

The study of *cis*- and *trans*-2 butene using mass spectrometry

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Abstract. Using mass spectrometric technique, the effect of geometrical isomerism on the first and higher appearance energy values for $C_4H_5^+$, $C_4H_7^+$ and $C_3H_3^+$ ions obtained from *cis*-2-butene and *trans*-2-butene is reported. The structure in the ionization efficiency curves (studied for 9 eV above threshold) for the same ions obtained from the two isomers is reported and compared. It is believed that at threshold $C_4H_7^+$ fragment is formed from the two isomers as methallyl ion. For $C_3H_3^+$ fragment formed from the *cis*-isomer at threshold the proposed structure is the propargyl ion with ΔH_f equal to 279.4 kcal/mole while for that ion obtained from *trans*-isomer the proposed structure is the allenyl ion with ΔH_f equal to 296.6 kcal/mole.

Keywords. *Cis*-2-butene; *trans*-2-butene; mass spectrometry; geometrical isomerism.

1. Introduction

The study of the effect of electrons on the ionization and fragmentation of geometrical isomers had been carried out by Natalis (1965). He concluded that the ionization energies of *cis*- and *trans*-isomers being the same imply that the same amount of energy is provided to the two types of molecules by the impinging particle, electron or photon. Also, geometrical isomerism disappears by fragmentation of ionized molecules, the extra energy content of *cis*-isomers due to steric conformation is released and used in the fragmentation process.

Cis- and *trans*-2-butene isomers had been investigated by Meisels *et al* (1970) using electron impact and by Morrison using the second derivative technique. They reported the appearance energies at threshold only of $C_2H_5^+$ and $C_2H_4^+$ fragments obtained from the two geometrical isomers.

Recently, Sunner (1980) using charge transfer technique reported the appearance energies at threshold only for 16 fragments obtained from *cis*-2-butene. His results also show that it is possible to distinguish isomers by charge transfer mass spectrometry, even if the molecular ions isomerize prior to fragmentation, by exploiting differences in the ionization probabilities.

The purpose of the present article is to report the effect of geometrical isomerism on the value of ionization energies, appearance energies and heats of formation for $C_4H_5^+$, $C_4H_7^+$ and $C_3H_3^+$ ions obtained from *cis*- and *trans*-2-butene for about

9 eV above threshold. The structures in the ionization efficiency (IE) curves for the same ions obtained from the two isomers are reported and compared.

2. Experimental technique

The IE data are obtained using the Atlas CH-4 mass spectrometer with a normal electron impact ion source (AN-4). The condition of measurements, experimental technique and calibration of energy scale had been reported previously (Selim *et al* 1978 ; Selin 1976). The experimental results are taken in the form of IE curves, i.e. ionization yield against accelerating voltage for the electrons (varied by 0.1 eV steps). These directly measured IE curves are then smoothed by seven-points smoothing method (Savitzky and Golay 1964). The smoothed data are treated by the energy distribution difference (EDD) technique (Winter *et al* 1966) by means of which the effective electron energy distribution can be reduced thus allowing an accurate determination of appearance energies and fine structure in the curves. The value of the constant b characterizing the EDD technique is taken to be 0.63 eV. This value of b is chosen so as to give the best results for Ar ionization energy value.

A computer technique is developed and used for determining the exact position of the breaks in the ion intensity difference curves. The technique is based upon straight line fitting procedure (Selim *et al* 1978 ; Allenson and Sedgwick 1968). In many cases, however, a step function may occur in the curves and can be detected when the sequence of increasing slopes is broken. The step function regions are further examined by manual plotting of the data. The numerical values of Student t used in the present study are that corresponding for 95% confidence limit which is proved to be suitable for the present results.

3. Results and discussion

The ionization efficiency (IE) curves for the ions, studied for 9 eV above threshold are given in figures 1-6. The initial portion of each curve is plotted on a magnified scale above the initial one. The ionization and appearance energies obtained from IE curves of the studied ions together with similar results previously reported by different authors using different techniques are reported in table 1. The values given are the average of six determinations while the errors quoted are the standard deviations. Only reproducible ionization and appearance energies are reported in the table. In table 2 the differences between the ionization energies as well as differences between appearance energies for the same ions obtained from the two isomers are reported. Heats of formation corresponding to the first and second appearance energies for the ions studied are also reported in table 2.

3.1. $C_4H_8^+$ ($m/z = 56$) parent ion

The measured first ionization energies for *cis*- and *trans*-2-butene are 9.26 and 9.25 eV respectively. The ionization energy for the two isomers is established (Watanabe *et al* 1962 ; Dewar and Worley 1969) at 9.13 eV. It is generally accepted that the ionization of butenes is produced by removal of one of the π electrons (from C=C bond). We opine that the values 9.26 and 9.25 eV obtained presently are not corresponding to adiabatic ionization energies.

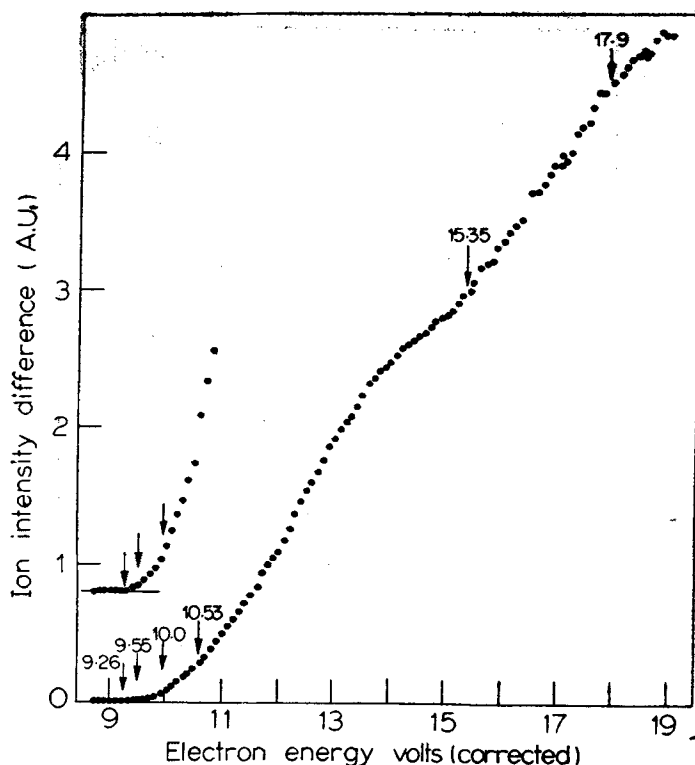


Figure 1. The ionization efficiency curve for *cis*-2-butene parent ion ($m/z = 56$).

Higher energy levels have been detected in the IE curves of *cis*- and *trans*-2-butene and reported in table 1. The differences between the values of the corresponding energy levels for the two isomers are within the limits of experimental errors (table 2). The only available similar energy levels in the literature to compare with are those reported by Dewar and Worley (1969) at 11.28, 12.40, (13.74), (14.75), 16.07 and (18.84) eV for *cis*-2-butene and at 11.46, 12.58 and 13.99 eV for *trans*-2-butene. No possible correlation can be obtained between the energy levels reported by these authors and that obtained from the present IE curves for the two isomers. However, many authors (White *et al* 1974 ; Kimura *et al* 1975) had detected vertical second ionization energy for *cis*-2-butene at 2.3 eV and for *trans*-2-butene at 2.5–2.6 eV above the corresponding vertical first ionization energy.

3.2. $C_4H_7^+$ ($m/z = 55$) fragment ion

The IE curve for $C_4H_7^+$ fragment obtained from *cis*-2-butene shows a somewhat sharp rise at the threshold while the curve for the same fragment from the *trans*-isomer exhibits a short tail at the threshold. The values measured for the appearance energy for $C_4H_7^+$ ion from *cis*- and *trans*-2-butene isomers are 11.51 and 11.52 eV respectively. The value 11.51 eV is in good agreement with photoionization value (Kramer and Dunbar 1973) 11.43 eV but is larger than electron impact values (Lossing 1972 ; Omura 1961 ; Dibelaar 1947) (table 2). For

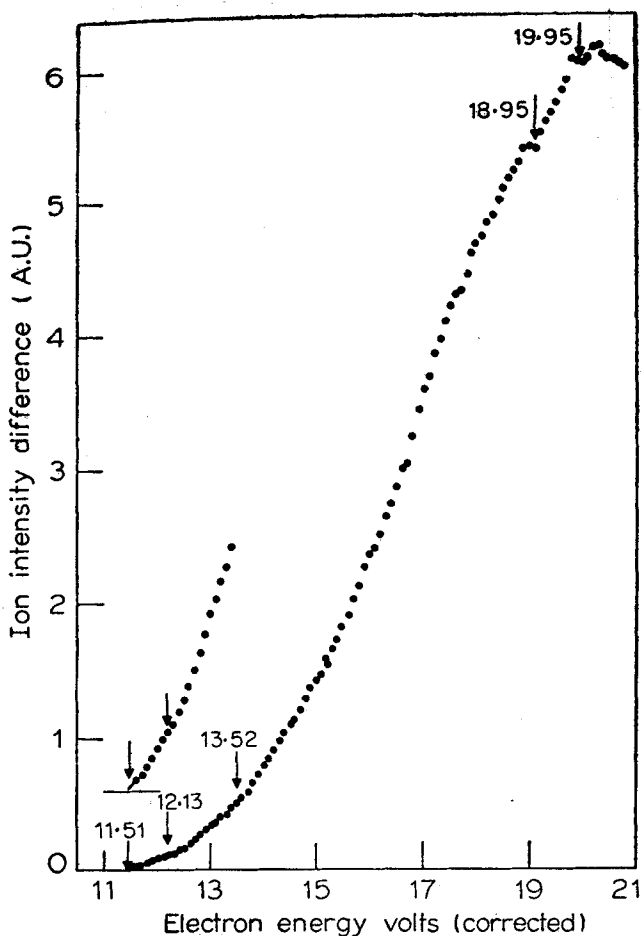


Figure 2. The ionization efficiency curve for fragment ion ($m/z = 55$) from *cis*-2-butene.

$C_4H_7^+$ fragment from *trans*-2-butene the only available value in the literature is the value reported early by Dibelar (1947) (11.24 eV).

The structure in IE curves for *cis*- and *trans*-2-butene are similar except for the higher appearance energy 12.50 eV which appears only in *trans*- isomer curve and appearance energy 13.52 eV which appears only in the *cis*-isomer curve.

The fragment $C_4H_7^+$ is formed from the two isomers by simple removal of H atom from $C_4H_8^+$ molecular ion. This process requires no reverse activation energy and the kinetic shift associated with the detectable threshold is believed to be small as a result of using : (a) zero draw-out potential and (b) high sensitivity electron multiplier as detector in the present study. The calculated ΔH_f values for $C_4H_7^+$ fragment obtained at threshold from *cis*- and *trans*-2-isomer respectively are 211.7 and 210.9 kcal/mole which may indicate that the same ion structure is obtained from the two isomers. These ΔH_f values are corresponding to methallyl structure $CH_3^+CHCH=CH_2$ with ΔH_f value equal to 204 kcal/mole as calculated

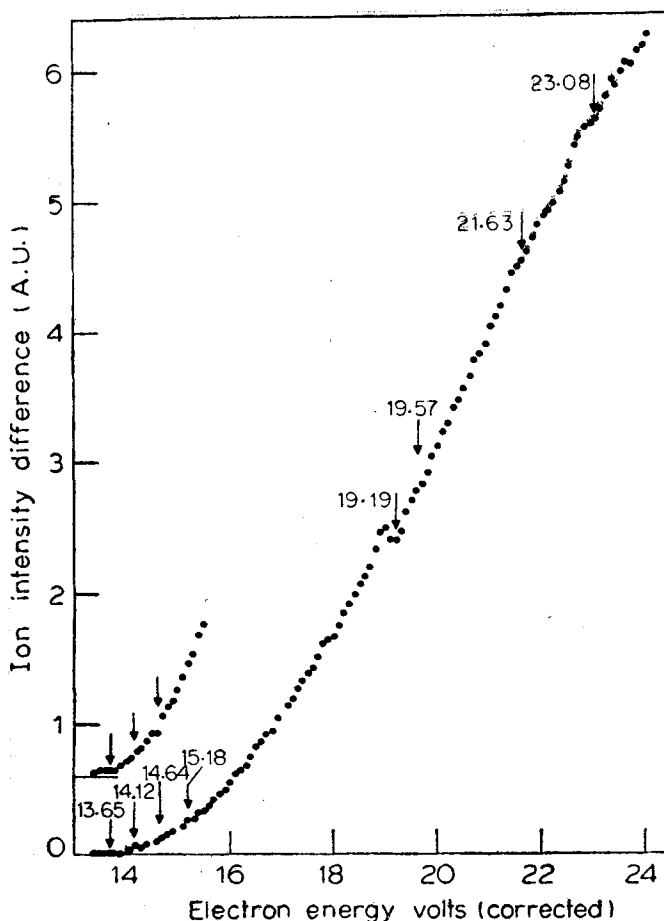


Figure 3. The ionization efficiency curve for fragment ion ($m/z = 39$) from *cis*-2-butene.

by Lossing (1972) from the ionization energy of methallyl radical. The present ΔH_f value for the ion suggests a kinetic energy shift of about 7 kcal/mole in the appearance energy of the ion. However, Lossing (1972) reported the value 206 kcal/mole for methallyl ion obtained from different sources with kinetic shift of only 2 kcal/mole.

It is possible that at higher energy than the threshold $C_4H_7^+$ fragment is formed as cyclic $C_3H_4CH_2^+$ ion with ΔH_f value (Franklin *et al* 1969) around 221 kcal/mole. There is evidence supporting this from the IE curves of $C_4H_7^+$ fragments obtained from both *cis*- and *trans*-isomers. These curves reveal second appearance energy* at 12.13 and 12.22 eV respectively and the corresponding calculated ΔH_f values are 226 and 227 kcal/mole. Taking into account a presumed small kinetic energy shift of about 6-7 kcal/mole in the appearance energy one can

* These values have no similars in $C_4H_7^+$ or $C_3H_5^+$ IE curves so, one cannot consider these values as the onset of formation of an excited state.

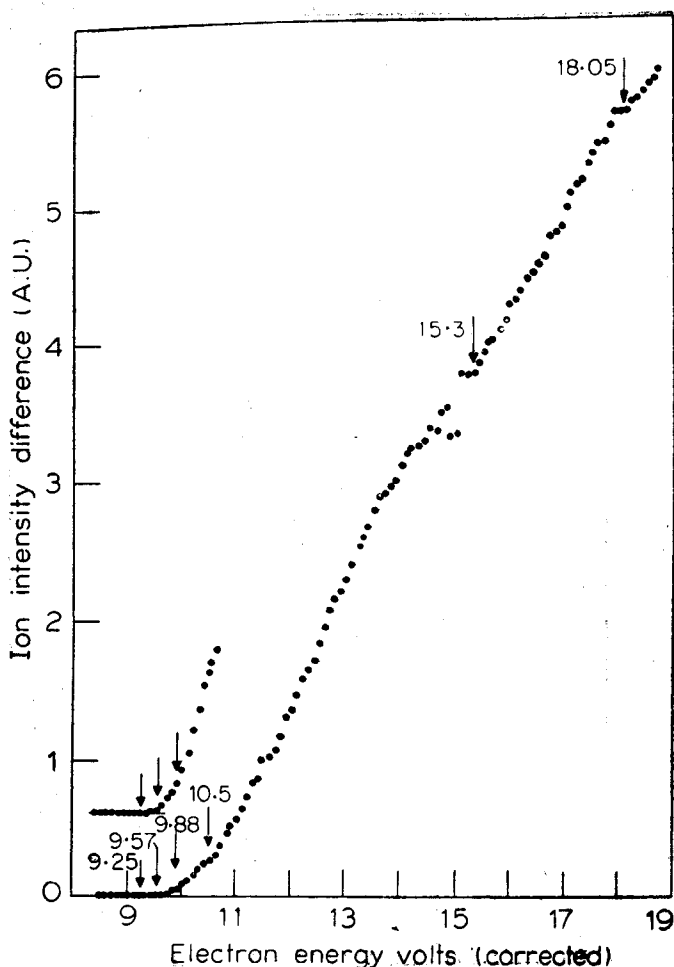


Figure 4. The ionization efficiency curve for *trans*-2-butene parent ion ($m/z = 56$).

suggest that ΔH_f values 226 and 227 kcal/mole correspond well to cyclic $C_3H_4CH_3^+$ structure with ΔH_f value equal to 221 kcal/mole as reported by Franklin *et al* (1969).

3.3. $C_3H_3^+$ ($m/z = 39$) fragment ion

The IR curves for the fragment ion obtained from the two isomers exhibit long tails at the threshold. The first appearance energy for $C_3H_3^+$ fragment obtained from the *cis*-isomer is measured at 13.65 eV and is in good agreement with the previously reported values (13.75, Omura 1961 and 13.80, Dibelaar 1947 eV) while the ion obtained from the *trans*-isomer is measured at 14.44 eV and is in reasonable agreement with the only previously reported value 14.20 eV (Dibelaar 1947). The difference between the appearance energy values for $C_3H_3^+$ fragment obtained from the two isomers is equal to 0.79 eV in the right direction since one expects that fragment ions obtained from *cis*-isomers is lower by the amount of

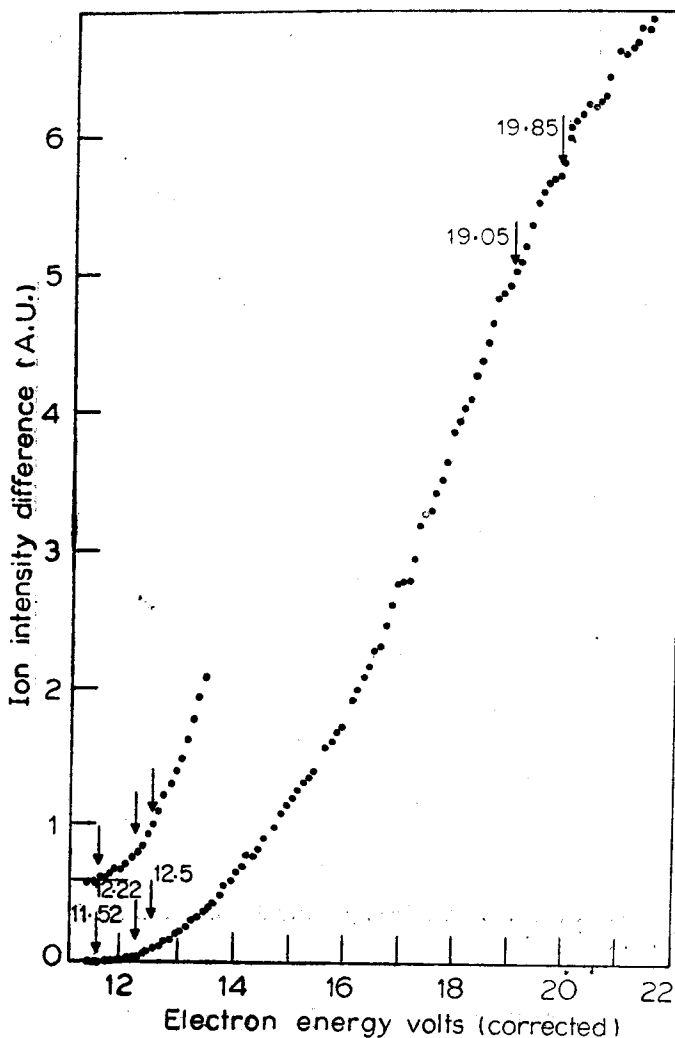


Figure 5. The ionization efficiency curve for fragment ion ($m/z = 55$) from *trans*-2-butene.

energy provided by steric conformation in the *cis*-isomer. However, one can argue that the value 0.79 eV is too a large value for the energy of steric conformation in the *cis*-isomer. Also, one may ask why similar energy of steric conformation does not appear in the fragmentation process leading to the formation of $C_4H_7^+$ fragment? The plausible explanation for the large difference between appearance energies obtained from the two isomers is that for unknown reason geometrical isomerism remains after the fragmentation of the two isomers and that the ground state of $C_3H_5^+$ fragment ion from *trans*-2-butene has a very low cross-section. As a result of that the measured appearance energy for $C_3H_5^+$ fragment from the *trans*-isomer is not the first one but higher appearance [energy.

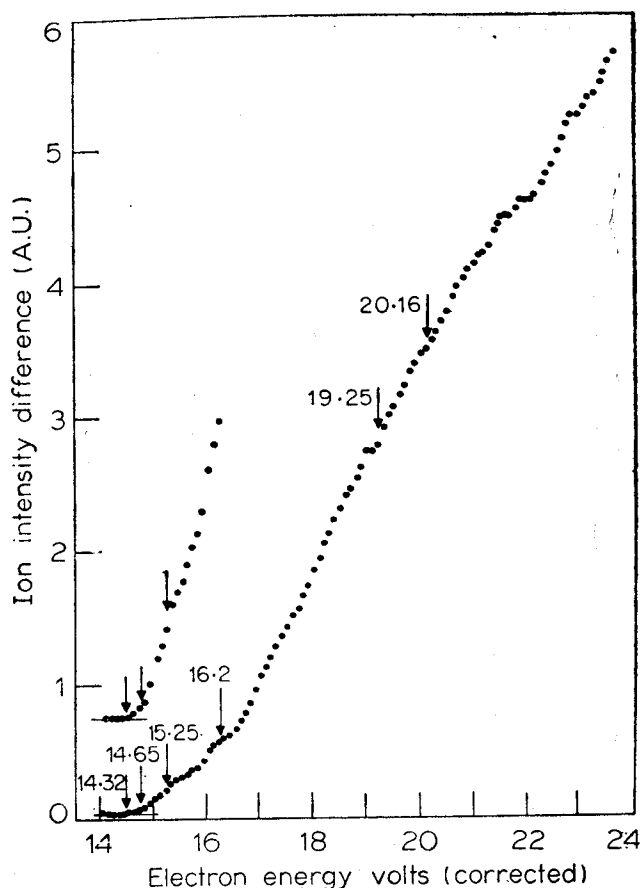


Figure 6. The ionization efficiency curve for fragment ion ($m/z = 39$) from *trans*-2-butene.

The structure in the IE curves of $C_3H_5^+$ fragments obtained from the two isomers are given in table 1. Three higher appearance energies appear at 19.57, 21.63, and 23.08 eV in the IE curve of $C_3H_5^+$ fragment produced from the *cis*-isomer but not in the IE curve of the fragment from the *trans*-isomer.

The $C_3H_5^+$ fragment ion is believed to be formed at the threshold from both isomers by the following processes having almost equal heats of formation :



Using charge transfer technique Sunner (1980) had detected two metastable peaks at m/z equal to 27.7 and 37.1 for the formation of $C_3H_5^+$ fragment from *cis*-2-butene. The first peak corresponds to the formation of $C_3H_5^+$ fragment from $C_6H_8^+$ fragment while the second peak corresponds to its formation from $C_4H_7^+$ fragment. The calculated ΔH_f values for $C_3H_5^+$ formation from *cis*-2-butene at the threshold are equal to 279.9 kcal/mole (process a) and 279.4 kcal/mole

Table 1. Ionization and appearance energies for $C_4H_8^+$, $C_4H_7^+$ and $C_3H_5^+$ ions obtained from *cis*- and *trans*-2-butene.

Ion	Ionization and appearance energies			
	<i>cis</i> -butene		<i>trans</i> -butene	
	Present study	Previous work	Present study	Previous work
$C_4H_8^+$ ($m/z = 56$)	9.26 ± 0.06	$9.16^{(1)}$, $9.00^{(2)}$, $9.13 \pm 0.01^{(3)}$	9.25 ± 0.05	$9.10 \pm 0.15^{(1)}$, $9.13 \pm 0.01^{(3)}$
	9.55 ± 0.10		9.57 ± 0.07	
	10.00 ± 0.07		9.88 ± 0.05	
	10.53 ± 0.06		10.50 ± 0.09	
	15.35 ± 0.06		15.30 ± 0.10	
	17.90 ± 0.08		18.05 ± 0.10	
$C_4H_7^+$ ($m/z = 55$)	11.51 ± 0.08	$11.32^{(1)}$, $11.20^{(4)}$, $11.10 \pm 0.11^{(5)}$, $11.43 \pm 0.01^{(6)}$	11.52 ± 0.06	$11.24 \pm 0.1^{(6)}$
	12.13 ± 0.09		12.22 ± 0.10	
	..		12.50 ± 0.10	
	13.52 ± 0.07		..	
	18.95 ± 0.12		19.05 ± 0.12	
	19.95 ± 0.10		19.85 ± 0.12	
$C_3H_5^+$ ($m/z = 39$)	13.65 ± 0.09	$13.75^{(4)}$, $13.80 \pm 0.3^{(6)}$		
	14.12 ± 0.10		14.32 ± 0.08	$14.20 \pm 0.3^{(6)}$
	14.64 ± 0.05		14.65 ± 0.09	
	15.18 ± 0.09		15.25 ± 0.06	
	..		16.20 ± 0.06	
	19.19 ± 0.07		19.25 ± 0.07	
	19.57 ± 0.07		..	
	..		20.16 ± 0.10	
	21.63 ± 0.08		..	
	23.08 ± 0.08			

(1) Lossing 1972, (2) Meisels *et al* 1970, (3) Watarabe *et al* 1962, (4) Omura 1961, (5) Dibelar 1947, (6) Kramer and Danbar 1973.

(process b). The mean value is equal to 279.4 kcal/mole which is in excellent agreement with ΔH_f value 281 kcal/mole for the propargyl ion $HC \equiv C^+CH_2$ reported by Lossing (1972). The presently reported ΔH_f value 279.4 kcal/mole is higher by about 23 kcal/mole than the heat of formation of $C_3H_5^+$ as cyclopropenyl ion reported by Lossing (1972) and Franklin *et al* (1969) which rules out the formation of cyclopropenyl ion in the present study at least

Table 2. Ionization and appearance energy differences and heats of formation for $C_4H_5^+$, $C_4H_7^+$ and $C_3H_3^+$ ions obtained from *cis*- and *trans*-2-butene.

Ion	Ionization and appearance energy differences (eV) <i>Trans-cis</i>	ΔH_f (kcal/mol)	
		<i>Cis</i> -	<i>Trans</i> -
$C_4H_5^+$ (<i>m/z</i> = 56)	-0.01	211.9	210.6
	0.02	218.6	218.0
	-0.12
	-0.03
	-0.05
	0.15
$C_4H_7^+$ (<i>m/z</i> = 55)	0.01	211.7	210.9
	0.09	226.0	227.0
$C_3H_3^+$ (<i>m/z</i> = 39)	..	279.4	..
	0.20	290.2	296.2

at the threshold. While the ΔH_f value for propargyl ion has not been established until now, the excellent agreement between the present result for this ion together with that of Lossing (1972) may indicate that ΔH_f for the ion is about 280 kcal/mole. Although, the processes (a and b) for formation of cyclopropenyl ion from *cis*-2-butene are multicenter dissociation processes which require reverse activation energy and probably also kinetic shift the presently reported value of ΔH_f for propargyl ion together with that calculated by Lossing (1972) may indicate that $C_3H_3^+$ is formed presently from *cis*-2-butene with almost zero excess energy.

The calculated ΔH_f value for the formation of $C_3H_3^+$ fragment from *trans*-2-butene according to process (a) is equal to 257.2 kcal/mole, while that value according to process (b) is equal to 296.1 kcal/mole. The mean value is equal to 296.6 kcal/mole and probably corresponds to the formation of $C_3H_3^+$ fragment with allenyl structure ($CH_2=C=CH^+$). The ΔH_f value for the formation of allenyl ion obtained from *i*-butene is calculated previously by Selim (1970) as 287.3 kcal/mole. It appears that the formation of $C_3H_3^+$ fragment from *trans*-2-butene needs more excess energy than the formation of the same ion from *i*-butene.

Finally, if one calculates the ΔH_f value for $C_3H_3^+$ fragment obtained from the *cis*-isomer corresponding to the second appearance energy (14.12 eV) the calculated value will be equal to 290.7 kcal/mole according to process (a) and 289.7 kcal/mole according to process (b). The mean value is equal to 290.2 kcal/mole and may indicate that at higher energy than the threshold the propargyl ion obtained from *cis*-2-butene (at the threshold) isomerizes to the allenyl structure.

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