed by Mohler et al.^{4)*} Thus, the reaction giving the two groups of ions m/e 12~15 and m/e 40 simultaneously is possible from this point of view.

The intensities of the m/e 15 KE ions of isobutane and isobutene are very large, and they might be produced in pairs with neutral fragments. As in the case of the H-M mechanism, the process can be considered as follows: From Table I, it is seen that the KE of isobutene is 2.7 eV. and that that of isobutane is 2.5 eV. Although the precision of the present experiment is ± 0.2 eV., the order of magnitude of the KE values is reliable, i. e., the m/e 15 KE value of isobutene is larger than that of isobutane. The C-C distance of isobutane is $1.54 \pm 0.02 \text{ \AA}$,⁸⁾ while that of isobutene between the tertiary carbon atom and the CH_3 radical is 1.50 \AA .⁹⁾ We assume that, in a section along the C-C bond of the potential energy diagram of the two substances, the potential energy curve for the ground states and for the upper repulsive state, along which a molecule dissociates into a CH_3^+ ion and

another fragment, are nearly the same. Since the C-C distance of isobutene is smaller than that of isobutane, the Franck-Condon region corresponding to isobutene crosses the potential energy curve for the upper state at a region higher than in isobutane; consequently, the KE of m/e 15 ion from isobutene is larger than that from isobutane.

Summary

Fragment ions produced by electron impact with excess kinetic energies from into nine hydrocarbons ranging from C_2 to C_4 have been investigated. Fragment ions of a higher mass-number could not be measured. The decomposition mechanism of propylene has been explained by the mechanisms proposed by Hustrulid and by Mohler et al. To explain the decomposition of other molecules, reactions producing ions with excess kinetic energy as well as neutral fragments must also be taken into consideration.

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* *n*-Butane, 2.9; Isobutene, 3.7; 1-Butene, 3.0 eV.

8) J. Y. Beach and J. Walter, *J. Chem. Phys.*, **8**, 303 (1940).

9) G. R. Somayajulu, *ibid.*, **31**, 919 (1959).

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