

Ionization and Dissociation of *cis*- and *trans*-2-Butene by Electron Impact*

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A study has been made of the appearance potentials and relative abundance of a number of ions from the mass spectra of *cis*- and *trans*-2-butene. The appearance potentials were found to be in generally good agreement with spectroscopic data. The mass spectra of the 2-butenes were compared with those of 1-butene and isobutene. The $C_2H_5^+$ ion was found to be the only ion showing a significant difference between the 2-butene isomers. This difference approached a maximum with ionizing electrons of 40-volt energy and remained constant up to energies of 100 volts.

I. Introduction

The ever increasing interest in the use of the mass spectrometer as an analytical instrument, especially for hydrocarbon analyses, has made it desirable to accumulate complete mass spectra for most of the hydrocarbons encountered in the petroleum and synthetic rubber industries below mass 150 or having a vapor pressure of not less than several millimeters of mercury at room temperature. No less important are the resultant data on energies and unimolecular reactions obtained from the mass spectrometric studies of ionization and dissociation by electron impact of gases at pressures of the order of 10^{-4} millimeter of mercury. Because a comparison of observations of dissociation processes of several related molecules will contribute more information about the properties of the ions produced and the manner in which they are produced than the study of one molecular species, it is the purpose of this paper to extend the data on the lower hydrocarbons to include the *cis* and *trans* isomers of 2-butene. Various authors have already reported data on methane [1],¹ ethylene [2, 3], ethane [4, 5], allene [6], propylene [6, 7], isobutene [7], 1-butene [8],

propane [6, 7], *n*-butane [5], and isobutane [5]. In most of these cases it has been possible to determine with the aid of the mass spectrometer what species of ions are produced from a particular molecule by a measure of the mass-to-charge ratio. It is also possible to determine the relative probabilities of formation of each ionic species under given conditions in the ionization chamber. If the energy of the bombarding electrons is controlled and measured, one is able to determine minimum energies necessary to produce any ionic species. In the case of a loss of an electron from the parent molecule, the minimum energy required is known as the ionization potential, $I (X^+)$, of the molecule. The energy at which the ionized parent molecule dissociates into two or more fragments, one of which is an ion, is called the appearance potential, $A (X^+)$, of the ion. The ionization potential is of interest for comparison with data obtained by spectroscopic or theoretical methods. The appearance potentials give information on the heat of dissociation of the molecule though in general they merely set an upper limit to the energies involved. The mass spectrometer data give no information as to the state of aggregation of the uncharged products of dissociation or as to the kinetic energy of the products of ionization. Nevertheless, these data are an important source of additional information on molecular structure and binding energies [9].

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¹ Figures in brackets indicate the literature references at the end of this paper.

II. Experimental Procedure

The mass spectrometer used for the present work has been described in several papers [10]. Therefore, only a brief review of the more important details will be presented. The ionization chamber and 180-degree analyser tube were horizontally supported between the pole pieces of an electromagnet. The strength of the magnetic field was such as to deflect ions of a mass-to-charge ratio of 12 along the axis of the analyser tube at an ion-accelerating potential of 2,500 v. A schematic drawing of the ionization chamber and voltage supplies is given in figure 1. The lines of force of the magnetic field are parallel to the electron ribbon. The path of the ion beam is

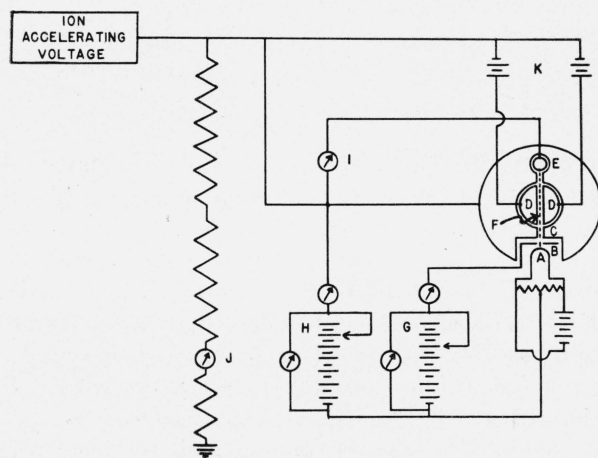


FIGURE 1.—Schematic drawing of the ionization chamber and power supplies.

A, Filament; B, first electron slit; C, second electron slit; D, ion pusher; E, electron catcher; F, electron ribbon; G, electron accelerating power supply and meters; H, ionizing power supply and meters; I, catcher current; J, ion accelerating meter; K, pusher voltage supply.

downward, perpendicular to the plane of the paper. The energies of the ionizing electrons obtained from a tungsten filament were controlled by a wirewound potentiometer and read on a calibrated University model sensitive research meter, which could be read directly to 0.2 v on the 15-v scale and to 1 v on the 75-v scale. The voltage of the second (ionizing) electron slit was varied, whereas that of the first slit was maintained at 5 v. The filament was mounted in a low-pressure region from which the electrons enter the ionization chamber through a very small slit to minimize interference from products of thermal

cracking. Observations on products of primary processes were assured by determining the linear variation of the positive ion current with electron emission and with the pressure of the sample in the ionization chamber.

The *cis*-2-butene and *trans*-2-butene were samples of high purity prepared by J. A. Hinckley, Jr., on the Koppers Fellowship at the Mellon Institute of Industrial Research, Pittsburgh, Pa. The amounts of impurity in these samples were determined by measurements of freezing points by A. R. Glasgow, Jr., under the supervision of Frederick D. Rossini, in the National Bureau of Standards section on Thermochemistry and Hydrocarbons, according to the method described by Glasgow, Streiff, and Rossini [11]. The mole fraction of impurity in *cis*-2-butene is 0.0044 ± 0.0010 ; that in *trans*-2-butene is 0.0181 ± 0.0012 . From the manner of preparation and purification of these samples, it is believed that the impurity in each case is substantially all the other isomer. Liquid samples of suitable size were sealed into lengths of 3-ml glass tubing for convenient introduction into the inlet system. The sensitivity, which we may define as the number of divisions of $C_4H_8^+$ ion on the photographic record per micron of sample pressure behind the leak, was such as to give approximately 350 divisions of $C_4H_8^+$ ion for 30 μ of sample pressure for both *cis*- and *trans*-2-butene. All data were automatically recorded by a photographic oscillograph.

The determination of ionization and appearance potentials has been thoroughly discussed by L. G. Smith [1] and Stevenson and Hipple [5, 12]. The procedure used in determining the values reported here was the method of "initial breaks" as described by Stevenson and Hipple [5]. The voltage scale for the hydrocarbon ions was corrected for "contact potential," using the initial break of the ionization efficiency curve of argon. The ionization potential of argon, $I(A^+) = 15.76$ electron volts (ev) was taken from the tables of Bacher and Goudsmit [13], using the conversion factor $1 \text{ ev} = 8,066 \text{ cm}^{-1}$ to convert from centimeters⁻¹ to electron volts. The observed ionization potentials of argon⁺ and argon⁺⁺ were 13.5 ± 0.1 ev and 41.5 ± 0.1 ev, respectively. The value of $I(A^{++}) - I(A^+) = 28.0 \pm 0.1$ ev is in agreement with values reported for electron impact methods [12] and spectroscopic methods [13].

III. Discussion of Results

Figure 2 shows the first portions of the ionization efficiency curves for several of the *cis*- and *trans*-2-butene ions and argon. The curves have been plotted with the ion current scale adjusted to make all slopes nearly equal. Although the appearance potentials were evaluated by extrapolating the smooth curve to intercept the abscissa,

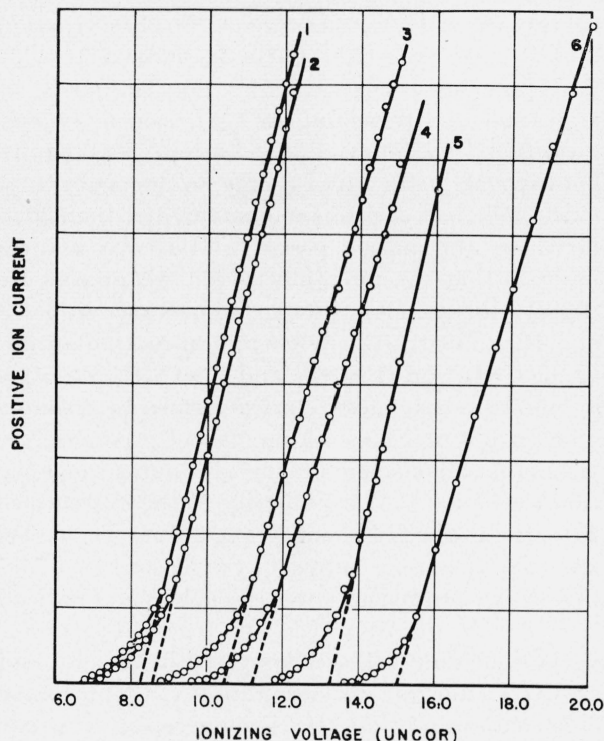


FIGURE 2.—Initial portions of the ionization efficiency curves for the ions *trans*-C₄H₈⁺ (1), *cis*-C₄H₈⁺ (2), *trans*-C₄H₇⁺ (3), *cis*-C₃H₅⁺ (4), *cis*-C₃H₃⁺ (5), and argon⁺ (6).

The ordinate is arbitrary and different for some ions.

close checks can be made by comparing the intercepts resulting from extrapolation of the linear portion of the curve to zero ion current.

Table 1 summarizes the appearance potentials of some of the ions in the mass spectra of *cis*- and *trans*-2-butene. Measurements on several ions of 1-butene were made in order to compare experimental details of the present work with that previously reported. Table 2 lists the probable processes by which each ion is formed. Included in table 1 are the values reported for 1-butene and isobutene by Stevenson [8] and Hipple and Stevenson [7] respectively.

TABLE 1.—Appearance potential of various ions in the mass spectra of *cis*- and *trans*-2-butene

Ion (X ⁺)	Appearance potential A (X ⁺) ev				
	<i>cis</i> -2-Butene	<i>trans</i> -2-Butene	1-Butene	1-Butene [8]	Isobutene [7]
C ₄ H ₈ ⁺	9.41 ±0.1	9.13 ±0.1	9.65 ±0.1	9.65 ±0.1	8.86 ±0.1
C ₄ H ₇ ⁺	11.11 ±0.1	11.24 ±0.1	-----	11.07 ±0.1	11.32 ±0.1
C ₃ H ₅ ⁺	11.66 ±0.1	11.76 ±0.1	11.76 ±0.1	11.65 ±0.1	11.51 ±0.1
C ₃ H ₄ ⁺	12.5 ±0.2	12.4 ±0.2	11.9 ±0.2	11.7 ±0.2	11.62 ±0.1
C ₃ H ₃ ⁺	13.8 ±0.3	14.2 ±0.3	13.6 ±0.2	13.8 ±0.2	14.2 ±0.5
C ₂ H ₅ ⁺	12.2 ±0.2	12.4 ±0.2	-----	11.97 ±0.1	15 ±1
C ₂ H ₄ ⁺	10.6 ±0.2	10.8 ±0.2	-----	-----	12.1 ±0.5
C ₂ H ₃ ⁺	13.8 ±0.3	14.0 ±0.3	-----	13.6 ±0.3	15.2 ±0.5

TABLE 2.—Probable process of ion formation

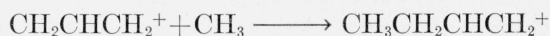
Ion	Process
C ₄ H ₈ ⁺	C ₄ H ₈ →C ₄ H ₈ ⁺ +e ⁻
C ₄ H ₇ ⁺	C ₄ H ₇ ⁺ +H+e ⁻
C ₃ H ₅ ⁺	C ₃ H ₅ ⁺ +CH ₃ +e ⁻
C ₃ H ₄ ⁺	C ₃ H ₄ ⁺ +CH ₄ +e ⁻
C ₃ H ₃ ⁺	C ₃ H ₃ ⁺ +CH ₃ +e ⁻
C ₂ H ₅ ⁺	C ₂ H ₅ ⁺ +C ₂ H ₃ ⁺ +e ⁻
C ₂ H ₄ ⁺	C ₂ H ₄ ⁺ +C ₂ H ₄ +e ⁻
C ₂ H ₃ ⁺	C ₂ H ₃ ⁺ +C ₂ H ₅ +e ⁻

Except for the first ionization potential, the appearance potentials of the *cis* and *trans* isomers agree within the estimated experimental error. The agreement of the electron-impact ionization potential (9.1 ev) of *trans*-2-butene with the value (9.2 ev) determined spectroscopically by Price and Tutte [14] is gratifying. The small difference in ionization potentials of *cis*- and *trans*-2-butene is in the opposite direction to the difference found by Sugden, Walsh, and Price [15] for *cis*- and *trans*-dichloroethylene, for which the ionization potentials are 9.6₁ ev and 9.9₁ ev, respectively. The ionization potentials of *cis* (9.4 ev) and *trans*-2-butene (9.1 ev) are to be compared with 9.6₅ ev for 1-butene [8], and 8.8₆ ev for isobutene [7].

Both 2-butenes resemble other unsaturated hydrocarbons so far studied by electron impact, with the exception of 1-butene, in that the difference in appearance potentials of the C₄H₈⁺ ion and the C₄H₇⁺ ion of both 2-butene isomers is about 2.0 ev. The difference in appearance potentials of the same ions in 1-butene is 1.4 ev [8]. This is very near to the value (1.2 ev) for the difference in appearance potential of the parent ion and the parent ion minus one hydrogen atom of the saturated hydrocarbons. The relative

abundance of the $C_4H_7^+$ ion in the 2-butenes is about the same as that in 1-butene and about 20 percent greater than the abundance of the same ion in isobutene.

Rossini [16] lists the relative stabilities of the butenes as 1-butene (0.00 ev), *cis*-2-butene (0.080 ± 0.005 ev), *trans*-2-butene (0.121 ± 0.005 ev), isobutene (0.167 ± 0.011 ev). The experimental error of the electron-impact values reported for the appearance potentials of the $C_3H_5^+$ ion does not allow stability measurements on the *cis* and *trans* isomers. Comparison with 1-butene and isobutene, however, is practical. From Rossini's list of relative stabilities given above, isobutene is more stable than *cis*-2-butene by approximately 0.09 ev. However, the appearance potentials determined in this work for the $C_3H_5^+$ ion from *cis*-2-butene is 11.6₆ ev, whereas that ion from isobutene is 11.5₁ ev, as determined by Stevenson and Hipple [7]. This indicates that the 2-butene configuration of the $C_3H_5^+$ ion is a total of 0.24 ev less stable than the corresponding isobutene ion. Again from Rossini, *cis*-2-butene is more stable than 1-butene by 0.08 ev. As the appearance potentials of the $C_3H_5^+$ ions from both these molecules agree within experimental error, the 1-butene structure of the $C_3H_5^+$ ion is apparently a total of 0.32 ev less stable than the isobutene configuration. This checks Stevenson's findings [8], and supports his assignment of about 0.4 ev as the lower limit for the activation energy of the reaction



(assuming that $CH_2CHCH_2^+ + H \longrightarrow C_3H_6^+$ requires no activation energy) to demonstrate that the allyl ion is at least 0.1 ev more stable than the isoallyl ion. Stevenson has also shown [8] that other electron-impact data and chemical evidence can be reconciled if activation energies for addition of radicals to the vinyl ion are assumed.

The ionization potential of methyl acetylene is 11.25 ev [15], whereas that of allene is 9.9 ev [6]. Although the exact appearance potential of the $C_3H_4^+$ ion is uncertain, the value for the 2-butenes (12.5 ev) being 0.8 ev higher than the same ion for 1-butene would seem to indicate that the $C_3H_4^+$ ion has the methyl acetylene structure rather than

the allene structure as reported for the same ion formed from 1-butene [8]. It seems probable then that the CH_3 group and the hydrogen atom forming the unionized products of the process originate from adjacent carbon atoms rather than the same carbon atom.

The appearance potential of the $C_2H_5^+$ ion of the 2-butenes (12.2 ev) combined with the ionization potential of the ethyl radical (8.6₇) reported by Hipple and Stevenson [5, 17], yields a dissociation energy $D(C_2H_5-C_2H_3) = 3.5$ ev for the reaction 2-butene $\longrightarrow C_2H_5^+ + C_2H_3$, in agreement with that previously reported [8]. The similarity of appearance potentials of the $C_2H_5^+$ ion of *cis* and *trans*-2-butene indicates that both isomers require approximately the same energy to dissociate to a $C_2H_5^+$ ion. At electron energies greater than 20 v, however, the mass spectra of the two isomers indicate that the probabilities for this process are slightly different for the two isomers (see tables 3 and 4). The relatively low appearance potentials of the $C_2H_4^+$ ion (10.6 ev) and the $C_2H_3^+$ ion (13.8 ev) indicate that these ions are formed by a simple dissociation process with one set of products and very probably a single unionized fragment in addition to the ion. The similarity of the appearance potential of the $C_2H_3^+$ ion of the 2-butenes to that ion from 1-butene supports Stevenson's calculation of the ionization potential of the vinyl radical.

The mass spectra of *cis*- and *trans*-2-butene for various ionizing voltages are given in tables 3 and 4. At an ionizing potential of 50 v, the intensity of ion current for the $C_4H_5^+$ ion is given an arbitrary value of 100, in accordance with the practice at this laboratory. The abundances of all other ions are made relative to this value. Some of the less abundant ions of each carbon group have been omitted for the sake of brevity. Also omitted for the same reason are the doubly charged ions with a mass to charge ratio of 25.5, 26.5, and 27.5 originating from the ions $C_4H_3^{++}$, $C_4H_5^{++}$, and $C_4H_7^{++}$, respectively. These first appear at about 40 ev for each isomer. Also omitted are the two metastable ions at 30.0 and 37.0 as reported by Hipple, Fox, and Condon [18] and an additional metastable ion at 15.3, probably originating in the same manner as that one reported for 2-pentene by the same authors. All three metastable ions appear below 20 ev for both isomers.

TABLE 3.—Mass spectrum of *cis*-2-butene ^a

V_I	m/e								
	56 (C ₄ H ₈ ⁺)	55 (C ₄ H ₇ ⁺)	54 (C ₄ H ₆ ⁺)	53 (C ₄ H ₅ ⁺)	52 (C ₄ H ₄ ⁺)	51 (C ₄ H ₃ ⁺)	50 (C ₄ H ₂ ⁺)	42 (C ₃ H ₆ ⁺)	41 (C ₃ H ₅ ⁺)
20	93.6	19.0	2.7	2.3				0.4	102
30	94.6	33.0	6.1	10.3	1.5	2.5	0.7	5.1	155
40	98.0	36.0	7.0	13.2	3.3	8.3	5.9	5.8	172
50	100	38.6	7.3	13.7	3.5	10.4	10.3	6.0	187
60	102	40.1	7.2	12.4	3.4	10.6	11.6	6.1	186
70	105	42.2	7.5	14.2	3.6	10.9	12.5	6.4	190
80	107	43.1	7.7	14.5	3.4	11.0	13.0	6.6	187
90	105	42.8	7.8	14.4	3.2	10.7	14.4	6.5	186
100	107	43.3	7.8	14.0	3.2	10.5	14.5	6.6	188
	40 (C ₃ H ₄ ⁺)	39 (C ₃ H ₃ ⁺)	29 (C ₂ H ₅ ⁺)	28 (C ₂ H ₄ ⁺)	27 (C ₂ H ₃ ⁺)	26 (C ₂ H ₂ ⁺)	15 (CH ₃ ⁺)	14 (CH ₂ ⁺)	2 (H ₂ ⁺)
20	6.0	14.4	11.6	30.6	4.7	0.9	1.0		0.4
30	10.7	49.1	22.5	48.3	37.1	5.8	3.7	0.4	.5
40	12.3	64.9	25.7	55.2	57.0	14.5	7.4	1.1	.5
50	13.2	69.2	26.7	57.7	62.6	20.0	9.9	1.8	.6
60	13.5	70.8	27.2	58.9	64.0	22.8	11.3	2.3	.7
70	14.0	73.3	28.0	60.8	64.9	24.6	11.9	2.7	.8
80	14.2	73.7	28.6	61.9	65.5	25.6	12.3	3.0	.9
90	14.1	72.7	28.3	61.0	63.4	25.3	12.2	2.9	(b)
100	14.1	72.4	28.1	61.6	62.9	25.4	11.9	2.9	(b)

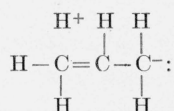
^a The relative abundances have not been corrected for presence of C¹³ and D.^b No measurement made.TABLE 4.—Mass spectrum of *trans*-2-butene ^a

V_I	m/e								
	56 (C ₄ H ₈ ⁺)	55 (C ₄ H ₇ ⁺)	54 (C ₄ H ₆ ⁺)	53 (C ₄ H ₅ ⁺)	52 (C ₄ H ₄ ⁺)	51 (C ₄ H ₃ ⁺)	50 (C ₄ H ₂ ⁺)	42 (C ₃ H ₆ ⁺)	41 (C ₃ H ₅ ⁺)
20	80.9	16.7	2.3	2.1				2.8	87.9
30	93.0	32.8	5.7	10.8	1.4	2.5	0.7	5.0	150
40	95.5	36.9	6.4	13.7	3.2	7.9	5.7	5.4	166
50	100	40.0	6.8	14.5	3.6	10.2	10.0	5.9	194
60	104	42.4	7.1	15.2	3.4	10.8	11.7	6.3	191
70	105	42.9	7.1	15.3	3.4	11.0	12.4	6.4	192
80	105	43.5	7.0	15.2	3.4	10.8	12.7	6.3	193
90	103	42.7	6.9	14.9	3.2	10.4	12.6	6.3	191
100	105	43.7	7.0	15.1	3.3	10.5	12.7	6.5	193
	40 (C ₃ H ₄ ⁺)	39 (C ₃ H ₃ ⁺)	29 (C ₂ H ₅ ⁺)	28 (C ₂ H ₄ ⁺)	27 (C ₂ H ₃ ⁺)	26 (C ₂ H ₂ ⁺)	15 (CH ₃ ⁺)	14 (CH ₂ ⁺)	2 (H ₂ ⁺)
20	4.7	14.8	11.5	25.1	3.7	0.5	0.7		0.3
30	9.8	46.3	25.7	46.4	35.3	5.2	3.2	0.4	.5
40	11.3	59.6	30.3	52.7	53.2	12.7	6.6	1.0	.6
50	12.3	65.7	32.3	56.3	59.1	18.1	9.0	1.6	.7
60	13.0	68.8	34.3	59.1	62.7	21.4	10.3	2.2	.7
70	13.2	69.5	34.2	59.4	62.4	22.6	11.0	2.5	.8
80	13.1	69.5	34.3	59.7	62.2	23.6	11.1	2.6	.8
90	13.0	68.2	33.9	58.9	59.9	23.1	11.0	2.7	(b)
100	13.2	69.1	34.5	59.9	60.5	23.3	11.0	2.5	(b)

^a The relative abundances have not been corrected for presence of C¹³ and D.^b No measurement made.

For electron energies of 50 v or more, there appears to be little difference in the *cis* and *trans* mass spectra, especially for ions resulting from the loss of an electron, or a single unit such as a methyl group, or hydrogen atom, or the fracture of the double bond splitting the molecule in half. See, for example, the similarity of the sensitivities of the two isomers and the similarity of abundance of the $C_4H_7^+$ ion, the $C_3H_5^+$ ion, and the $C_2H_4^+$ ion in both *cis* and *trans* isomers.

For 50-v electrons, the relative abundance of the $C_2H_5^+$ ion is 27 percent for *cis*-2-butene and 32 percent for *trans*-2-butene compared to 48 percent for 1-butene and 28 percent for isobutene. The abundance of the $C_2H_5^+$ ion in the 2-butenes is interesting because a $C_2H_5^+$ ion is not expected from the structures of *cis*- and *trans*-2-butene. There are two possible explanations for the presence of this ion. The first possibility is the tendency for some molecules of this type to resonate between several possible structures, each structure contributing to the general characteristics of the molecule. For example, to account for dipole moments of 0.35 for propylene, and 0.37 for 1-butene, Hurdis and Smyth [19] point out that three structures can be written for propylene of the type



Although the contribution of such structures is probably small, the fact that one hydrogen bond may have a partially ionic character is of interest as it is already known that the $C_3H_5^+$ ion in propylene is about 30 percent more abundant than the $C_3H_6^+$ ion. Also it might reconcile the anomaly reported by Stevenson in his work on 1-butene, where the difference in appearance potentials of the $C_4H_5^+$ ion and the $C_4H_7^+$ ion is 1.4 ev. This value is near the difference between the $C_4H_{10}^+$ ion and the $C_4H_9^+$ ion (1.2 ev) of the butanes, although the relative abundance of the $C_4H_7^+$ ion in 1-butene is larger than the relative abundance of the $C_4H_7^+$ ion in isobutene, whereas the abundance of the $C_4H_5^+$ ion in isobutane is about five times the abundance of that ion in

n-butane. Similar structures for the 2-butenes can be shown to be capable theoretically of dissociating to give $C_2H_5^+$ ions.

A second and more usual explanation of the formation of the $C_2H_5^+$ ion is the process common to many of the hydrocarbons studied by electron impact, namely, isomerization that occurs in the very short time between formation of the ion and subsequent dissociation into fragments. Incidentally, as the shape of the recorded peaks resulting from an isomerization process is exactly the same as that resulting from simpler dissociation processes, one would conclude that the isomerization and dissociation is accomplished before the ion is accelerated by the electrostatic field. Knowing the dimensions of the ionization chamber, it is possible to calculate an upper limit for the time required for a 2-butene ion to isomerize and dissociate to give a stable $C_2H_5^+$ ion. Assuming that an ion of mass M , and charge e , in coulombs, is accelerated from rest in an electric field of E volts, the velocity (cm/sec) after falling through the total potential E , is given by

$$V = \sqrt{\frac{2eE10^7}{M}}$$

Assuming a pusher potential of 4 v and a distance of 3 mm between the electron ribbon and the ion accelerating slit, the maximum time allowable for isomerization and dissociation to form a stable $C_2H_5^+$ ion is of the order of 10^{-4} second.

Both 2-butene patterns are generally lower than those of 1-butene and isobutene except in the C_2 group, where the abundances of the ions are about half way between 1-butene and isobutene, the former having the highest values. In the C_4 group, all 2-butene ions with the exception of the $C_4H_7^+$ ion, are more abundant than the same ions from either 1-butene or isobutene. The 2-butene $C_4H_7^+$ ion is slightly less abundant than 1-butene and 20 percent more abundant than isobutene.

Figure 3 is a plot of some of the data in tables 3 and 4. All the curves are for ions originating from *cis*-2-butene, with the exception of the $C_2H_5^+$ ion, data for which are given for both *cis* and *trans* isomers. The flat portion of each curve occurs above 50 v, indicating rather stable con-

ditions for recording relative abundances above that voltage. The $C_2H_5^+$ ion is the only ion with significant differences in abundance between *cis*- and *trans*-2-butene. It is obvious from figure 3 that even this difference is small and very constant with increasing ionizing voltage.

It was hoped that the variation of mass spectra of the 2-butenes with energy of the ionizing electrons would be such as to make possible the selection of an ionizing voltage which would allow a more accurate separation of the *cis*- and *trans*-2-butenes in a mixture of the other butenes. Unfortunately, the relatively low abundance of the $C_2H_5^+$ ion, which is the only ion exhibiting a significant difference in abundance between the two isomers, reduces its effectiveness as a means of

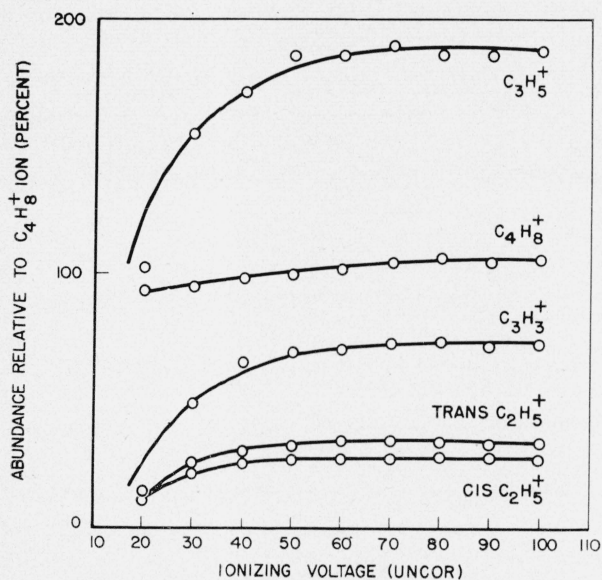


FIGURE 3.—Upper portion of the ionization efficiency curves for the ions *cis*- $C_3H_5^+$, *cis*- $C_4H_8^+$, *cis*- $C_3H_3^+$, *cis*- $C_2H_5^+$, and *trans*- $C_2H_5^+$.

The abundance of each ion is relative to the abundance of the *cis*- $C_4H_8^+$ ion at electron energies of 50 v.

accomplishing the separation with any reasonable degree of accuracy. Under standard operating conditions the energy of the electron beam is 50 v.

There is no evidence to indicate that an advantage can be gained by operating at some other value.

IV. Summary

The appearance potentials and relative abundances of a large portion of the mass spectra of *cis*- and *trans*-2-butene are reported. The ionization potentials of *cis*-2-butene and *trans*-2-butene were found to be $9.4_1 \pm 0.1$ and $9.1_3 \pm 0.1$ ev, respectively. The latter is in agreement with previously determined spectroscopic data. The values for the heat of dissociation of the $C_2H_5-C_2H_3$ bond and the ionization potential of the vinyl radical calculated from *cis*- and *trans*-2-butene are found to be in agreement with those values reported by Stevenson. The mass spectra of *cis*- and *trans*-2-butene are compared with each other and with 1-butene and isobutene. There is no evidence to indicate an advantage in using ionizing energy other than the normal operating value of 50 v when analysing mixtures containing *cis*- and *trans*-2-butene.

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V. References

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