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Metastable Ions Formed by Electron Impact in Hydrocarbon Gases

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It has been recently reported that the non-integral masses appearing in the mass spectra of various hydrocarbons may be explained by the spontaneous dissociation of some of the ions into fragments of lighter mass after they have been accelerated and emerge from the ion gun. By means of an energy filter, an energy analysis of the non-integral masses in *n*-butane, butadiene, and ethane has been made and the values obtained agree with those predicted on the basis that they arise from metastable ions. Variation of the pressure and electrode potentials confirms that the dissociation is spontaneous. The formation of metastable ions appears to be a general occurrence in the ionization and dissociation of hydrocarbons and is shown here to occur in ethane, propane, 1,3-butadiene, butene-1, *cis*-butene-2, isobutylene, normal butane, iso-butane, pentene-2, normal pentane, iso-pentane, and methyl-cyclo-pentane.

INTRODUCTION

A PRELIMINARY report[1] has been made on evidence obtained with the mass spectrometer indicating that some kinds of primary ions formed by electron impact in several hydrocarbon gases are metastable. They are apparently stable enough to hold together for a time of the order of 10^{-6} sec. during which they are drawn out of the ion source region and accelerated, but dissociate before completing their trip through the analyzing magnetic field. The observed facts are in accord with the interpretation that the metastable ions simply fall apart so that the fragments have a small energy of relative motion. This "small" energy may amount to some volts but is small compared to the 500 to 1000 electron volts of energy which the ions are given for analysis in the mass spectrometer.

This paper reports further data obtained by means of the mass spectrometer with energy analysis of the ions which fully confirms and considerably extends the results given earlier. Broadly the phenomenon here discussed bears some resemblance to pre-dissociation, first discovered by Henri[2] in optical band spectra, but it should be observed that when pre-dissociation results in broadening of the lines in the band spectrum, the mean life of the molecule for pre-dissociation must be short compared to the usual radiative life of 10^{-8} sec. Hence optical pre-dissociation studies deal with cases in which the mean life is much smaller than in the cases described in this paper. The range of values of the mean life which may be studied in a particular mass spectrometer is of course dependent on potentials of the electrodes and the dimensions of the tube in the ion source and ion accelerating regions.

These studies grew out of a desire to understand the origin of several broad peaks, some of which occur at positions corresponding to non-integral masses, which were observed in the mass spectrometer. In the first experiments, reported

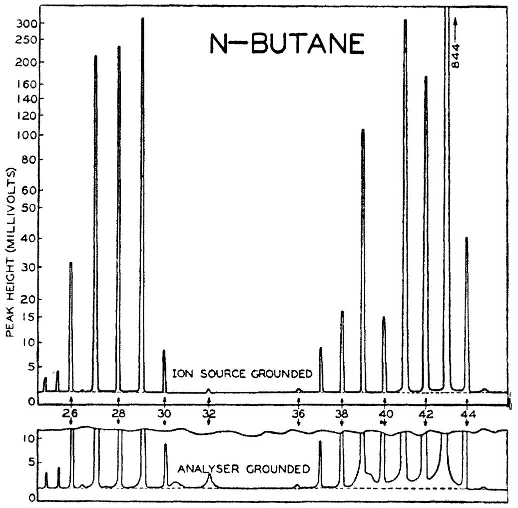

FIG. 1. Showing effect on observed mass spectrum of *n*-butane of operating with ion source grounded instead of with analyzer grounded.

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[1] J. A. Hipple and E. U. Condon, Phys. Rev. **68**, 54 (1945).

[2] V. Henri, Comptes rendus **177**, 1037 (1923).

earlier, an experiment was performed on the effect on the mass spectrum of operating with the ion source and the collector both at ground while the main accelerating potential was applied to the analyzer section of the tube. Since the ions are formed in a region that is one or two volts above ground, only those ions reach the collector which have essentially as much energy on leaving the analyzer as they acquired on entering it.

Figure 1 shows the mass spectrum of normal butane taken in the two ways, the ion source grounded curve being superposed above the curve taken in the more familiar way in which the analyzer is grounded. Comparing the two curves, the following differences are at once evident:

(a) The broad background from mass 38 to 44 is removed.
(b) The hump on the side of the mass 39 peak is removed.
(c) The mass 32 peak is considerably reduced and sharpened indicating that in the usual spectrum it is really compounded of a broad peak, which is removed when the ion source is grounded, together with a small sharp peak which is unaffected by the change. In later experiments with a tube that was vacuum-tight this mass 32 peak (O_2) was entirely eliminated when the ion source was grounded.
(d) The broad peak at mass 30.5 is removed.

The material which is not collected with the ion source grounded must consist of ions which lose energy in some way in going through the tube. Of course, it is possible that some energy losses occur by impact with the residual gas in the tube but it was thought that this could only account for a general raising of the background around regions of intense ionization.

The hypothesis was considered that these effects might be due to unstable ions which hold together long enough to be accelerated through all or most of the accelerating potential drop but which dissociate, perhaps with a small release of internal energy, somewhere in the tube before they have entered the analyzer, or at least before they have gone through the field. Let the potential be reckoned as zero at the place where the ion is first formed, and suppose the ion has mass m_0 which it retains until it has moved to a place where the potential is V_1. At this place suppose it dissociates with negligible release of internal energy into an ion of mass m and a neutral fragment of mass (m_0-m). The new ion will continue on with little immediate change of velocity, but will in turn be accelerated by the electric field in going from the region of potential V_1 to that of the full voltage V of the accelerating field.

Its kinetic energy just before dissociation is eV_1 but after dissociation the ion fragment has only the kinetic energy, $(m/m_0)eV_1$, the other part being carried off by the neutral fragment. After traversing the whole accelerating field the kinetic energy of the ion fragment is

$$T=(m/m_0)eV_1+e(V-V_1).$$

Now the radius in which it moves in the analyzer is determined by the usual formula,

$$R=\frac{c}{eH}(2mT)^{\frac{1}{2}}.$$

Therefore the ion fragment will appear at the collector for the same combination of V and H as does a normal ion of mass m^* where

$$m^*=\frac{m^2}{m_0}\frac{V_1}{V}+m\left(1-\frac{V_1}{V}\right).$$

If dissociation occurs before the ion is accelerated, then its effective mass is m. However, if dissociation occurs after full acceleration but before entering the analyzer then $(V_1=V)$

$$m^*=m^2/m_0.$$

It has been found that the observations correlate with this expression. The peaks have width which is partly due to the fact that some dissociations occur elsewhere and partly to the effect of the neglected release of internal energy. An additional reason for the diffuseness of the metastable peaks is the focusing property of the instrument. The instrument has been designed to focus ions that maintain a constant m/e in passing through the analyzer. Thus it is probable that the observed diffuse peaks are caused by transitions occurring very close to the exit slit of the ion gun and before the ion has traversed very far into the analyzer. This is confirmed by the spectrum of *n*-butane obtained by Washburn, Wiley, and Rock[3] on an instrument employing a deflection in the magnetic field of 180°. Although there is no field-free

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[3] H. W. Washburn, H. F. Wiley, and S. M. Rock, Ind. Eng. Chem. Anal. Ed. **15**, 541 (1943).

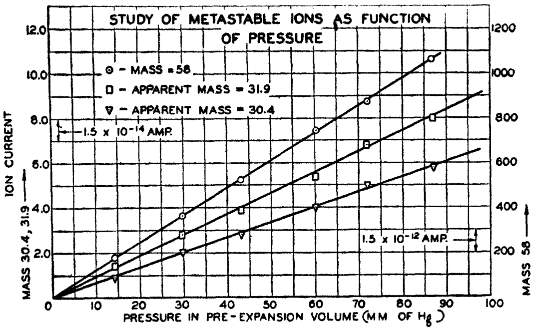

FIG. 2. Variation of ion current with pressure. The linearity of the curves shows that the peaks at 30.4 and 31.9 are not induced by ion-molecule collisions.

region between the ion source and the analyzer, the diffuse peaks at mass 32 and 39.2 are quite prominent, and there is some indication that those at 25.2 and 30.4 are also present. The ions dissociating elsewhere in the tube will contribute to the background with no pronounced peaks appearing.

Of course, an observation of m^* alone does not suffice to determine both m_0 and m and hence to fix the particular dissociation process responsible for a peak. This was done by arranging to measure the kinetic energy of the ions after they have gone through the analyzer by adjusting the retarding field between the analyzer region and the ion collector, as explained in a later section.

Peaks arising from reactions occurring during the transit of the ions through the mass spectrometer have previously been reported. Smyth reported two peaks in hydrogen[4] having an apparent mass less than one (throughout this paper singly charged ions are being discussed unless explicitly stated). Smyth[5] also reported a peak at mass 7 in N_2 which occurred at low electron voltages. The size of these peaks relative to the parent ion was very sensitive to the pressure in the instrument and they were attributed to collisions with other molecules during the transit through the instrument. Discussing the case of N_2, Smyth[6] concludes "that there are N_2^+ ions, probably those formed at the first ionization potential which dissociate on collision after acquiring large kinetic energies." Hogness and Lunn[7] reported a similar effect in NO—". . . some of the NO^+ ions are unstable toward collision with gas molecules, and on collision dissociate into either N^+ or O^+."

Dissociation of molecules during transit has been observed in several mass spectrographs by the appearance of diffuse traces at non-integral mass numbers on the photographic plate. These are greatly enhanced by increasing the pressure in the field-free region between the electrostatic energy filter and the magnetic analyzer. A very careful study of these "bands" has been made by Mattauch and Lichtblau,[8] who have described 28 different processes of dissociation of this type induced by collision. All of these processes differ from those reported in the present work which it is believed are not induced by collision.

With the improved techniques now available, mass spectrometers are now operated at a pressure 100 to 1000 times lower than in the early experiments and the possibility of dissociation induced by collision is remote. For instance, Smyth found a peak at mass 7 with 30-volt electrons amounting to 3 percent of mass 28 in N_2 in one experiment.[5] Hagstrum and Tate[9] reported the same peak having an appearance potential of 64±2 volts and an abundance relative to N_2^+ of 0.006 percent. This relative abundance was confirmed approximately in the course of the present investigation using 100-volt electrons and no ionization was evident at 50 volts. This work was done with an automatic recorder without pushing the sensitivity beyond 1 part in 20,000, but the ionization below 50 volts at mass 7 must be less than the above figure in our equipment. The conclusion is that mass 7 ($m/e=7$) in N_2 must be attributed to N^{++} in present instruments at the usual operating pressures and the large peak at this mass observed in the early experiments arises from dissociation induced by ion-molecule collisions.

In order to show that the ions at non-integral masses occurring in the spectra of hydrocarbons are caused by spontaneous dissociation and are

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[4] H. D. Smyth, Phys. Rev. **25**, 452 (1925).

[5] H. D. Smyth, Proc. Roy. Soc. **A104**, 121 (1923).

[6] H. D. Smyth, Rev. Mod. Phys. **3**, 373 (1931).

[7] T. R. Hogness and E. G. Lunn, Phys. Rev. **30**, 26 (1927).

[8] J. Mattauch and H. Lichtblau, Physik. Zeits. **40**, 16 (1939); see also F. W. Aston, *Mass Spectra and Isotopes* (Edward Arnold and Company, London, 1942), page 61.

[9] H. D. Hagstrum and J. T. Tate, Phys. Rev. **59**, 354 (1941).

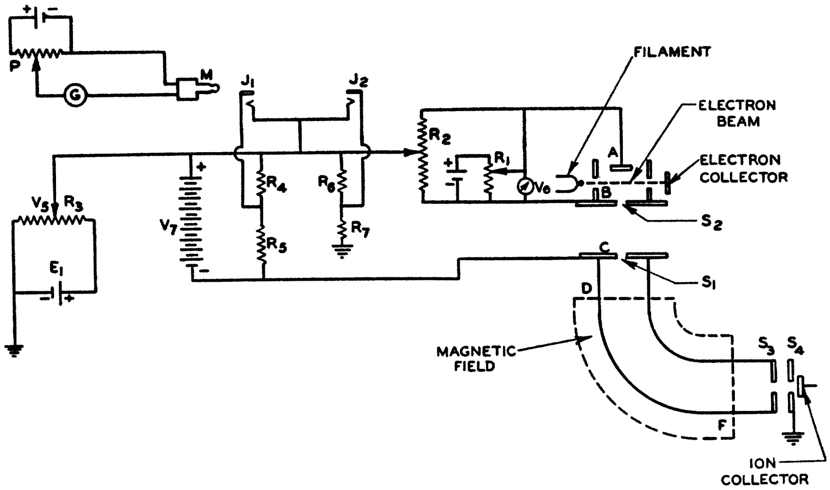

FIG. 3. Arrangement for studying energies of ion fragments from metastable ions.

not to be attributed to ion-molecule collisions, the spectrum of *n*-butane was studied as the pressure in the tube was varied. This tube did not have differential pumping[6] and the analyzer section was not pumped separately; therefore, the pressure in the analyzer varied in the same manner as that in the ion source and any peaks conditioned by collisions in the analyzer should not vary linearly with the pressure. The pressure in back of the leak bleeding the gas into the mass spectrometer tube was used as a measure of the pressure in the tube—the leak had previously been found to have a linear flow characteristic in the range used. The pressure in the large gas reservoir used for stabilizing the flow through the leak was determined by measuring the pressure in a smaller pre-expansion volume with a manometer before the sample was expanded into the larger reservoir. In this way the pressure could be measured accurately. In Fig. 2 the pressure in the pre-expansion reservoir is taken as the abscissa since it is a linear function of the pressure in the tube. This is evident by the linearity of the ion current corresponding to the parent ion $C_4H_{10}^+$ in normal butane. The other curves show that the peaks arising from the metastable ions

$$C_4H_{10}^+ \rightarrow C_3H_7^+ + CH_3, \quad m^* = 31.9,$$
$$C_4H_{10}^+ \rightarrow C_3H_6^+ + CH_4, \quad m^* = 30.4,$$

also vary linearly with the pressure and are, therefore, to be attributed to a primary process. Other strong evidence for this is the effect of the ion-draw-out voltage (V_6 in Fig. 3) on the intensity of the metastable ions relative to the rest of the spectrum which is described in detail later. When less time is spent in the ion source, the abundance of the metastable ions rises rapidly as compared with the rest of the spectrum.

APPARATUS AND EXPERIMENTAL PROCEDURE

The mass spectrometer employed in these experiments was of the type with a sectored magnetic field in which the ions were deflected through 90 degrees on a five-inch radius. An ion accelerating voltage variable from 300–1300 volts was available. The electron energies could be varied by changing the accelerating voltage on the electrons from 0–100 volts.

The ions were measured with a pen recording system whose sensitivity enabled signals of 0.2 millivolts to be recorded. This represented an ion current of about 5×10^{-15} ampere. This recorder, along with certain features of the mass spectrometer has been previously described.[10]

In order to obtain the retarding potential which formed the energy filter, the electrical circuit was arranged as shown in Fig. 3.

An electron beam creates the ions in the region *AB*. By means of a small potential V_6 these ions are drawn through slit S_2 into the accelerating field *BC*. The ions emerging from slit S_1 pass through a field-free region *CD* into the magnetic

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[10] J. A. Hipple, D. J. Grove, and W. M. Hickam, Rev. Sci. Inst. **16**, 69 (1945).

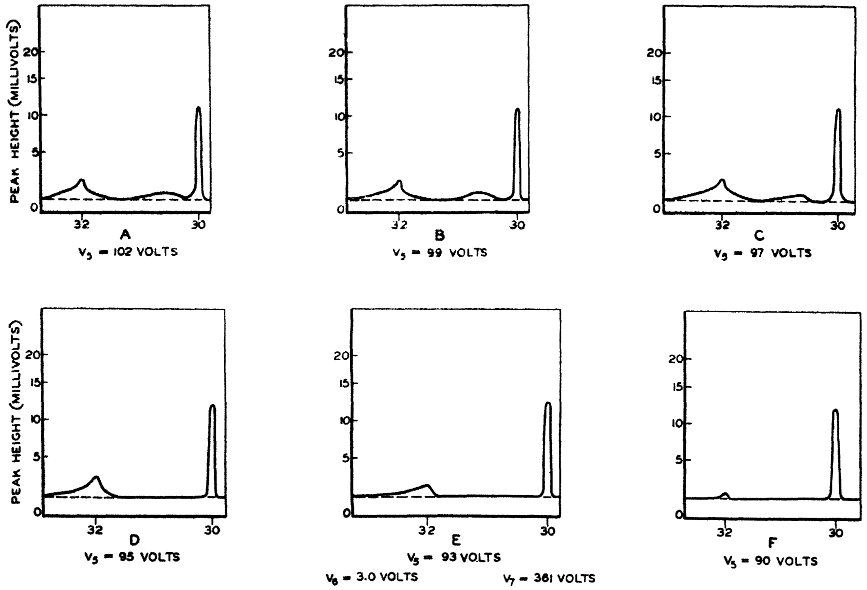


FIG. 4. Effect of energy filter on mass spectrum of *n*-butane in the mass 30 region.

field *DF*. After leaving the magnetic field, they pass through a slit S_3 into the retarding field which is applied between S_3 and S_4. Those ions which are able to penetrate this retarding field are caught by the ion collector and measured with the recording system.

An ion accelerating voltage V_7 was applied between slits S_1 and S_2 in which S_1 was negative with respect to S_2. The ion source was connected to ground through a variable voltage supply V_5. S_4 was maintained at ground potential. Since the potential of the ion source and analyzer could be varied with respect to ground potential by means of R_3, the retarding potential between S_3 and S_4 could be adjusted so as to allow the metastable ions to be completely filtered. A measure of the voltage V_5 which would just enable these ions to get through to the ion collector would then be a measure of the energy lost in the dissociation. The potentials V_5 and V_7 were obtained with banks of batteries.

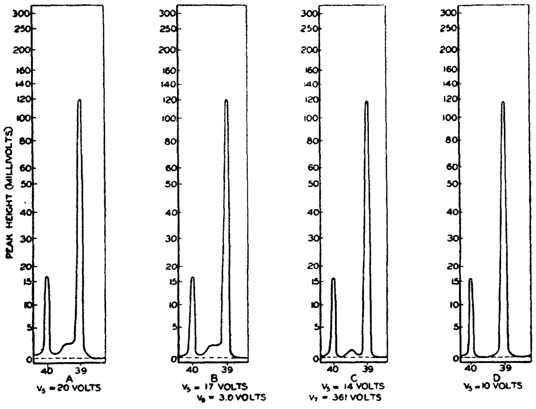


FIG. 5. Effect of energy filter on mass spectrum of *n*-butane in the mass 39 region.

Since the ions are drawn out of *AB* with about 3 volts, it was necessary to take this voltage into consideration as the ions would then not be formed at ground potential. This was done by means of the resistor R_2. This resistor was placed across plates *A* and *B* and in parallel with the source of potential used to draw out the ions from that region. R_3 was adjusted so that V_5 was zero. R_2 was then adjusted until the primary ions were just beginning to be cut off. Thus the voltage V_5 which just cut off the ions in question was then a good measure of the energy lost.

The voltages V_5 and V_7 were measured with a potentiometer *P*. This potentiometer measured the voltage drop across the bleeder resistors R_4 and R_6. The potential drop across the resistor R_4 gave a value of the voltage V_7 while that across R_6 gave the voltage V_5. R_4 and R_6 were 1500 ohms each while R_5 and R_7 were 3×10^6 ohms each. The resistors in each bleeder were matched to better than 0.1 percent. The potentiometer

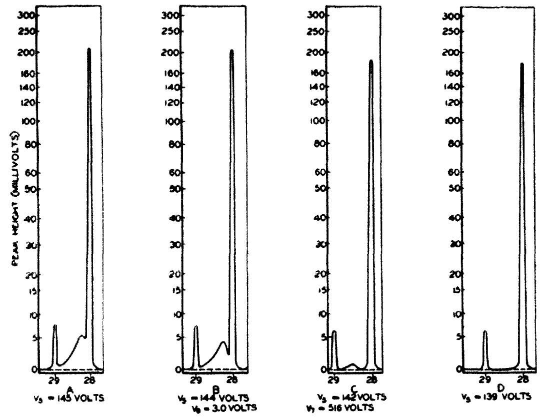


FIG. 6. Effect of energy filter on mass spectrum of 1,3-butadiene in the mass 28 region.

circuit measured each of the voltages by means of the two jacks J_1 and J_2, the accuracy being about 0.2 volt.

With this arrangement the spectra of *n*-butane, 1,3-butadiene and ethane were studied to determine the transitions giving rise to the metastable ions. The spectra were scanned by varying the magnetic field.

DISCUSSION OF SOME HYDROCARBON SPECTRA

1. Normal Butane

In addition to the normal sharply defined peaks in the mass spectrum, there are broad peaks at effective masses about 32 and 30.5 and a large hump on the side of the 39 peak which appears to be superposed on the normal 39 peak. There is also a slight hump at 25.2.

The peak at 32 is associated with the transition

$$C_4H_{10}^+\ (58) \rightarrow C_3H_7^+\ (43) + CH_3\ (15),$$

for which $m^* = (43)^2/58 = 31.9$. This assumption has in its favor the fact that mass 43 is a very prominent peak in the normal spectrum. If the assumption is correct, then the ions responsible have only (43/58) of the kinetic energy corresponding to the total applied potential of 361 volts. This means that in the energy filter this peak should disappear if the ions are caused to go against a retarding field of more than

$$(43/58) \times 361 = 268 \text{ volts}.$$

They, therefore, will have lost 93 electron volts of kinetic energy, which actually went to the unobserved neutral methyl radical.

Figure 4 shows the effect of the energy filter on the mass 32 region as V_5, the potential of the ion source with respect to ground is varied. The diffuse peak is present for $V_5 = 95$ volts but begins to go out as V_5 is further diminished and is quite gone at $V_5 = 90$ volts. In curve F of Fig. 4 the remaining small sharp peak at mass 32 is due to O_2^+ from a small trace of that gas in the tube.

Similarly the diffuse peak at $m^* = 30.5$ also shown in Fig. 4 may be associated with

$$C_4H_{10}^+\ (58) \rightarrow C_3H_6^+\ (42) + CH_4\ (16),$$

for which $m^* = (42)^2/58 = 30.4$. In this transition 16/58 of the original energy is lost to the ion fragment on dissociation. This is 99.5 volts and in Fig. 4 it is clearly seen that the 30.5 peak starts to disappear at 99 volts and is cleaned out at 95 volts—a higher value of V_5 than the diffuse 32 peak, in accord with this interpretation.

The hump at $m^* = 39$ is associated with the transition

$$C_3H_7^+\ (43) \rightarrow C_3H_5^+\ (41) + H_2\ (2)$$

giving a calculated $m^* = 39.2$. The calculated energy loss of the ion fragment is 2/43 of 361 or 16.3 volts. Figure 5 shows the effect of the energy filter on this region of the mass spectrum. Again the expected behavior is obtained, a considerable portion of the hump being removed in going from 17 to 14 volts.

The weak ion current appearing at 25^+ may be explained by the transition

$$C_2H_5^+\ (29) \rightarrow C_2H_3^+\ (27) + H_2\ (2)$$

from which $m^* = (27)^2/29 = 25.1$. It has been found that this diffuse peak may be erased from the spectrum when $V_5 = 24.0$ which agrees well with the deduced value of $(2/29) \times 361 = 24.8$ volts.

It should be emphasized that these experiments do not reveal the nature of the neutral fragment that is formed. Thus, in the preceding equations what we write as CH_4 may possibly represent production of this material in dissociated form such as $CH_3 + H$ or $CH_2 + H_2$, etc.

2. Propane

It is interesting that the two transitions observed with propane are the same as two of those found in *n*-butane. Diffuse peaks were observed at 39.2 and 25.2 corresponding to the transitions

$C_3H_7^+ (43) \rightarrow C_3H_5^+ (41) + H_2 (2), \quad m^* = 39.2,$

and

$C_2H_5^+ (29) \rightarrow C_2H_7^+ (27) + H_2 (2), \quad m^* = 25.2.$

These transitions were not studied with the energy filter.

3. Ethane

Diffuse peaks are observed at 24^+, 25^+, and 26^+. These may be explained by the transitions

$$C_2H_6^+ (30) \rightarrow C_2H_4^+ (28) + H_2 (2), \quad m^* = 26.2, \quad V_L = 34.4,$$

$$C_2H_5^+ (29) \rightarrow C_2H_3^+ (27) + H_2 (2), \quad m^* = 25.2, \quad V_L = 35.4,$$

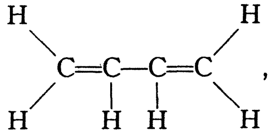
$$C_2H_4^+ (28) \rightarrow C_2H_2^+ (26) + H_2 (2), \quad m^* = 24.2, \quad V_L = 36.8,$$

where V_L is the energy lost by the ion to the neutral fragment.

In this study an ion accelerating voltage of 516 volts was used and the measured value of voltages at which the peaks started to disappear were 35.0, 36.0, and 37.0 volts, respectively—in nice agreement with the values of V_L given above.

4. 1,3-Butadiene

In the mass spectrum of 1,3-butadiene,



there is a large diffuse peak at about mass 28.2 and a smaller one at about mass 13.8. The parent mass is 54 and the large diffuse peak at 28.2 can be associated with the transition $54^+ \rightarrow 39^+ + 15$ for which the calculated m^* is $(39)^2/54 = 28.2$ although not immediately evident from the structure. However, 39^+ and 54^+ are the largest peaks in 1,3-butadiene.

Figure 6 shows the effect of the energy filter on the mass 28 region which shows that the peak begins to disappear for $V_5 = 144$ volts and is removed when $V_5 = 139$ volts. The expected loss is $(15/54) \times 516 = 143$ volts.

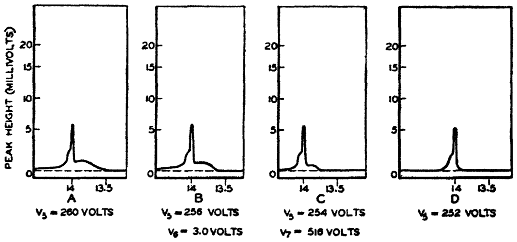


FIG. 7. Effect of energy filter on mass spectrum of 1,3-butadiene in the mass 14 region.

The diffuse peak at mass 13.5 is shown in Fig. 7 for various values of V_5. This peak is associated with a simple splitting in half of the parent ion, $54^+ \rightarrow 27^+ + 27$, which leads to a calculated m^* of 13.5. On this view the ion fragment has only one-half of the original energy and so can be stopped by a retarding potential of 258 volts in good agreement with the experimental value ($V_5 = 256^+$ volts) shown in the figure. The remaining asymmetry on mass 14 is caused by the production of CH_2 with kinetic energy.

These interpretations indicate that there are two different ways in which the parent ion can break up, the dropping off of a methyl group being considerably more probable than the process of splitting in half.

5. Iso-butane

Iso-butane shows the same broad peaks as normal butane except for some differences in relative intensity. The peaks at 31.9 and 30.5 are much weaker than those from *n*-butane, and the "hump" at 39.2 is about twice as strong as in the case of *n*-butane.

These differences correlate with the fact that 58^+, which is interpreted as giving rise to 31.9 and 30.5, is relatively stronger in *n*-butane than isobutane, whereas 43^+, which is interpreted as the source of the 39.2 hump, is relatively stronger in isobutane than *n*-butane.

6. The butenes

The spectra of butene-1, *cis* butene-2, and isobutylene were studied and no important differences were noted with respect to peaks due to metastable ions.

A broad diffuse peak appears at mass 30 similar in appearance to the 31.9 peak in the butanes.

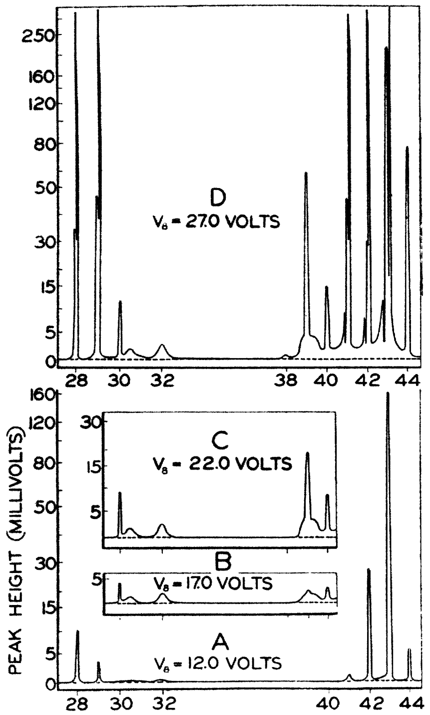


FIG. 8. Mass spectrum of *n*-butane in the mass 28–44 region showing the effect of variation of the electron voltage. The discontinuities indicate a change to $\frac{1}{10}$ sensitivity to record the tops of the large peaks.

This is interpreted as being due to decomposition of the parent ion by the dropping of a methyl group,

$$56^+ \rightarrow 41^+ + 15,$$

the calculated m^* being $(41)^2/56 = 30.0$.

The "hump" now appears at mass 37 instead of mass 39 and may be associated with the transition,

$$41^+ \rightarrow 39^+ + 2.$$

7. Normal pentane

With normal pentane there is a very diffuse peak at mass 24.5. This peak can be associated with the transition

$$72^+ \rightarrow 42^+ + 30, \quad m^* = 24.5.$$

TABLE I. Peak heights in normal butane spectrum.

Mass	$V_6 = 1.0$	2.0	3.0	4.0	5.0
58	246.0	425.6	437.9	431.3	430.2
57	41.08	68.67	71.22	70.25	69.55
43	1243	2016	2129	2119	2129
42	174.6	278.2	291.6	288.2	287.2
41	349.0	541.1	563.4	553.5	553.5
40	15.38	24.16	25.66	25.93	26.00
39	114.0	178.9	189.5	187.6	189.7
39.2	1.28	2.84	3.36	3.99	4.26
31.9	0.88	1.94	2.39	2.61	2.89
30.5	0.27	1.03	1.37	1.49	1.64

There is also a very broad peak between 29 and 30 which can be regarded as due to

$$57^+ \rightarrow 41^+ + 16, \quad m^* = 29.5.$$

A "hump" is also present on the 39 peak as in the butanes.

This spectrum has not been studied with the energy filter to give detailed confirmation of the suggested transitions. It might be expected that the parent 72^+ ion could drop a methyl group. This would lead to a predicted diffuse peak at $m^* = 45.3$ but there is no indication of such a process in our observations.

8. Iso-pentane

The same diffuse peaks are observed here as with *n*-pentane, presumably arising from the same transitions. In iso-pentane the 57 peak is about twice that for *n*-pentane and correspondingly the diffuse 29.5 peak is about twice as intense as in *n*-pentane. On the other hand the situation is reversed with regard to the parent ion 72^+ and its associated diffuse peak at 24.5 where the *n*-pentane intensity is about four times that in iso-pentane.

9. Pentene-2

Pentene-2 shows diffuse peaks at masses 24, 15.3, 27.8, and 51. These peaks can be interpreted by the following transitions, with the corresponding calculated m^*,

$$70^+ \rightarrow 41^+ + 29, \quad m^* = 24.0,$$

$$55^+ \rightarrow 39^+ + 16, \quad m^* = 27.7,$$

$$55^+ \rightarrow 29^+ + 26, \quad m^* = 15.3,$$

$$55^+ \rightarrow 53^+ + 2, \quad m^* = 51.1.$$

TABLE II. Relative peak heights at various voltages.

Ion-draw-out voltage	Mass 58	57	43	42	41	40	39	39.2	31.9	30.5
1.0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2.0	1.73	1.67	1.62	1.59	1.55	1.57	1.57	2.22	2.21	3.82
3.0	1.78	1.73	1.71	1.67	1.61	1.67	1.66	2.62	2.72	5.26
4.0	1.75	1.71	1.70	1.65	1.59	1.69	1.65	3.11	2.97	5.52
5.0	1.75	1.70	1.71	1.65	1.59	1.69	1.66	3.33	3.29	6.07

10. Methyl Cyclo-Pentane

Diffuse peaks are observed in methyl cyclopentane at 56.8 and 37.4. The following transitions could account for these:

$$C_6H_{12}^+ (84) \rightarrow C_5H_7^+ (69) + CH_3 (15), \quad m^* = 56.7,$$

$$C_6H_{12}^+ (84) \rightarrow C_4H_8^+ (56) + C_2H_4 (28), \quad m^* = 37.4.$$

EFFECT OF ION-DRAW-OUT POTENTIALS

Since the ions spend a considerable portion of their lifetime in the ion source, it should be possible to change the magnitude of those peaks originating from the metastable ions by changing the time spent in this region. This can be accomplished by changing the potential with which the ions are drawn from the ion source into the main accelerating field. This potential is represented by V_6 in Fig. 3. With an increase in this voltage the ions are drawn out faster and hence they spend a shorter time in this region. Thus more ions have a chance to dissociate in the regions where the effect can be detected.

A complication arises, however, in that an increase in V_6 not only increases these metastable peaks, but also affects all of the peaks in general because of the change in the focusing conditions. In order to obtain some idea as to the effect of V_6 on the dissociation phenomenon, it is necessary to look at the peak ratios.

Table I presents the peak heights in arbitrary units of some masses in the normal butane spectrum taken at several values of V_6.

Table II is derived from Table I. The data are normalized to show more clearly the relative change in the peak heights as V_6 is increased. From this table it is noted that from 2.0 through 5.0 volts, peaks 58, 57, 43, 42, 41, 40, and 39 remained fairly constant, and that they all changed by approximately the same percentage between 1.0 and 2.0 volts. However, those peaks which are attributed to the metastable ions changed by a greater percentage between 1.0 and 2.0 volts, and they continued to increase as V_6 was increased. In fact it is noted that the 30.5 peak is six times as large at 5.0 volts as at 1.0 volt, while the 31.9 peak is over three times as large.

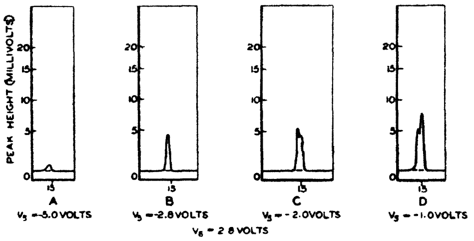


FIG. 9. Study of mass 15 in *n*-butane with the energy filter to show that the doublet is caused by the formation of CH_3^+ with kinetic energy and not by a metastable ion.

EFFECT OF ELECTRON ENERGY

A study of the metastable ions in *n*-butane[11] as a function of the electron voltage V_8 is shown in Fig. 8. The spectrum in the 28–44 mass region is shown with $V_8 = 12$, 17, 22, and 27 volts. With 12-volt electrons the metastable ions at 30.5 and 31.9 are just appearing whereas the "hump" at 39.2 has not appeared. At 17 volts the 39.2 peak has appeared, although the true mass 39 peak is barely evident. Since the metastable peaks are weak, it is difficult to measure their appearance potentials accurately. However, it is interesting that mass 43 and the apparent mass 31.9 appear at the same voltage within the accuracy of the measurements (about 0.5 volts); in the former case the reaction

$$C_4H_{10}^+ \rightarrow C_3H_7^+ + CH_3$$

occurs before the acceleration in the ion gun (region *AB* in Fig. 3), and in the latter case after this acceleration (after *BC* in Fig. 3). The appearance potential of 39.2 is about 2.5 volts higher than that for 31.9.

IONS FORMED WITH KINETIC ENERGY

Since the mass spectrometer of the type used in this work will not focus ions of the same *m/e* which differ in energy, those ion fragments which are formed from the parent molecule with appreciable kinetic energy will give rise to asymmetrical peaks. A measurement of the kinetic energy released in the ionization and dissociation of some less complicated molecules has provided a greater insight into the dissociation processes involved in these molecules.[12,9] Part of the

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[11] D. P. Stevenson and J. A. Hipple, J. Am. Chem. Soc. 64, 1588 (1942).

[12] W. Bleakney, Phys. Rev. 35, 1180 (1930).

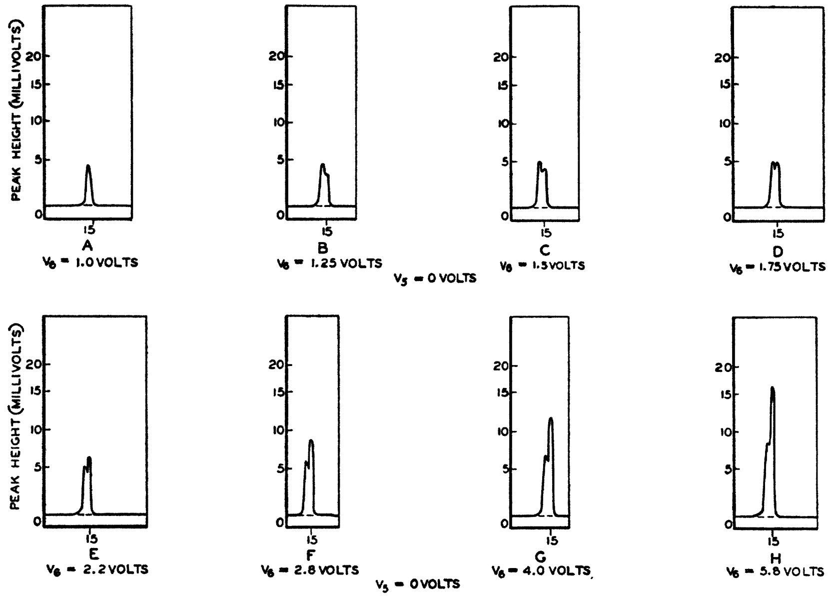

FIG. 10. Showing the difference in the effect of the ion-draw-out voltage (V_6) on the CH_3^+ in *n*-butane formed with considerable kinetic energy as compared with the fragment formed with little or no kinetic energy.

asymmetry in Fig. 7 was ascribed to the formation of CH_2^+ with kinetic energy in butadiene. Similarly, in *n*-butane there appears to be a weak kinetic energy peak at mass 14 and a pronounced one at mass 15. These ions still reached the ion collector when electrode *A* (Fig. 3) was grounded, eliminating all the other peaks in the spectrum between mass 15 and mass 60. Under this condition only those ions formed initially with kinetic energy can reach the ion collector. Although this is not a metastable effect, the investigation of mass 15 is described in this paper as there is a non-integral mass involved here which might be mistakenly interpreted as arising from a metastable ion unless proven otherwise. If the ion formed with kinetic energy is designated $^*CH_3^+$, it is seen in Fig. 9 that this ion is relatively unaffected when V_5 is varied from -1.0 volts to -2.8 volts whereas CH_3^+ disappears at -2.8 volts. In fact, $^*CH_3^+$ is still present when $V_5=-5.0$ volts. Figure 10 shows that $^*CH_3^+$ is less affected by V_6 in the range studied than CH_3^+ which is reasonable on geometrical considerations. Similar studies have shown the presence of ions formed with considerable kinetic energy in the C_2 and C_3 regions.