Kinetic Energies of Fragment Ions from n-Butane Resulting from Electron Impact

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Fragment ions from polyatomic molecules produced by electron impact sometimes possess considerable kinetic energy, the so-called initial energy, which may amount to several electron volts. In early studies the initial energy of ions was measured to determine the ionization potential of ions from their appearance potential. Recently, however, the kinetic energy has come to be of importance in itself, because it provides valuable information on the molecular structure and on the primary processes of the radiation chemistry.

The kinetic energy of fragment ions from *n*-butane produced by electron impact has been studied by many workers. Using the retarding potential method, Fox and Hipple[1] reported that fragment ions of a small mass and those formed by complex dissociation processes always had a high kinetic energy. Taubert[2] carried out a systematic measurement of the kinetic energy of fragment ions from some paraffins and mono-olefines; varying the repeller voltage, he showed that more abundant fragment ions normally have lower kinetic

1) R. E. Fox and J. A. Hipple, *Rev. Sci. Instr.*, **19**, 462 (1948).

2) R. Taubert, "Advances in Mass Spectrometry," p. 486 (1959).

energies. Mohler et al.[3] observed some ions of a high kinetic energy from polyatomic molecules, and they proposed that these ions are produced from the decomposition of doubly-charged molecule-ions. On the other hand, Washburn and Berry[4] attempted to estimate the initial energies of various ions from *n*-butane, using a discrimination method.

Conventional mass spectrometers exhibit a phenomenon called "discrimination," in which ions having initial energies tend to fail to pass through the slit system of the ion-source and the analyzer tube because of the effect of the velocity components perpendicular to the principal motion through the system. On the basis of his experiments, Berry[5] pointed out that the initial velocity distribution could be obtained from the discrimination data and that it was possible to utilize the discrimination effect to determine the average value of initial kinetic energies; he studied theroretically and experimentally the effects of discrimination using the slit system of a mass spectrometer.

The purposes of the present work are two: (a) To investigate the influence of the initial kinetic energy of ions on the relative intensity of the mass spectrum. We studied the difference between the discrimination for ions produced from rare gases in which the initial energy was in equilibrium with the thermal energy, and that for some fragment ions produced from *n*-butane, ions which were believed to have a certain amount of initial energy. (b) On the basis of the information gained about the discrimination effect of the ions with some kinetic energy, the amount of kinetic energy for fragment ions is estimated and the mechanisms of dissociation processes from doubly-charged molecule-ions are considered.

Experimental

A model 21-103-C C.E.C. mass spectrometer was used in the present research. The temperature of the ion-source was kept at 250°C as determined by a thermocouple. The energy of the ionizing electrons was 70 V. and the current was 9.5 μamp. in all experiments. In the instrument, the ions formed in the electron beam are forced through the first slit by a weak repeller voltage and are accelerated in the region between the first and second slits by a high voltage. Between the second slit and the collector slit, the ions travel at a constant speed, but they are caused to move in a circular path by the uniform magnetic field. The mass analyzer tube which is immersed in the magnetic field is a 180° type.

As the instrument is the electric-field scanning type, the ion-accelerating voltage varies in inverse proportion to the mass-chage ratio, m/e, of the ions. To determine the discrimination curve, the relative intensity of various ions was measured by scanning accelerating voltage at several magnetic fields.

The samples used in this experiment were standard samples for mass spectrometric analysis and were 99.9% pure.

Experimental Results

The Effect of the Initial Energy on the Relative Intensities of the Mass Spectrum.—The discrimination efficiency is defined as the ratio of the number of ions of a given mass passing through the collector slit in a unit of time to the number of ions initially produced by electron impact. Since the discrimination efficiency depends on the initial energy of ions, on the accelerating voltage, on the repeller voltage, and on the geometry of the

TABLE I. RELATIVE ABUNDANCE FOR FRAGMENT IONS FROM *n*-BUTANE AT TWO DIFFERENT MAGNETIC FIELDS

Electron impact voltage was 70 V.

Ion	m/e	Low magnetic field mag. curr. =255 mamp.	High magnetic field mag. curr. =300 mamp.
C_2^+	24	0.07	0.10±0.002
C_2H^+	25	0.78±0.01	0.93±0.004
$C_2H_2^+$	26	9.19±0.04	10.12±0.01
$C_2H_3^+$	27	45.76±0.01	47.60±0.07
$C_2H_4^+$	28	35.27±0.15	36.13±0.20
$C_2H_5^+$	29	45.32±0.01	45.52±0.06
$C_2H_6^+$	30	1.06±0.003	1.06±0.004
C_3^+	36	0.14±0.004	0.15±0.003
C_3H^+	37	1.72±0.004	1.92±0.003
$C_3H_2^+$	38	3.06±0.003	3.35±0·01
$C_3H_3^+$	39	18.13±0.10	19.44±0.02
$C_3H_4^+$	40	2.67±0.01	2.87±0.002
$C_3H_5^+$	41	33.22±0.04	33.65±0.02
$C_3H_6^+$	42	13.03±0.03	13.08±0.01
$C_3H_7^+$	43	100.	100.
$C_3H_8^+$	44	3.44±0.02	3.49±0.005
C_4^+	48	1.00±0.003	0.12±0.003
C_4H^+	49	0.63±0.001	0.69±0.003
$C_4H_2^+$	50	1.97±0.002	2.11±0.003
$C_4H_3^+$	51	1.48±0.001	1.56±0.002
$C_4H_4^+$	52	0.35±0.003	0.36±0.004
$C_4H_5^+$	53	0.97±0.001	1.01±0.001
$C_4H_6^+$	54	0.24±0.001	0.24±0.001
$C_4H_7^+$	55	1.11±0.003	1.13±0.001
$C_4H_8^+$	56	0.87±0.004	0.89±0.01
$C_4H_9^+$	57	2.54±0.012	2.60±0.004
$C_4H_{10}^+$	58	11.64±0.008	11.78±0.03
$C_4H_{10}^+$ (i)	59	0.51±0.007	0.52±0.002

3) F. L. Mohler, V. H. Dibeler and R. M. Reese, *J. Chem. Phys.*, **22**, 394 (1954).
4) H. W. Washburn and C. E. Berry, *Phys. Rev.*, **70**, 559 (1946).
5) C. E. Berry, ibid., **78**, 597 (1960).

slit system, it is possible to find information on the initial energy of ions from the experimental relation between the discrimination efficiency and the accelerating voltage.

TABLE II. RELATIVE ABUNDANCE FOR THE KRYPTON ISOTOPE IONS AT TWO DIFFERENT MAGNETIC FIELDS

Ion m/e	Low magnetic field mag. curr. =240 mamp.	High magnetic field mag. curr. =316 mamp.	Sensitivity ratio H_{316}/H_{240}
78	0.635±0.01	0.645±0.002	1.051
80	4.07 ±0.01	4.03 ±0.01	1.059
82	20.43 ±0.005	20.36 ±0.004	1.061
83	20.25 ±0.01	20.23 ±0.003	1.064
84	100.	100.	1.064
86	30.35 ±0.00	30.38 ±0.09	1.066

At the normal repeller voltage and at the fixed geometry of the slit system, the measured relative abundance for ions with an initial energy was measured as a function of the ion-accelerating voltage. Table I shows the relative abundance of fragment ions from *n*-butane at two different magnetic fields. The second column of the table shows the relative intensity for fragment ions preduced at a lower magnetic field (the magnetic current was 255 mamp), while the third column shows those at a higher magnetic field (the magnetic current was 300 mamp). The relative intensities for most of the fragment ions, such as the ions of $m/e=$ 58, 42 and 29, are nearly independent of the magnetic field strength and are all about the same, varying only within a few per cent. On the other hand, the relative intensities for

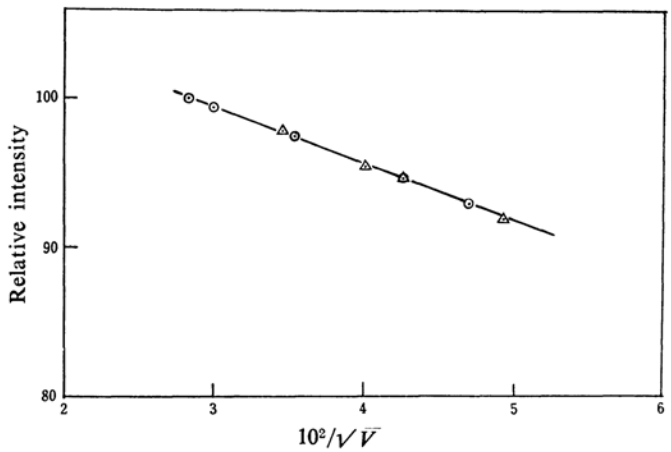

Fig. 1. Discrimination curve for $^{40}Ar^+$ and $^{80}Kr^+$.
⊙ Argon-40 △ Krypton-80

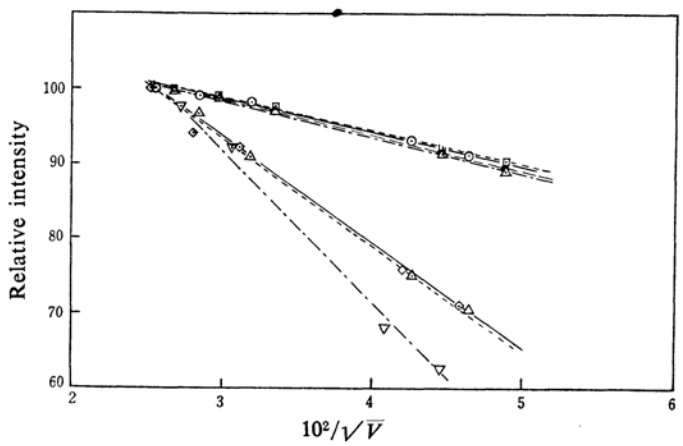

Fig. 2. Discrimination curves for argon, carbon dioxide, propane and some fragment ions from *n*-butane.

—⊙— Argon-40
—△— Carbon dioxde-44
---▣--- Propane-44
--O-- *n*-Bu-43
—△— *n*-Bu-40
---◇--- *n*-Bu-39
---▽--- *n*-Bu-37

certain ions, such as the ions of m/e =39, 40 and 26, are considerably dependent on the field strength. For instance, the change in relative intensity at the two different magnetic field strengths is about 7% for $m/e=39$ and about 10% for $m/e=26$.

Table II shows the relative intensities for krypton isotopes at two different magnetic field strengths. The relative intensities for each isotope ion at the different field strengths are nearly equal, but they have a small dependence on the field strength; that is, the relative intensity of isotopes gradually increases at a high magnetic field as the mass-charge ratio of the ions increases.

Figure 1 shows the relation between the relative intensity of the isotopes of krypton and argon and the accelerating voltage. In this experiment, the accelerating voltage was determined by using the relation between the accelerating voltage and the magnetic field strength, which was adjusted by means of the magnetic current. Although there is a great difference between the mass of argon ($m=40$) and krypton ($m=80$), the relative intensities of both ions lie on the same discrimination curve, since the ions for argon and krypton are produced with no initial energy but have only thermal energy which is determined by the temperature of the ions-source, From this finding, it may be concluded that the ions which have only thermal energy but whose mass-charge ratios are different receive the same discrimination effect.

In this instrument, since ions are analyzed by the electric-field scanning, the ions are accelerated by the voltage obtained from the following eqation:

$$V_1/V_2=(B_1/B_2)^2 \qquad (1)$$

where V is the accelerating voltage, B is the magnetic field strength, and the subscripts represent two different magnetic fields. Since the accelerating voltage decreases with an increase in the mass-charge ratio of ions, the discrimination efficiency for ions with the same mass increases with an increase in the magnetic field strength, as is shown in Fig. 1. This is a reason why the sensitivity ratios for krypton isotopes measured at different magnetic fields increase with an increase in the mass of ions, as is shown in Table II.

The relative intensities for fragment ions from *n*-butane were measured at different magnetic fields. Figure 2 shows the discrimination curves for several ions of *n*-butane. In this figure, the discrimination curves for argon, carbon dioxide and propane ions which were produced with no initial energy are also shown. The relative intensity of the most abundant ion ($m/e=43$) from *n*-butane lies on the same discrimination curve as argon, carbon dioxide and propane ions. On the other hand, the curves for the fragment ions, such as ions of $m/e=37$, 39 and 40, are seen to be extremely steep compared with the former curves. It is reasonable to conclude that these ions are produced with certain amounts of initial energy from the dissociation processes. Furthermore, from the slope of the curves it may be seen that the initial energy for the ion of $m/e=37$ is greater than those of ions of $m/e=39$ and 40.

From the effect of discrimination, it may be concluded that the relative intensity of fragment ions with initial kinetic energies greater than the thermal energy is markedly dependent on the conditions of measurement, such as the accelerating voltage or the magnetic field strength.

The Kinetic Energy of the Fragment Ions from *n*-Butane.—Since the discrimination efficiency for ions with an initial energy markedly depends on the accelerating voltage and on the geometry of the slit system, there is a possibility of utilizing the discrimination effect to determine the average value of initial energies. Berry[5] pointed out that the collection efficiency, N, namely, the ratio of the number of ions of a given mass-charge ratio passing through the collector slit in a unit of time to the number of ions passing the second slit is given by the following equation:

$$N=\frac{1}{2}\left[(1+k)-\frac{L}{w}\sqrt{\frac{V_0}{V}}\right] \qquad (2)$$

where k, w and L are constants determined by the geometry of the slit system, V is the accelerating voltage, and V_0 is the initial energy of the ions. When the initial energy of ions is not so large as the thermal energy, the discrimination effect at the second slit is not so appreciable that the above equation can be applied. On the basis of the results of Figs. 1 and 2, Eq. 2, seems to give a good approximation for the collection efficiency of these ions, because the discrimination effect for ions with the same kinetic energy is not dependent on the mass of ions, as is shown in Figs. 1 and 2, and because the discrimination curves for fragment ions linearly decrease with an increasing $1/\sqrt{V}$, as is shown in Fig. 2.

On the basis of Eq. 2, the kinetic energy for a given ion can be estimated as in Fig. 3. Line (a) in the figure shows a discrimination curve for the A^+ ion with the known kinetic energy of V_{0a}. The dotted lines on both sides of the line are extrapolations of the observed points to $V\rightarrow\infty$, or to the relative intensity, $\rightarrow 0$. The line (b) shows a discrimination curve

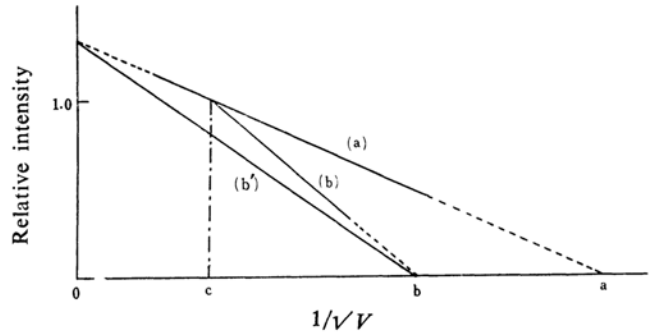

Fig. 3. Calculation of the kinetic energy for ions having initial energy by a graphical method.

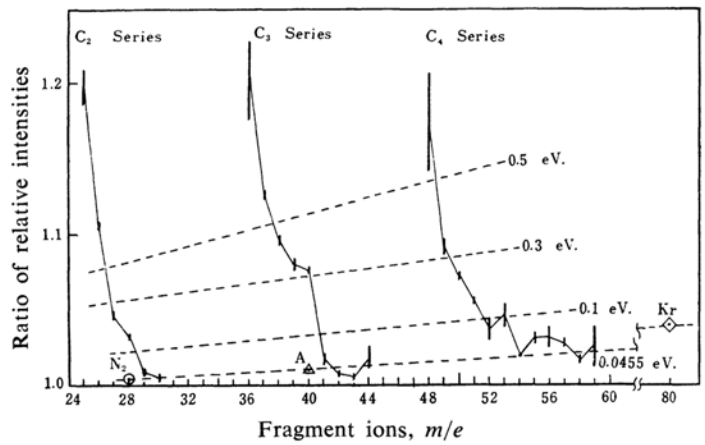

Fig. 4. Ratio of relative intensities at two different magnetic fields and kinetic energies for fragment ions from *n*-butane. Low magnetic field strength was 2386 G and the high field strength was 2807 G.

for the B^+ ion with the unknown kinetic energy of V_{ob}, and the relative intensity for B^+ is normalized at a point C, which is usually the highest voltage obtained. To compare the kinetic energies for the A^+ and B^+ ions, line (b) must be transferred to line (b′), which is normalized at $1/\sqrt{V}=0$. Line (b′) is easily obtained as shown in Fig. 3. Let the slopes of lines (a) and (b′) be t_a and $t_{b'}$; then the kinetic energy of the B^+ line is given by the following equation:

$$V_{ob}=(t_{b'}/t_a)^2 V_{oa} \qquad (3)$$

Since the kinetic energy of the argon ion of $m/e=40$ is in equilibrium at the wall of the ion-source and is estimated to be 0.0455 eV. at 250°C, the kinetic energy for the fragment ion of $m/e=40$ is estimated to be about 0.31 eV. from the results of Fig. 2 and from the relation of Eq. 3.

The ratio of the relative intensities for a given ion at two different magnetic fields, or at two difierent accelerating voltages of V_1 and V_2, provides information about the initial energy of the ion. Figure 4 shows the ratio of relative intensities for fragment ions from *n*-butane obtained by successive operations (to eliminate an error arising from the pressure drop). In this figure, the dotted lines show the iso-energy curve obtained by the above method for ions with difierent initial energies. The curves for ions of N_2^+, Ar^+ and Kr^+ were obtained with this instrument. The other curves for 0.3 and 0.5 eV. were calculated from Eq. 3, assuming that the kinetic energies for N_2^+, Ar^+ and Kr^+ were thermal energy. From the results of Fig. 4, some information about the initial energy for fragment ions from *n*-butane is obtained: (1) All ions produced from *n*-butane by the scission of CH_3 or C_2H_5 have lower kinetic energies, energies which are comparable with the thermal energy. (2) The ions which are represented by the following formulas have high kinetic energies;

$$C_nH_m^+,\ n=2,3,4 \quad m=0,1,\ldots,n+1 \qquad (4)$$

In general, the kinetic energy of these ions increases with a decrease in the number of hydrogen atoms; that is, as the number of scissions of the C–H bond increases, the initial

TABLE III. INITIAL ENERGIES AND RELATIVE ABUNDANCES FOR FRAGMENT IONS FROM *n*-BUTANE PRODUCED BY ELECTRON IMPACT

	Parent ion	Fragment ion			
		Thermal energy		Kinetic energy	
	1	2	3	4	5
C_4-Series	$C_4H_{10}^+$ (11.6)	$C_4H_9^+$ (2.5)	$C_4H_7^+$ (1.1)	$C_4H_5^+$ [0.1] (1.0)	$C_4H_3^+$ [0.15] (1.5)
		$C_4H_8^+$ (0.9)	$C_4H_6^+$ (0.2)	$C_4H_4^+$ [0.08] (0.3)	$C_4H_2^+$ [0.25] (2.0)
C_3-Series	$C_4H_{10}^+$ or $(C_4H_{10})^{2+}$	$C_3H_8^+$ (3.4)	$C_3H_6^+$ (13)	$C_3H_4^+$ [0.31] (2.6)	$C_3H_2^+$ [0.45] (3.6)
		$C_3H_7^+$ (100)	$C_3H_5^+$ (33)	$C_3H_3^+$ [0.35] (18)	C_3H^+ [0.55] (1.7)
C_2-Series	$C_3H_{10}^+$ or $(C_4H_{10})^{2+}$		$C_2H_6^+$ (1.0)	$C_2H_4^+$ [0.15] (35)	$C_2H_2^+$ [0.7] (9.1)
			$C_2H_5^+$ (45)	$C_2H_3^+$ [0.25] (46)	C_2H^+ [2.0] (0.9)

[ ]: Kinetic energy ( ): Relative abundance

energy for the ions rapidly increases.

Discussion

Fragment ions from *n*-butane produced by electron impact are divided into C_2, C_3 and C_4 series depending on the number of carbon atoms in the ions. The $C_4H_{10}^+$ ion is the parent ion, but its relative intensity is small compared with that of the $C_3H_7^+$ ion, which is the most abundant. This result indicates that the $C_4H_{10}^+$ ion is so unstable that the ion decomposes further into a number of fragment ions as soon as it is formed.

The initial energies obtained in the present experiment for various fragment ions are summarized in Table III. The fragment ions in the second and third columns of the table have only thermal energy. On the other hand, the ions in the fourth and fifth columns have initial kinetic energies larger than the thermal energy. With regard to the relative abundances, in the C_3 series, the intensities of the $C_3H_7^+$ and $C_3H_5^+$ ions are larger than those of the $C_3H_6^+$ and $C_3H_4^+$ ions, and in the C_4 series the intensities of the $C_4H_9^+$ and $C_4H_7^+$ ions are larger than those of the $C_4H_8^+$ and $C_4H_6^+$ ions. In general it is found that the relative intensities of ions with odd numbers of hydrogen atoms are larger than those with even numbers of such atoms. Therefore, it is reasonable to conclude that the fragment ions in a series are formed by splitting hydrogen molecules successively.[6]

However, in the C_2 series the above relation does not hold, because the relative intensity of the $C_2H_4^+$ ions is quite large; it is, in fact, of nearly the same order as that of the $C_2H_5^+$ and $C_2H_3^+$ ions. Moreover, with regard to the initial energies, the $C_2H_5^+$ ion has only thermal energy, while the $C_2H_4^+$ and $C_2H_3^+$ ions have certain amounts of initial energy. Therefore, it is not always true that the less abundant ions have higher initial energies, as Taubert[2] proposed.

It was pointed out by Berry[5] and Mohler et al.[3] that the CH_3^+ ion from *n*-butane produced by electron impact possessed an initial energy of several electron volts. Mohler et al. proposed the mechanism leading to the high initial energy of the CH_3^+ ion. The ion with a high kinetic energy comes from the dissociation of the doubly-charged molecule-ion, because the Coulomb repulsion of these two charges can dissociate the molecule and most of this Coulomb energy will appear as kinetic energy of the fragment ions. The maximum kinetic energy of the CH_3^+ ion was measured as 1.6 eV. by Berry and as 2.2 eV. by Mohler et al. If the high energy of the CH_3^+ ion is produced by the dissociation of doubly charged molecules, the remaining fragment ions will also possess a high kinetic energy.

On the basis of the above assumption, the process for producing the kinetic energies for the $C_3H_3^+$ and $C_3H_4^+$ ions may be explained as follows:

$$(C_4H_{10})^{2+} \rightarrow CH_3^+ + 2H_2 + C_3H_3^+$$
$$\rightarrow CH_4^+ + H_2 + C_3H_4^+$$

When the kinetic energy for the CH_3^+ ion is selected as 1.6 eV., the kinetic energy for the $C_3H_3^+$ ion formed by the above dissociation

6) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York (1957), p. 88.

process is calculated as 0.61 eV. On the other hand, the kinetic energy for the $C_3H_4^+$ ion is estimated as 0.64 eV., provided that the kinetic energy of the CH_4^+ ion is of the same magnitude as that of the CH_3^+ ion.

In the case of the C_2 series, the processes for producing the kinetic energies for the $C_2H_3^+$ and $C_2H_4^+$ ions may also be explained by the same assumption:

$$(C_4H_{10})^{+2} \rightarrow C_2H_3^+ + 2H_2 + C_2H_3^+$$
$$\rightarrow C_2H_4^+ + H_2 + C_2H_4^+$$

The kinetic energies for the $C_2H_3^+$ and $C_2H_4^+$ ions are measured as about 0.25 eV. and 0.15 eV. respectively.

In the present experiment, however, the initial energy distribution for ions could not be obtained, although the average energy for mixtures of thermal and high energy ions was obtained. The discrimination effect is larger for high energy ions than for low energy ions. Therefore, the observed values of 0.35 eV. for the $C_3H_3^+$ ion and of 0.31 eV. for the $C_3H_4^+$ ion may turn out to be somewhat smaller than the actual kinetic energy. Using a deflection method, Berry obtained the maximum value of the initial energy for the $C_3H_3^+$ ion as 1.2 eV.[5]; its average value is calculated to be about 0.3 eV. Therefore, the present results are in good agreement with his result. Moreover, these results indicate that a considerable portion of the $C_3H_3^+$ ions is produced by the dissociation of doubly-charged molecule-ions.

Summary

The discrimination effect on the fragment ions from *n*-butane produced by electron impact has been investigated using a conventional mass spectrometer. From the effect of discrimination, it has been concluded that the relative intensity of fragment ions with initial energies larger than their thermal energy is markedly dependent on the conditions of measurement. On the basis of the information gained about the effect of discrimination on ions, the amount of the kinetic energy for fragment ions from *n*-butane has been estimated. From the results of our experiments, it is reasonable to consider that considerable portions of $C_3H_3^+$, $C_3H_4^+$, $C_2H_4^+$ and $C_2H_3^+$ ions are produced with high kinetic energies from the dissociation of the doubly-charged molecule-ion, according as the high kinetic enegy of the CH_3^+ ion is produced.

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