Mass Spectra at Low Ionizing Voltage and Bond Dissociation Energies of Molecular Ions from Hydrocarbons

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Since Eyring and co-workers(1) first introduced the statistical theory to the interpretation of mass spectra of hydrocarbons, several authors(2-4) have reported similar results on simple organic molecules. King and Long(3) pointed out that the theory is inadequate at low ionizing voltages although it seems qualitatively satisfactory at high ionizing voltages such as 70 V. except for some of the rearrangement and hydrogen abstraction processes. Hence, it seems very important for the purpose of clarifying ion dissociation mechanisms to study mass spectra at low ionizing voltages.

In this paper, the experimental results on the mass spectra of some paraffins and olefins, especially on the characteristic features of ion yield in relation to the ionizing voltages, are

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1) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaffig and H. Eyring, *Proc. Natl. Acad. Sci.*, **38**, 669 (1952).

2) L. Friedman, F. A. Long and M. Wolfsberg, *J. Chem. Phys.*, **27**, 613 (1957).

3) A. B. King and F. A. Long, ibid., **29**, 374 (1958).

4) A. Krope, E. M. Eyring, A. L. Wahrhaffig and H. Eyring, ibid., **32**, 149 (1960).

presented, and discussion is carried out on the bond dissociation of molecular ions.

Experimental

The instrument used in this work is a Hitachi mass spectrometer: type RMS-3, of a single focusing, 60° sector type with a radius of 100 mm. Positive ions going into the ion collector are detected through a negative feedback amplifier with an electrometer tube, Raytheon 5886 tetrode. In order to measure appearance potentials, however, some slight modifications are made in the ion source and the electric circuit belonging to it. A shielding electrode is inserted between the filament and the ionization chamber of an ordinary ion source, the filament is heated by DC currents and the ionizing voltage can be changed by 0.1 V. step by means of a potentiometer.

In the experiment, the pressure in the sample reservoir and the operating conditions, except the ionizing voltage, of the ion source are kept nearly constant.

The extrapolation method[5] is applied to obtain the appearance potentials, and krypton (ionization potential spectroscopically obtained: 14.03 eV.[6]) is used as the calibrating gas.

TABLE I. APPEARANCE POTENTIALS AND ACTIVATION ENERGIES OF PARAFFINS, eV.

$C_2H_6^+$ 11.78	$\xrightarrow{1.19}$	$C_2H_5^+$ 12.97	$\longrightarrow$	$C_2H_3^+$
	$\xrightarrow{0.38}$	$C_2H_4^+$ 12.16	$\longrightarrow$	$C_2H_2^+$
$C_3H_8^+$ 11.20	$\xrightarrow{0.56}$	$C_3H_7^+$ 11.76	$\xrightarrow{3.0}$	$C_3H_5^+$ 14.76
	$\xrightarrow{1.0}$	$C_3H_6^+$ 12.20	$\longrightarrow$	$C_3H_4^+$
	$\xrightarrow{1.04}$	$C_2H_5^+$ 12.24	$\xrightarrow{3.22}$	$C_2H_3^+$ 15.46
	$\xrightarrow{0.64}$	$C_2H_4^+$ 11.84	$\longrightarrow$	$C_2H_2^+$
n-$C_4H_{10}^+$ 10.23	$\xrightarrow{0.78}$	$C_4H_9^+$ 11.11		
	$\xrightarrow{0.63}$	$C_3H_7^+$ 10.86	$\xrightarrow{2.54}$	$C_3H_5^+$ 13·40
	$\xrightarrow{0.54}$	$C_3H_6^+$ 10.77		
	$\xrightarrow{2.32}$	$C_2H_5^+$ 12.55	$\longrightarrow$	$C_2H_3^+$
	$\xrightarrow{1.22}$	$C_2H_4^+$ 11.45		
iso-$C_4H_{10}^+$ 10.23	$\xrightarrow{1.37}$	$C_4H_9^+$ 11.6		
	$\xrightarrow{0.93}$	$C_3H_7^+$ 11.16	$\xrightarrow{3.39}$	$C_3H_5^+$ 14.55
	$\xrightarrow{0.65}$	$C_3H_6^+$ 10.88		
	$\xrightarrow{3.57}$	$C_2H_5^+$ 13.80	$\longrightarrow$	$C_2H_3^+$
	$\xrightarrow{3.84}$	$C_2H_4^+$ 14.07		

Experimental Results

Paraffins.—The appearance potentials obtained for straight and branched paraffins are shown in Table I together with bond energies calculated from the appearance potentials. Numerals under the chemical formula of ions represent the appearance potentials in electron volts and those above the arrows the bond energies or the activation energies in unimolecular decomposition. These energy values are in good agreement with the values reported by Field and Franklin[7].

In Figs. 1, 2 and 3, relative yields of principal ions are shown in relation to the ionizing voltage. The abscissa, V_e-I, is the excess energy of the ionizing electron over the ionization potential of the parent molecules. Since M/e 29 peak in a mass spectram of isobutane results from the summation of a rearrangement peak ($C_2H_5^+$) and isotopic peaks, correction is necessary for the estimation of

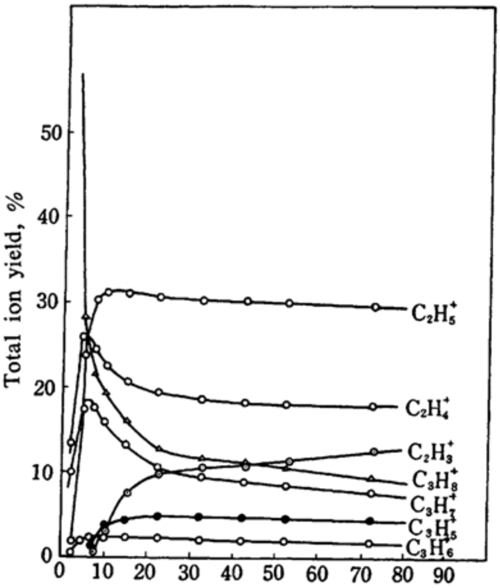

Fig. 1. Low voltage yield of ions from propane.

△ : Type I ○ : Type II
● : Type III ⊙ : Type IV

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[5] T. Mariner and W. Bleakney, *Phys. Rev.*, **72**, 807 (1947).

[6] J. D. Morrison, *Revs. Pure Appl. Chem.*, **5**, 22 (1955).

[7] F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions", Academic Press Inc., New York (1957).

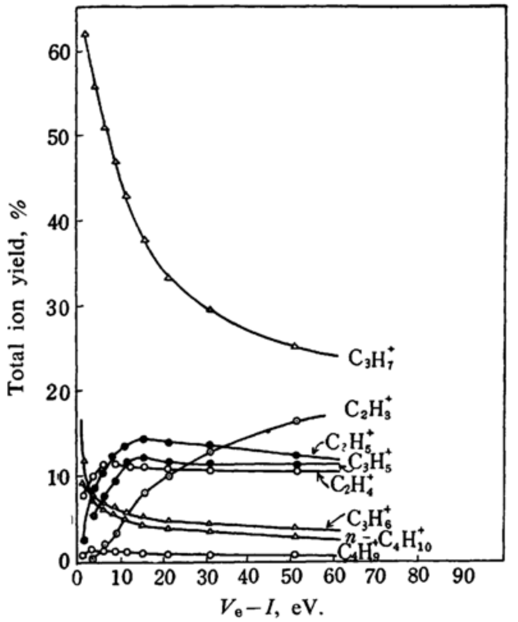

Fig. 2. Low voltage yield of ions from *n*-butane.
△ : Type I ○ : Type II
● : Type III ⊙ : Type IV

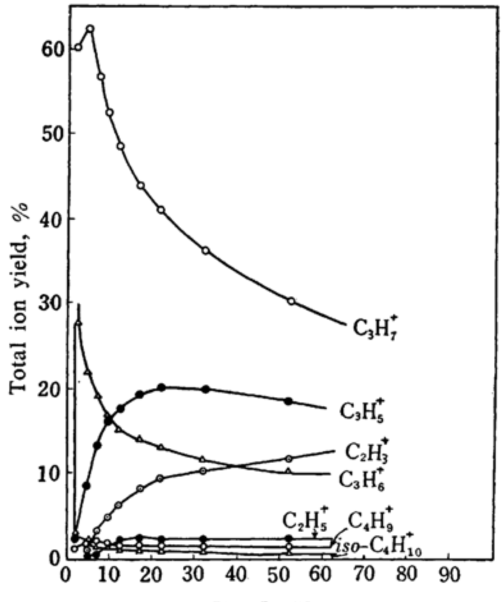

Fig. 3. Low voltage yield of ions from isobutane.
△ : Type I ○ : Type II
● : Type III ⊙ : Type IV

the $C_2H_5^+$ yield from the spectrum. The curve for $C_2H_5^+$ in Fig. 3 is a curve corrected by Washburn's method[8].

These curves can be classified into four types, though it is difficult to classify some ions because they show medium aspects between two neighboring types. Type I curves are for those ions whose relative yield is very high at very low excess energies and decreases rapidly with the increase of ionizing voltage. Type II curves are for those ions whose relative yield rises rapidly to a maximum at an excess energy of 5∼10 eV., and decreases to a nearly constant value. Type III curves are for those ions whose relative yield rises to a nearly constant value without passing a distinct maximum or after passing through a slight maximum at an excess energy higher than 10 eV. Type IV curves are for those ions whose relative yield increases slowly and does not level off until much higher ionizing voltages.

Parent ions and fragment ions of low activation energies belong to Type I. The activation energies of ions belonging to Type II are in a range between about 0.3. and 2 eV., and those to Type III in a range between about 2 and 3.5 eV., while those to Type IV are larger than 3 eV. The classification of principal ions from four paraffins are listed in Table II.

TABLE II. CLASSIFICATION OF PRINCIPAL IONS

Type	Substance			
	Ethane	Propane	*n*-Butane	Isobutane
I	$C_2H_6^+$	$C_3H_8^+$	*n*-$C_4H_{10}^+$ $C_3H_7^+$ $C_3H_6^+$	iso-$C_4H_{10}^+$ $C_3H_6^+$
II	$C_2H_5^+$ $C_2H_4^+$	$C_3H_7^+$ $C_3H_6^+$ $C_2H_4^+$	$C_4H_9^+$ $C_2H_4^+$	$C_4H_9^+$ $C_3H_7^+$
III	$C_2H_3^+$ $C_2H_2^+$	$C_3H_5^+$ $C_3H_4^+$ $C_2H_6^+$ $C_2H_5^+$	$C_4H_8^+$ $C_3H_5^+$ $C_2H_5^+$	$C_4H_8^+$ $C_4H_7^+$ $C_8H_5^+$ $C_2H_5^+$
IV	CH_3^+	$C_3H_3^+$ $C_3H_2^+$ $C_2H_3^+$ $C_2H_2^+$ C_2H^+ CH_3^+	$C_4H_7^+$ $C_3H_3^+$ $C_2H_3^+$	$C_3H_4^+$ $C_3H_3^+$ $C_2H_4^+$ $C_2H_3^+$

Olefins.—Similar results are obtained for straight olefins. The appearance potentials and the activation energies obtained are shown in Table III. These data are also in good agreement with the values of Field and Franklin[7]. Comparing Table III with Table I, the ionization potentials of olefins are considerably lower than those of paraffins with the same carbon numbers. This may be caused by the fact that π-electrons are concerned in the ionization of olefins. Activation energies, on the other hand, are higher for olefins than for paraffins.

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[8] G. P. Barnard, "Modern Mass Spectrometry", the Institute of Physics, London (1953), p. 201.

TABLE III. APPEARANCE POTENTIALS AND ACTIVATION ENERGIES OF OLEFINS, eV.

$C_2H_4^+$ 10.64 $\xrightarrow{3.72}$ $C_2H_3^+$ 14.36
$C_2H_4^+$ 10.64 $\xrightarrow{2.97}$ $C_2H_2^+$ 13.61

$C_3H_6^+$ 9.74 $\xrightarrow{2.37}$ $C_3H_5^+$ 12.11
$C_3H_6^+$ 9.74 $\xrightarrow{2.78}$ $C_3H_4^+$ 12.52
$C_3H_6^+$ 9.74 $\xrightarrow{3.09}$ $C_2H_4^+$ 12.83
$C_3H_6^+$ 9.74 $\xrightarrow{4.06}$ $C_2H_3^+$ 13.80

1-$C_4H_8^+$ 9.72 $\xrightarrow{2.29}$ $C_4H_7^+$ 12.01
1-$C_4H_8^+$ 9.72 $\xrightarrow{2.06}$ $C_3H_5^+$ 11.78 $\xrightarrow{2.04}$ $C_3H_3^+$ 13.82
1-$C_4H_8^+$ 9.72 $\xrightarrow{2.61}$ $C_2H_4^+$ 12.33

cis-2-$C_4H_8^+$ 9.25 $\xrightarrow{1.95}$ $C_4H_7^+$ 11.20
cis-2-$C_4H_8^+$ 9.25 $\xrightarrow{2.35}$ $C_3H_5^+$ 11.60 $\xrightarrow{2.15}$ $C_3H_3^+$ 13.75
cis-2-$C_4H_8^+$ 9.25 $\xrightarrow{3.0}$ $C_2H_5^+$ 12.25 $\longrightarrow$ $C_2H_3^+$
cis-2-$C_4H_8^+$ 9.25 $\xrightarrow{2.94}$ $C_2H_4^+$ 12.19 $\longrightarrow$ $C_2H_2^+$

TABLE IV. CLASSIFICATION OF PRINCIPAL IONS

Type	Substance			
	Ethylene	Propylene	1-Butene	*cis*-2-Butene
I	$C_2H_4^+$	$C_3H_6^+$	*l*-$C_4H_8^+$	2-$C_4H_8^+$
II		$C_3H_5^+$ $C_3H_4^+$	$C_4H_7^+$ $C_3H_5^+$ $C_3H_4^+$	$C_4H_7^+$ $C_3H_5^+$
III	$C_2H_3^+$ $C_2H_2^+$	$C_3H_3^+$ $C_3H_2^+$ $C_2H_5^+$ $C_2H_2^+$	$C_4H_6^+$ $C_4H_5^+$ $C_4H_4^+$ $C_4H_3^+$ $C_3H_7^+$ $C_3H_6^+$ $C_3H_3^+$ $C_2H_5^+$ $C_2H_4^+$ $C_2H_2^+$	$C_4H_6^+$ $C_4H_5^+$ $C_4H_4^+$ $C_4H_3^+$ $C_3H_6^+$ $C_3H_4^+$ $C_3H_3^+$ $C_3H_2^+$ $C_2H_5^+$ $C_2H_4^+$
IV	C_2H^+ C_2^+	C_3H^+ C_3^+ $C_2H_4^+$ $C_2H_3^+$ C_2H^+ CH_3^+ CH_2^+	$C_4H_2^+$ $C_3H_2^+$ C_3H^+ $C_2H_3^+$	$C_2H_3^+$ $C_2H_2^+$

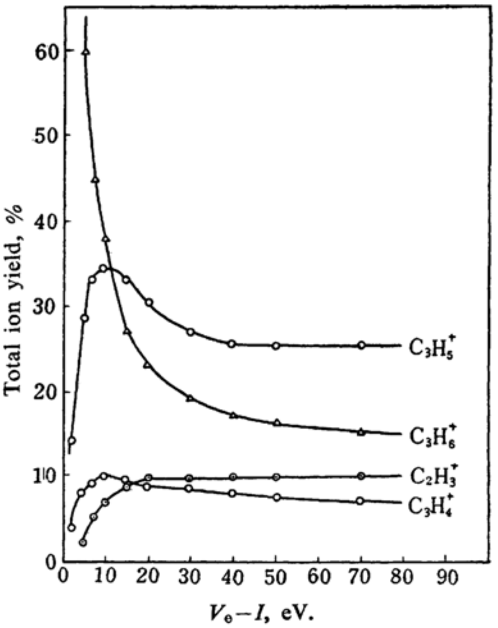


Fig. 4. Low voltage yield of ions from propylene.

△ : Type I ○ : Type II
● : Type III ⊙ : Type IV

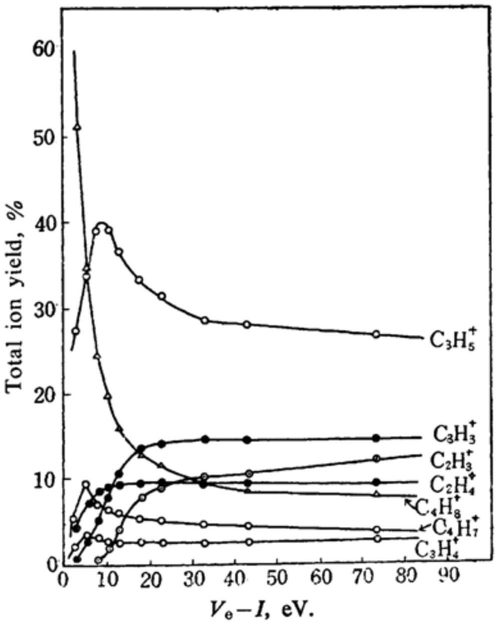


Fig. 5. Low voltage yield of ions from isobutene.

△ : Type I ○ : Type II
● : Type III ⊙ : Type IV

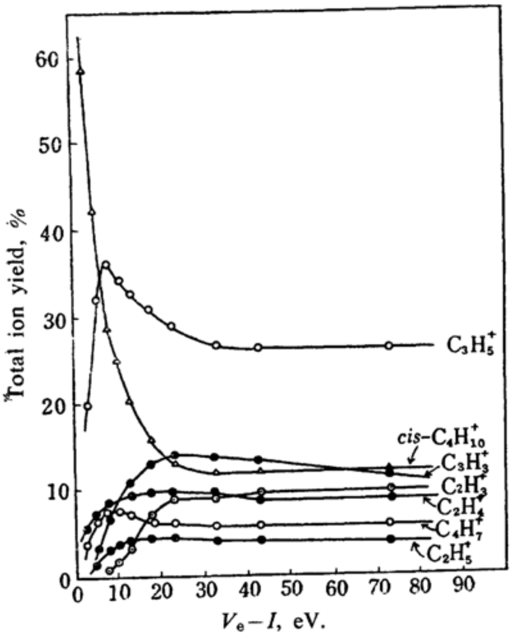


Fig. 6. Low voltage yield of ions from *cis*-2-butene.
△ : Type I ○ : Type II
● : Type III ⊙ : Type IV

Relative yields of principal ions are shown in Figs. 4, 5 and 6. The $C_2H_5^+$ yield in Fig. 6 is a corrected curve by Washburn's method[8]. As in the case of paraffins, the curves can be classified into four groups and the activation energies generally become larger from Type I to Type IV.

Discussion

It has been believed that the statistical theory of unimolecular reaction[1] can be applied to the interpretation of decomposition of molecular ions by the impact of electrons with comparatively high energies. The theory is based on the presumption that molecular ions do not decompose instantaneously into ionized and neutral fragments, but the electron energies are uniformly distributed to whole bonds of molecular ions and then they are concentrated in a specific bond, causing the decompotision related with the electronic state of fragment ions.

According to the theory, a positive charge is distributed to a C-C or C-H bond and the bond rupture of a molecular ion is closely related with the distribution of the positive charge[7]. For instance, a parent ion of propane is presumed to be a hybrid of the following three structures[1] explained in terms of resonance:

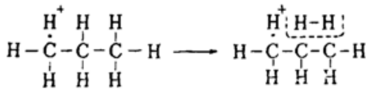
$$H_3{\equiv}C\dotplus CH_2-C{\equiv}H_3 \tag{1}$$

$$H_3{}^+\dot{=}C-CH_2-C{\equiv}H_3 \tag{2}$$

$$H_3{}^+\dot{=}\overset{H-H}{C-CH}{=}CH_2 \tag{3}$$

Fragment ions $C_2H_5^+$ and $C_3H_7^+$ can be expected from simple primary decompositions of the first and second structures, respectively. If a neutral molecule H-H is removed from the third structure, an ionic structure would be expected, $H_3{}^+\dot{=}C-CH=CH_2$, regarded as an olefinic molecular ion[9]. Thus the ionic structures concerned with the distribution of positive charge are very important for the primary rupture of C-C or C-H bond.

As mentioned above, a probable process for the $C_3H_6^+$ creation from $C_3H_8^+$ is a primary decomposition as follows:


(4)

or simply

$$C_3H_8^+ \longrightarrow C_3H_6^+ + H_2 \tag{5}$$

As seen in Table I, the activation energy of $C_3H_6^+$ is a little less than twice the activation energy of C_3H_7. This seems to be an energy transfer effect showing that the energy in the rearrangement of hydrogen atoms is given away from a hydrogen molecule to a resonant ion. From the relation of decomposition energy, the $C_3H_6^+$ ions can not be expected through a secondary decomposition given by[9]

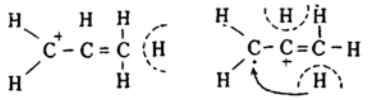
$$C_3H_8^+ \longrightarrow C_3H_7^+ + H \longrightarrow C_3H_6^+ + 2H \tag{6}$$

The fragment ions $C_3H_5^+$, on the other hand, are expected through a secondary decomposition as follows:

$$C_3H_8^+ \longrightarrow C_3H_7^+ + H \longrightarrow C_3H_5^+ + H_2 + H \tag{7}$$

In this case, energy transfer may also take place between a neutral hydrogen molecule and a resonant ion.

The $C_3H_5^+$ ions from paraffins are caused by a secondary decomposition, but those from olefins by a primary decomposition. For instance, the $C_3H_5^+$ ions from propylene are produced through both or either of the following process:


(8)

These two ionic structures are based on the assumption of electron migration[10], though

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[9] D. P. Stevenson and J. A. Hipple, Jr., *J. Am. Chem. Soc.*, 64, 1586 (1942).

[10] G. R. Lester, "Advances in Mass Spectrometry", Symposium Publications Division, Pergamon Press (1959), p. 287.

unfortunately their relative importance has not been exactly proved by experiment. The positive charge is distributed more probaly on C-C bond than on C-H bond, but the principal ions intensities have shown that the "no-bond structures" give an effect of greater importance for the bond rupture. In case of butene, however, the rupture of C-C bond is more probable. The reason may be in the fact that the effects of double bond or no-bond structures are weaker in case of butene than in case of propylene.

It was reported that there might be a simple relation between the yield of fragment ions caused by the rupture of C-H bond of the parent ions and the number of bonds11), but this theory has not been proved by experiment1). The results of the present experiment shown in Table V also contradict the theory. If the distribution of positive charge on C-C and C-H bonds are calculated more precisely by the orbital theory, the process of decomposition of molecular ions might be explained more clearly.

TABLE V. RELATIVE AMOUNT OF PRINCIPAL IONS TO TOTAL IONS AND RATIO OF C-H BONDS TO TOTAL BONDS IN A HYDROCARBON

Substance	$\frac{\text{C-H bonds}}{\text{Total bonds}}$	$\frac{C_nH^+_{2n+1}}{\text{Total ions}}$	$\frac{C_nH^+_{2n-1}}{\text{Total ions}}$
C_2H_6	0.87	0.09	
C_3H_8	0.80	0.08	
n-C_4H_{10}	0.77	0.007	
iso-C_4H_{10}	0.77	0.008	
C_2H_4	0.8		0.24
C_3H_6	0.75		0.24
1-C_4H_8	0.74		0.05
cis-2-C_4H_8	0.74		0.05

Since the fragment ions $C_2H_4^+$ from isobutane are believed to be of olefinic structure and can not be expected to result from $C_2H_5^+$ ions, the process may be as follows:

$$\text{iso-}C_4H_{10}^+ \longrightarrow CH_3-\underset{\cdot}{C}H^+ + CH_3-CH_3$$

$$\longrightarrow CH_2\dot{-}CH_2^+ + C_2H_6 \qquad (9)$$

The energy necessary for reaction 9 is about 3.84 eV. The fragment ions $C_2H_5^+$ from isobutane also seem to be caused by primary decomposition; and a referred process may be as follows:

$$\text{iso-}C_4H_{10}^+ \longrightarrow CH_3-\underset{\cdot}{C}H^+ + CH_3-CH_3$$

$$\longrightarrow CH_3-CH_2^+ + C_2H_5 \qquad (10)$$

The energy necessary for the $C_2H_5^+$ creation is about 3.57 eV. and a little less than that for the $C_2H_4^+$. These processes 9 and 10 may be explained by the presumption of hydrogen transfer and rearrangement respectivly.

The $C_2H_4^+$ and $C_2H_5^+$ ions from *cis*-2-butene may be produced through the following processes, respectively:

$$cis\text{-2-}C_4H_8^+ \longrightarrow CH_3-\underset{\cdot}{C}H^+ + CH-CH_3$$

$$\longrightarrow CH_2\dot{-}CH_2^+ + C_2H_4 \qquad (11)$$

and

$$cis\text{-2-}C_4H_8^+ \longrightarrow CH_3-\underset{\cdot}{C}H^+ + CH-CH_3$$

$$\longrightarrow CH_3-CH_2^+ + C_2H_3 \qquad (12)$$

Hydrogen migration and rearrangement are related, as in cases of the reactions 9 and 10. Contrary to the case of isobutane, the activation energy for $C_2H_5^+$ ions is much greater than that for the $C_2H_4^+$ ions. This may be one of the double bond effects. Another double bond effect is shown in Table VI. The activation energy for a bond rupture is greater in cases of 1-butene and *cis*-2-butene than in the case of *n*-butane, especially for the rupture of C-C bond.

TABLE VI. DOUBLE BOND EFFECT OF OLEFINS

Substance	Ionization potential	Activation energy		Type of total ion yield	
		C-H	C-C	C-H	C-C
n-C_4H_{10}	10.23	1.57	0.63	2	1
1-C_4H_8	9.72	2.29	2.06	2	2
cis-2-C_4H_8	9.25	1.95	2.35	2	2

In order to examine chain branching effects, the results on propane, *n*-butane, and isobutane are compared in Table VII. The activation energies for both C-C bond rupture and C-H bond rupture of iso-$C_4H_{10}^+$ are between those of $C_3H_8^+$ and *n*-$C_4H_{10}^+$, respectively.

TABLE VII. CHAIN BRANCHING EFFECT OF PARAFFINS IONS

Substance	Ionization potential	Activation energy		Type of total ion yield	
		C-H	C-C	C-H	C-C
C_3H_8	11.20	0.56	1.04	2	3
n-C_4H_{10}	10.23	1.57	0.63	2	1
iso-C_4H_{10}	10.23	1.37	0.93	2	2

Summary

Relative yields of parent and principal fragment ions from four paraffins and olefins by electron impact are measured for the first time. The characteristic features of the ion yields can be classified into four types related with the ionizing voltages. The decomposition processes for some fragment ions can be explained under some assumptions, and those for forbidden ions $C_2H_5^+$ from isobutane and *cis*-2-butene under the assumption of hydrogen rerrangement.

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11) F. L. Mohler, L. Williamson and H. M. Dean, *J. Research NBS*, 45, 235 (1950).

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