

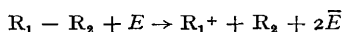
IONIZATION AND DISSOCIATION BY ELECTRONIC IMPACT

THE IONIZATION POTENTIALS AND ENERGIES OF FORMATION OF *SEC.*-PROPYL AND *TERN.*-BUTYL RADICALS. SOME LIMITATIONS ON THE METHOD

BY D. P. STEVENSON

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It is shown that the mass spectrometrically measured appearance potentials of a variety of ions in a number of different substances are mutually consistent with the assumption that there are electron impact induced ionization and dissociation processes



such that the appearance potential of R_1 , $A(R_1^+)$, is given by the equality

$$A(R_1^+) = I^*(R_1) + D(R_1 - R_2)$$

where $I^*()$ and $D()$ are the ionization potential and dissociation energy of the parenthetic substances, respectively. It is further shown that a necessary condition for the equality is $I^*(R_1) < I^*(R_2)$. If $I^*(R_1) > I^*(R_2)$, then it is found that $A(R_1^+) > I^*(R_1) + D(R_1 - R_2)$ and probably the neutral product accompanying the formation of R_1^+ is not R_2 but either R_2^* or $F_1 + F_2$ where the asterisk indicates electronic excitation and the F's smaller dissociation fragments.

The appearance potentials of $C_3H_8^+$, $C_3H_7^+$, $C_4H_9^+$ and $C_4H_8^+$ in the mass spectra of a number of branched alkanes have been measured. It is found that in these cases that the condition, $I^*(R_1) < I^*(R_2)$, is satisfied, the appearance potentials of the ions $C_3H_7^+$ and $C_4H_8^+$ are mutually consistent and the

intercombination of the appearance potentials with the appropriate thermochemical data lead to

$$D(\text{sec.-C}_3\text{H}_7\text{—H}) = 4.07 \pm 0.1 \text{ eV.}$$

$$D(\text{tert.-C}_4\text{H}_9\text{—H}) = 3.88 \pm 0.1 \text{ ,,}$$

$$I^*(\text{sec.-C}_3\text{H}_7) = 7.46 \pm 0.1 \text{ ,,}$$

$$I^*(\text{tert.-C}_4\text{H}_9) = 6.90 \pm 0.1 \text{ ,,}$$

It is thus found that the ionization potentials of the free radicals, CH_3 , C_2H_5 , $\text{sec.-C}_3\text{H}_7$ and $\text{tert.-C}_4\text{H}_9$ do not parallel the ionization potentials of the corresponding alkanes. It is suggested that it would be of interest to determine whether the quantum theory offers an explanation of this lack of parallelism.

It is shown that in certain mass spectrometers employing wolfram cathodes, there is insufficient differential pumping between the cathode and ionization chambers, and thus the apparent appearance potentials and intensities of certain ions in the mass spectra of some substances are falsified by the back diffusion of pyrolysis products in these mass spectrometers.

The measurement of the so-called appearance potentials of the ions characteristic of the mass spectra of substances as excited by single electron impact in the dilute gas provides a potentially powerful means of studying the energetics of not only ions but also unstable molecules such as free radicals. The same difficulties are encountered in the interpretation of data obtained with mass spectrometers as are encountered in the interpretation of optical spectra. These are the experimental ones of extrapolating observable intensities to limiting ones to determine characteristic energies and then associating the characteristic energies so determined with particular products and energy levels of the products. The mass spectrometric method has an advantage over optical methods in that in general the empirical formula of at least one of the products, the ionic one, is uniquely determined. This advantage is also a limitation on the method since it is thus required that only processes that lead to at least one ionic product can be studied.

The experimental problem of extrapolating observations on ionization efficiency curves of ions in mass spectra to obtain the so-called appearance potentials that can be associated with definite energies has been solved by semi-empirical means. Methods of extrapolation have been found that not only yield reproducible limiting energies, the appearance potentials, but yield energies in agreement with those found by other methods. Thus extrapolating ionization efficiency curves for the molecule-ions in the mass spectra of a number of olefins in the manner found appropriate for agreement between the appearance potentials of rare gas ions and the spectroscopically determined ionization potentials of the rare gases, leads to essential equality of the appearance potentials of the olefin molecule-ions and the ionization potentials of the olefins as determined from Rydberg series in their spectra in the vacuum ultra-violet.¹

The interpretation of the appearance potentials of fragment ions in the mass spectra of complex substances involves the following problems. What are the neutral fragments that are simultaneously formed, and what are the states of electronic excitation of the neutral products and the ionic one? In addition to these problems the possibility arises that due to peculiarities of the potential hyper-surface of the state of the molecule-ion from which the fragments have been formed, it has been necessary to endow the molecule-ion with more than the minimum energy necessary for the formation of the particular set of fragments in a particular set of states. In the simplest case this would correspond to an activation energy for the formation of the molecule-ion, $\text{R}_1\text{—R}_2^+$, from the radical R_1 and the ion R_2^+ .

It is the purpose of this discussion to show that in a number of cases the simplest set of assumptions suffice for the interpretation of the data to yield an apparently reliable determination of the energy of formation

¹ Honig, *J. Chem. Physics*, 1948, **16**, 105.

of the methyl radical. The methods employed for the determination of this energetic datum are employed to obtain the energies of formation and the ionization potentials of the *sec.*-propyl and *tert.*-butyl radicals from new experimental data on various C_5 — C_8 alkanes.

It has been found² that the appearance potentials of certain ions in the mass spectra of propane and butanes could not be interpreted by means of a simple set of assumptions concerning their processes of formation. Similar phenomena have been found with higher alkanes and a general rule is formulated for the prediction of those processes that may be interpretable through the simple assumptions. The origin of the failure of the simple assumptions has been explored by means of studies of isotopically labelled hydrocarbons.

Experimental

Measurements reported in this paper were made with a Westinghouse Type LV mass spectrometer somewhat modified in these laboratories. The modifications and the method of measurement have been described.^{3,4} The additive constant in the ionizing electron energy scale was determined by association of the initial break in the ionization efficiency curve of the argon ion, $40A^+$, with the spectroscopically determined ionization potential of argon, 15.76 eV.⁵ The possibility that the hydrocarbons might cause variation in the contact potentials associated with the electron gun was eliminated by making the measurements on argon simultaneously with those on the ions $C_3H_5^+$, $C_3H_6^+$, and $C_3H_7^+$ in the mass spectra of the hydrocarbons. The contributions of the ion, $C_3H_4^+$, to the $m/q = 40$ current were corrected for by determining the relation between the ratios $C_3H_4^+/C_3H_7^+$ and $C_3H_5^+/C_3H_7^+$ as a function of apparent ionizing electron energy characteristic of the hydrocarbon mass spectrum in the absence of argon. The ratio $C_3H_5^+/C_3H_7^+$ was then used as a pseudo-energy scale for the determination of the contributions of $C_3H_4^+$ to the $m/q = 40$ positive ion current at any given apparent ionizing electron energy in the presence of argon. No detectable difference was found between ionization efficiency curves of argon as measured in the presence or absence of hydrocarbons.

The appearance potentials were taken from the initial breaks of the ionization efficiency curves. The effects of range of the specific intensities of different ions were eliminated by the method of Smith,⁶ i.e. adjusting the intensity scale so that the linear portions of the ionization efficiency curves were all of the same slope.

The hydrocarbons upon which measurements were made were taken from the pure compound bank maintained by the Spectroscopic Department for calibration in spectrometric analyses. Linde Company spectroscopically pure argon was used. The appearance potentials that have been measured are given in Table I. Typical ionization efficiency curves are shown in Fig. 1-3.

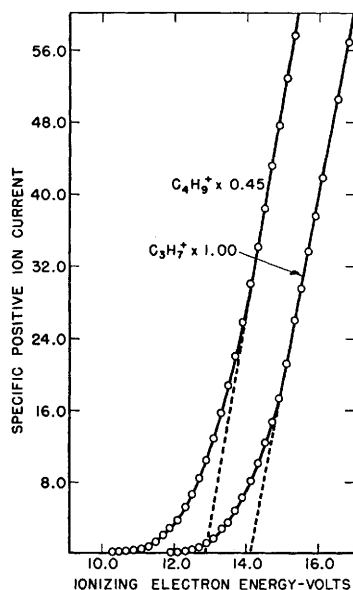


FIG. 1.—Ionization efficiency curves for the ions $C_4H_9^+$ and $C_3H_7^+$ of the 2 : 2 : 3-trimethylbutane mass spectrum.

² Stevenson and Hipple, *J. Amer. Chem. Soc.*, 1942, **64**, 1588.

³ Stevenson, *J. Chem. Physics*, 1950, **18**, 1347.

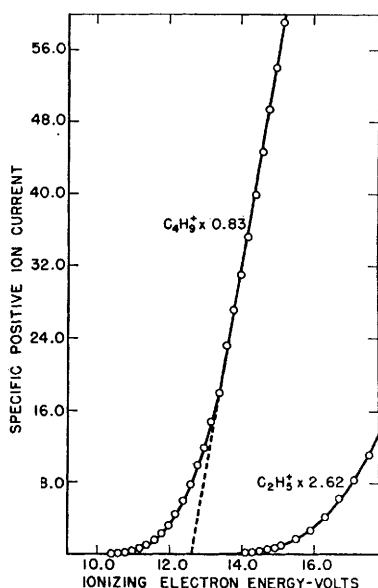
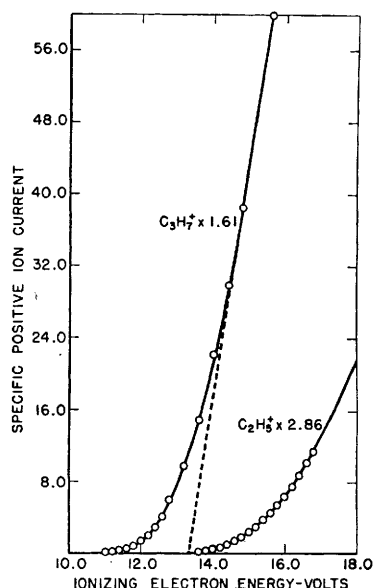
⁴ Stevenson and Wagner, *J. Chem. Physics*, 1951, **19**, 11.

⁵ Moore, *Atomic Energy Levels* (I Circular, Nat. Bur. Stand., c-467 (Washington, D.C., 1949).

⁶ Smith, *Physic. Rev.*, 1937, **51**, 263.

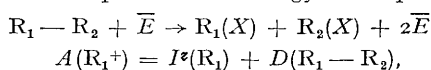
TABLE I.—APPEARANCE POTENTIALS OF ALKYL IONS IN ALKANE MASS SPECTRA

Molecule	$A(C_2H_5^+)$	$A(C_3H_7^+)$	$A(C_3H_7^+)$	$A(C_4H_9^+)$	$A(C_4H_9^+)$
<i>iso</i> -C ₄ H ₁₀	—	10·5 ₂ ± 0·1	11·0 ₁ ± 0·1	—	—
<i>iso</i> -C ₅ H ₁₂	13·2 ± 0·2	10·2 ₄ ± 0·1	10·8 ₄ ± 0·1	—	—
<i>neo</i> -C ₅ H ₁₂	—	—	—	10·3 ₂ ± 0·1	10·2 ₉ ± 0·1
2 : 3-Me ₂ -Butane	—	9·8 ₄ ± 0·2	10·7 ₉ ± 0·1	—	—
2 : 2-Me ₂ -Butane	13·6 ± 0·2	—	—	9·3 ± 0·2	10·1 ₉ ± 0·1
2 : 2 : 3-Me ₃ -Butane	—	—	11·8 ₄ ± 0·2	9·5 ₂ ± 0·2	10·0 ₉ ± 0·1
2 : 2 : 3 : 3-Me ₄ -Butane	—	—	—	9·2 ₄ ± 0·1	9·7 ₉ ± 0·1

FIG. 2.—Ionization efficiency curves for the ions C₄H₉⁺ and C₂H₅⁺ of the 2 : 2-dimethylbutane mass spectrum.FIG. 3.—Ionization efficiency curves for the ions C₃H₇⁺ and C₂H₅⁺ of the *isopentane* mass spectrum.

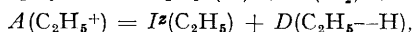
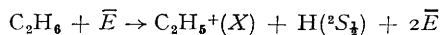
Discussion

The simplest assumption that can be made with respect to the significance of the appearance potential of an alkyl ion in the mass spectrum of an alkane is that it corresponds to the energy of the process,

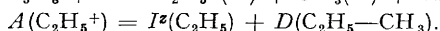
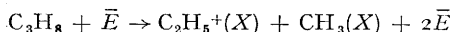


where X indicates the ground electronic state, $A()$ the appearance potential, $I^\circ()$ the ionization potential and $D()$ the dissociation energy. If such conditions obtain for the formation of an ion in the mass spectra of two substances, then the combination of the appearance potentials of the ion with the appropriate thermochemical data permits the determination of a dissociation energy. For example, the appearance potentials of the ethyl ion in the mass spectra of ethane and propane in combination with the heats of formation of methane, ethane and propane, and the

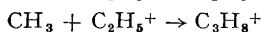
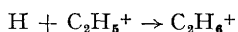
dissociation energy of hydrogen into hydrogen atoms would yield the dissociation energy of methane, $D(\text{CH}_3\text{—H})$, if



and

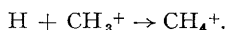


The dissociation energy of methane, $D(\text{CH}_3\text{—H})$, computed in this manner (termed the indirect method) could be in error if the two processes did not yield the ethyl ion in the same state, if the methyl radical were formed in an excited state or if either or both processes,



require an activation energy.

It has been found that the appearance potentials of molecule-ions themselves can be reasonably accurately associated with the ionization potential of the molecule. Thus, the dissociation energy of methane, $D(\text{CH}_3\text{—H})$, can be alternately calculated as the difference between the appearance potential of the methyl ion in the methane mass spectrum and the appearance (ionization) potential of the methyl ion in the methyl radical mass spectrum. Such a determination of $D(\text{CH}_3\text{—H})$ would of necessity be greater than or equal to the true value, and it would be greater only by virtue of an activation energy for the process

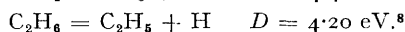
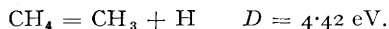
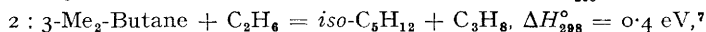
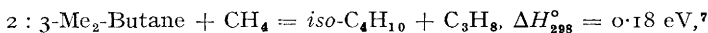


This second method of obtaining dissociation energies from appearance potentials is termed "the direct method". Agreement between determinations by the two methods would be strong argument for the validity of the simple assumption concerning these electron impact induced processes stated above.

In the case of $D(\text{CH}_3\text{—H})$, five pairs of processes have been examined and found to yield values that agree well within their experimental error. Furthermore, a direct measurement of the ionization potential of the methyl radical combined with either of two appearance potentials of the methyl ion gives $D(\text{CH}_3\text{—H})$ in excellent agreement with the values deduced from the appearance potential pairs by the indirect method. These data and results are summarized in Table II. There are also shown in this Table the results of determination of $D(\text{CH}_3\text{—H})$ from the kinetics of photochemical reactions and pyrolyses.

The complete agreement between the various determinations of $D(\text{CH}_3\text{—H})$ shown in Table II can be taken as evidence that electron impact induced processes of the simple type described above do exist. It further suggests that the data in Table I may be similarly interpreted to yield dissociation energies of propane and isobutane, $D(\text{sec.-C}_3\text{H}_7\text{—H})$ and $D(\text{tert.-C}_4\text{H}_9\text{—H})$, respectively.

The combination of the appearance potential, $A(\text{C}_3\text{H}_7^+)$ in the mass spectra of isobutane, isopentane and 2:3-dimethylbutane with the auxiliary data,



⁷ Rossini *et al.*, *Selected Values of Properties of Hydrocarbons* (Circular of the Nat. Bur. Stand., c-461, Washington D.C., 1947).

⁸ See (a) of Table II.

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TABLE II.—VARIOUS DETERMINATIONS OF $D(\text{CH}_3\text{—H})$

Method	Process	$D(\text{CH}_3\text{—H})$ eV
Direct E.I.	(a) $\text{CH}_3 \rightarrow \text{CH}_3^+ + \bar{E}$ with	
	(b) $\text{CH}_4 \rightarrow \text{CH}_3^+ + \text{H} + \bar{E}$	4.44 ± 0.2
	(c) $\text{CH}_3\text{OH} \rightarrow \text{CH}_3^+ + \text{OH} + \bar{E}$	4.48 ± 0.4
Indirect E.I.	(d) $\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5^+ + \text{H} + \bar{E}$ with	4.38 ± 0.2
	$\text{C}_3\text{H}_8 \rightarrow \text{C}_2\text{H}_5^+ + \text{CH}_3 + \bar{E}$	
	(e) $\text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_7^+ + \text{H} + \bar{E}$ with	4.34 ± 0.2
	$\text{iso-C}_4\text{H}_{10} \rightarrow \text{C}_3\text{H}_7^+ + \text{CH}_3 + \bar{E}$	
	(f) $\text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_5^+ + \text{H} + \bar{E}$ with	4.48 ± 0.2
	$\text{iso-C}_4\text{H}_8 \rightarrow \text{C}_3\text{H}_5^+ + \text{CH}_3 + \bar{E}$	
	(g) $n\text{-C}_3\text{H}_7\text{Cl} \rightarrow \text{C}_3\text{H}_7^+ + \text{Cl} + \bar{E}$ with	4.42 ± 0.2
	$n\text{-C}_4\text{H}_{10} \rightarrow \text{C}_3\text{H}_7^+ + \text{CH}_3 + \bar{E}$	
	(h) $\text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{OH}^+ + \text{H} + \bar{E}$ with	4.42 ± 0.2
	$\text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_2\text{OH}^+ + \text{CH}_3 + \bar{E}$	
Electron Impact		
Average		4.42 ± 0.04
Photochemical	(i) $\text{CH}_4 + \text{Br} \rightarrow \text{CH}_3 + \text{HBr}$	4.43 ± 0.05
	$\text{HBr} \rightarrow \text{H} + \text{Br}$	
Pyrolysis	(j) $\text{CH}_3\text{I} \rightarrow \text{CH}_3 + \text{I}$	$4.45 \pm ?$
	$\text{HI} \rightarrow \text{H} + \text{I}$	

(a) Hipple and Stevenson, *Physic. Rev.*, 1943, **63**, 121.

(b) Ref. (6) of text.

(c) Cumming and Bleakney, *Physic. Rev.*, 1940, **58**, 787.(d) Stevenson, *J. Chem. Physics*, 1942, **10**, 291.(g) Stevenson and Hipple, *J. Amer. Chem. Soc.*, 1942, **64**, 2766.

(h) See (c).

(i) Kistiakowsky *et al.*, *J. Chem. Physics*, 1942, **10**, 305 and 653; 1943, **11**, 6.(j) Polanyi *et al.*, *Nature*, 1940, **146**, 129 and 685; 1941, **147**, 542; *Trans. Faraday Soc.*, 1941, **37**, 377 and 648; 1943, **39**, 19.

result in

$$D(\text{sec.-C}_3\text{H}_7\text{—H}) = 4.07 \pm 0.1 \text{ eV,}$$

$$I^2(\text{sec.-C}_3\text{H}_7) = 7.45 \pm 0.1 \text{ eV,}$$

while from $A(\text{C}_4\text{H}_9^+)$ in the mass spectra of neopentane, 2:2-dimethylbutane, 2:2:3-trimethylbutane and 2:2:3:3-tetramethylbutane and the auxiliary data

$$2:2:3:3\text{-Me}_4\text{-Butane} + \text{CH}_4 = \text{neo-C}_5\text{H}_{12} + \text{iso-C}_4\text{H}_{10}, \Delta H_{298}^\circ = 0.03 \text{ eV,}^7$$

$$2:2:3:3\text{-Me}_4\text{-Butane} + \text{C}_2\text{H}_6 = 2:2\text{-Me}_2\text{-Butane} + \text{iso-C}_4\text{H}_{10}, \Delta H_{298}^\circ = -0.07,^7$$

$$2:2:3:3\text{-Me}_4\text{-Butane} + \text{C}_3\text{H}_8 = 2:2:3\text{-Me}_3\text{-Butane} + \text{iso-C}_4\text{H}_{10}, \Delta H_{298}^\circ = -0.07,^7$$

and $D(\text{CH}_3\text{—H})$ and $D(\text{C}_2\text{H}_5\text{—H})$

$$D(\text{tert.-C}_4\text{H}_9\text{—H}) = 3.87 \pm 0.2 \text{ eV,}$$

$$I^2(\text{tert.-C}_4\text{H}_9) = 6.92 \pm 0.2 \text{ eV,}$$

as summarized in Table III.

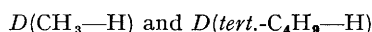
These dissociation energies for secondary and tertiary C—H bonds are in approximate agreement with the values given by Butler and Polanyi,

$$D(\text{sec.-C}_3\text{H}_7\text{—H}) = 3.86 \text{ eV and } D(\text{tert.-C}_4\text{H}_9\text{—H}) = 3.73 \text{ eV.}$$

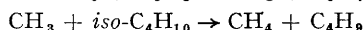
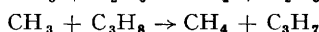
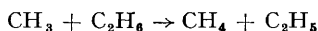
TABLE III.—VARIOUS INDIRECT ELECTRON IMPACT DETERMINATIONS OF $D(sec.-C_3H_7-H)$ AND $D(tert.-C_4H_9-H)$, AND OF $I^2(sec.-C_3H_7)$ AND $I^2(tert.-C_4H_9)$

Process	$D(R-H), I^2(R)$	
$iso-C_4H_{10} \rightarrow C_3H_7 + CH_3 + \bar{E}$	4.0 ₂	7.5 ₄
2:3-Me ₂ -Butane $\rightarrow C_3H_7 + C_3H_7 + \bar{E}$		
$iso-C_5H_{12} \rightarrow C_3H_7 + C_2H_5 + \bar{E}$	4.1 ₁	7.3 ₆
2:3-Me ₂ -Butane $\rightarrow C_3H_7 + C_3H_7 + \bar{E}$		
av. R = $sec.-C_3H_7$	4.0 ₇ \pm 0.1	7.4 ₆ \pm 0.1
$neo-C_5H_{12} \rightarrow C_4H_9 + CH_3 + \bar{E}$	3.8 ₉	6.8 ₈
2:2:3:3-Me ₄ -Butane $\rightarrow C_4H_9 + C_4H_9 + \bar{E}$		
2:2-Me-Butane $\rightarrow C_4H_9 + C_2H_5 + \bar{E}$	3.8 ₇	6.9 ₂
2:2:3:3-Me ₄ -Butane $\rightarrow C_4H_9 + C_4H_9 + \bar{E}$		
av. R = $tert.-C_4H_9$	3.8 ₈ \pm 0.1	6.90 \pm 0.1
2:2:3-Me ₃ -Butane $\rightarrow C_4H_9 + C_3H_7 + \bar{E}$	$D(sec.-C_3H_7-H) - D(tert.-C_4H_9-H) = 0.2$	
2:2:3:3-Me ₄ -Butane $\rightarrow C_4H_9 + C_4H_9 + \bar{E}$		
	vs.	4.0 ₇ - 3.8 ₈ = 0.1 ₉

The electron impact values for the dissociation energy of alkyl-hydrogen bonds differ in several respects from those from pyrolysis kinetics. These differences are: (i) a smaller range between



according to the electron impact method, i.e. 0.54 eV compared with 0.72 eV and (ii) the electron impact method gives less difference between $D(C_2H_5-H)$ and $D(sec.-C_3H_7-H)$ and greater difference between $D(sec.-C_3H_7-H)$ and $D(tert.-C_4H_9-H)$, respectively, than does the pyrolysis method. According to Steacie⁹ the activation energies for the reactions



are 8, 6.8 and 4.2 kcal./mole, respectively. To the extent that these activation energies reflect the strengths of the primary, secondary and tertiary carbon-hydrogen bonds, they suggest the order of the inequalities, $D(C_2H_5-H) > D(sec.-C_3H_7-H) > D(tert.-C_4H_9-H)$, by the electron impact method to be preferable to that given by the alkyl iodide pyrolysis method. It may be noted in this connection that the difference between the ionization potentials of propane and isobutane (0.9-1.0 eV)^{2,10} is greater than the difference between the ethane and propane ionization potentials (0.4 eV).^{2,10}

The ionization potentials of the alkyl radicals, CH_3 , C_2H_5 , $sec.-C_3H_7$ and $tert.-C_4H_9$, 10.0₇, 8.6₈, 7.4₅ and 6.9₂ eV, respectively, roughly parallel those of the corresponding alkanes, namely, 13.3,⁶ 11.7,² 11.3¹⁰ and 10.4² eV, respectively. However, the free radical ionization potentials do not show the discontinuity of trend between C_2 and C_3 shown by the alkane ionization potentials. It is not obvious to the author whether or not exact parallelism would be expected to exist between the ionization potentials of these two homologous series on theoretical grounds.

⁹ Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corp., New York, 1946), p. 520.

¹⁰ Delfosse and Bleakney, *Physic. Rev.*, 1939, **56**, 256.

Comparison of the mass spectrum of ordinary propane with those of *n*-propyl deuteride and *sec*.-propyl deuteride ⁴ has conclusively shown that in the formation of $C_3H_7^+$ in the propane mass spectrum it is one of the secondary hydrogens that dissociates. The sum of the ionization potential of the *sec*.-propyl radical and the dissociation energy of the secondary carbon-hydrogen bond given above is $11.5_2 \pm 0.1$ eV. This agrees within experimental error with the value found for the appearance potential of $C_3H_7^+$ in the propane mass spectrum, $11.6_7 \pm 0.1$ eV.¹¹

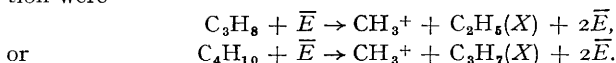
It has also been shown ⁴ that in the formation of $C_4H_9^+$ from *isobutane*, it is the tertiary hydrogen that dissociates. The sum of the ionization and dissociation energies, $I^*(tert.-C_4H_9)$ and $D(tert.-C_4H_9-H)$, given above, is 10.8 ± 0.3 eV. This is considerably less than the value found for the appearance potential of $C_4H_9^+$ in the *isobutane* mass spectrum, $11.5_7 \pm 0.2$ eV.² Since there are no sufficiently low states of the hydrogen atom, the difference between the calculated and observed appearance potential must be associated with excitation of the butyl ion.

If the previously found appearance potential of $C_4H_9^+$ in the mass spectrum of *tert*.-butyl chloride, $10.2_7 \pm 0.1$ eV,¹² is combined with the heat of formation of *tert*.-butyl chloride (-1.83 eV) and the dissociation energy of HCl (4.43 eV),¹³ the energy required for the formation of $C_4H_9^+ + H$ from *isobutane* is calculated to be $10.8_8 \pm 0.1$ eV, in excellent agreement with the value from the sum of ionization potential, $I^*(tert.-C_4H_9)$, and of dissociation energy, $D(tert.-C_4H_9-H)$, given above. Since the appearance potential of $C_4H_9^+$ in the *tert*.-butyl chloride mass spectrum is thus shown to be compatible with the data reported in this discussion, the dissociation energy of the tertiary carbon-chlorine bond may be taken as the difference between this appearance potential and the ionization potential of the *tert*.-butyl radical,

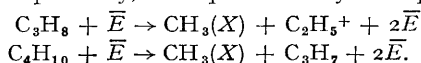
$$D(tert.-C_4H_9-Cl) = 10.2_7 - 6.9_0 = 3.3_7 \text{ eV.}$$

It may be noted that neither the appearance potential of $C_2H_5^+$ in the *isopentane* or 2 : 2-dimethylbutane mass spectra nor that of $C_3H_7^+$ in the 2 : 2 : 3-trimethylbutane mass spectrum has been employed to deduce dissociation energies. The reason for these omissions will now be discussed.

It was found that the appearance potentials of the methyl ion in the mass spectra of propane and the butanes ² were considerably greater (*ca.* 5-8 eV) than the minimum values to be expected from the sum of the ionization potential of the methyl radical (10.0_7 eV) and the dissociation energy of the carbon-carbon bonds being broken, if the processes of formation were



Thus, we may conclude the processes are not represented by the equations as written, although the seemingly complementary processes giving ethyl and propyl ions, respectively, are represented by the equations



Examination of the mass spectra of the monodeutero-propanes and butanes reveals the processes yielding CH_3^+ must be quite different from those yielding $C_2H_5^+$ (propane) or $C_3H_7^+$ (butanes). The intensities of the ions $C_2H_5D^+$ in the mass spectra of the isotopic propanes, *n*- C_3H_7D and *sec*.- C_3H_7D are approximately those to be expected from their molecular structure, and similarly for the intensities of the ions $C_3H_8D^+$ in the mass spectra of the monodeutero-butaness.⁴ However, contrary to

¹¹ Stevenson and Hipple, *J. Amer. Chem. Soc.*, 1942, **64**, 2769.

¹² Ref. (g) of Table II.

¹³ Herzberg, *Molecular Spectra and Molecular Structure* (Prentice Hall, New York, 1939).

expectations based on their molecular structure, CH_2D^+ appears in quite good yield in the mass spectra of *sec*.- $\text{C}_3\text{H}_7\text{D}$, *sec*.- $\text{C}_4\text{H}_9\text{D}$ and *tert*.- $\text{C}_4\text{H}_9\text{D}$. Thus, the formation of CH_3^+ from propane or butane must require the intermediate formation of an excited state of the molecule-ion, one in which there is considerable "reshuffling" of the atoms prior to dissociation. Examination of the ionization efficiency curves for the ions CH_3^+ and CH_2D^+ in the mass spectra of propane, *n*-propyl deuteride and *iso*-propyl deuteride reveals but a single state of C_3H_8^+ to be involved. This follows from the manner in which the ionization efficiency curves for CH_3^+ from C_3H_8 , *n*- $\text{C}_3\text{H}_7\text{D}$ and *sec*.- $\text{C}_3\text{H}_7\text{D}$ and CH_2D^+ from *n*- $\text{C}_3\text{H}_7\text{D}$ and *sec*.- $\text{C}_3\text{H}_7\text{D}$ can be superimposed. This is illustrated in Fig. 4 where there are shown the ionization efficiency curves for $\text{CH}_3^+(\text{C}_3\text{H}_8)$ and $\text{CH}_2\text{D}^+(\text{sec}.\text{-C}_3\text{H}_7\text{D})$.

Closer scrutiny of the mass spectra of the various isotopic propanes and butanes suggests a possible reason for requirement of an excited state of the molecule-ions, C_3H_8^+ and $\text{C}_4\text{H}_{10}^+$ for the formation of CH_3^+ . Although the intensities of C_2H_5^+ and $\text{C}_2\text{H}_4\text{D}^+$ in the mass spectra of *n*-propyl deuteride, and of C_3H_7^+ and $\text{C}_3\text{H}_8\text{D}^+$ in the mass spectra of the butyl deuterides were approximately those to be expected from the molecular structures, it was found that $n\text{-C}_3\text{H}_7\text{D} \quad \text{C}_2\text{H}_4\text{D}^+ \approx 1.2 \text{ C}_2\text{H}_5^+$ and similarly for *n*-butyl deuteride.⁴ Since such a large fraction of the propane and butane molecule-ions formed by electron impact dissociate, it does not seem likely that such an isotope effect can arise from differences in the amplitudes of oscillation in the various modes of propane and butane molecules. Rather, the isotope effects must arise from the small differences in zero point energy of the alternate dissociation products, e.g. $\text{C}_2\text{H}_4\text{D}^+ + \text{CH}_3 < \text{C}_2\text{H}_5^+ + \text{CH}_2\text{D}$. If this origin of the isotope effect is accepted, i.e. that a difference of the order of a few hundredths of an electron volt in the zero point energy of alternate dissociation paths on an energy hypersurface can effect the relative probability of the processes to the extent of 20 %, it would be expected that a process requiring an additional 1.2 eV would not be observable on that surface. Instead, to observe the ion requiring the higher energy it would be expected that a different intermediate surface (electronic state of the molecule-ion) would be required.

On the basis of the foregoing argument, it would be expected that the appearance potential of the ethyl ion in the *isopentane* and *neohexane* mass spectra and of the propyl ion in the *triptane* mass spectrum should be considerably greater than the sum of ionization potential and dissociation energy. Referring to Table II, it is found that

$$\text{isopentane, } A(\text{C}_2\text{H}_5^+) - A(\text{C}_3\text{H}_7^+) = 2.4 \text{ eV,}$$

$$\text{neohexane, } A(\text{C}_2\text{H}_5^+) - A(\text{C}_4\text{H}_9^+) = 3.4 \text{ eV,}$$

while the differences between the ionization potentials of the complementary pairs of ions are

$$I^\circ(\text{C}_2\text{H}_6) - I^\circ(\text{sec}.\text{-C}_3\text{H}_7) = 8.67 - 7.44 = 1.23 \text{ eV,}$$

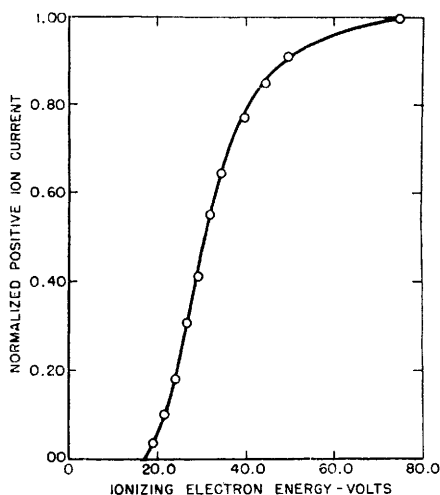


FIG. 4.—Normalized ionization efficiency curves for CH_3^+ from C_3H_8 (curve) and CH_2D^+ from *sec*.- $\text{C}_3\text{H}_7\text{D}$ (O).

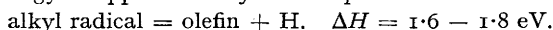
IONIZATION POTENTIALS

and $I^{\circ}(\text{C}_2\text{H}_5) - I^{\circ}(\text{tert.-C}_4\text{H}_9) = 8.67 - 6.92 = 1.75 \text{ eV}$,

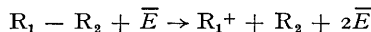
while triptane, $A(\text{C}_3\text{H}_7^+) - A(\text{C}_4\text{H}_9^+) = 1.75 \text{ eV}$,

and $I^{\circ}(\text{sec.-C}_3\text{H}_7) - I^{\circ}(\text{tert.-C}_4\text{H}_9) = 0.52 \text{ eV}$.

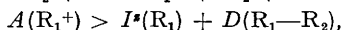
It is seen that extra energy of the magnitude of 1.2–1.7 eV is required. It may be of significance for the nature of the process that in these cases the extra energy is approximately that required for reactions of the type



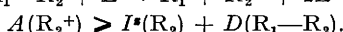
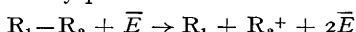
These results suggest the phenomenon first observed in the formation of the methyl ion in the mass spectra of propane and the butanes is indeed a general one and that there exists the general rule that for $I^{\circ}(\text{R}_1) > I^{\circ}(\text{R}_2)$, the process



requires

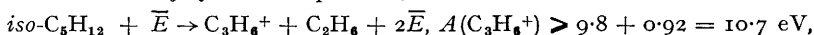


while for the complementary process



The existence of this rule greatly limits the potential of the electron impact method of determining dissociation energies. Having reliable values for the ionization potentials of the methyl and ethyl radicals, it was hoped that measurements of the appearance potentials of either CH_3^+ or C_2H_5^+ in the mass spectra of $\text{CH}_3\text{—R}$ or $\text{C}_2\text{H}_5\text{—R}$ would suffice to determine the energy of formation of the radical R by the formulae $D(\text{CH}_3\text{—R}) = A(\text{CH}_3^+) - I^{\circ}(\text{CH}_3)$ or $D(\text{C}_2\text{H}_5\text{—R}) = A(\text{C}_2\text{H}_5^+) - I^{\circ}(\text{C}_2\text{H}_5)$. However, for this direct procedure to be applicable, it is necessary that $I^{\circ}(\text{R}) > I^{\circ}(\text{CH}_3)$ or $I^{\circ}(\text{R}) > I^{\circ}(\text{C}_2\text{H}_5)$. These conditions make the method inapplicable to all C_3 and higher alkyl radicals.

The appearance potentials of the olefin ions, C_3H_6^+ and C_4H_8^+ , in the mass spectra of the *iso*-alkanes, Table I, present an interesting example of a difficulty that may beset electron impact studies. In agreement with previous findings² the appearance potential of C_3H_6^+ in the mass spectrum of *isobutane*, $10.5 \pm 0.1 \text{ eV}$, equals the sum of the ionization potential of propylene¹ ($9.80 \pm 0.05 \text{ eV}$) and the heat of the reaction, $\text{iso-C}_4\text{H}_{10} = \text{C}_3\text{H}_6 + \text{CH}_4$, $\Delta H_{298}^{\circ} = 0.80 \text{ eV}$. However, this appearance potential in the *isopentane* mass spectrum is lower than the least energy for the formation of C_3H_6^+ from *isopentane*,



and this appearance potential ($A(\text{C}_3\text{H}_6^+)$) in the 2 : 3-dimethylbutane mass spectrum equals the ionization potential of propylene! It can only be concluded that *isopentane* to a small extent and 2 : 3-dimethylbutane to a greater extent pyrolyze at the wolfram cathode to give propylene among other substances, and that this propylene diffuses back into the ionization chamber and thus falsifies measurements of C_3H_6^+ .

The appearance potential of C_4H_8^+ in the *neopentane* mass spectrum, $A(\text{C}_4\text{H}_8^+) = 10.3 \pm 0.1 \text{ eV}$ is equal to the sum of the ionization potential of *isobutylene* (9.35 eV)¹ and the heat of the reaction, $\text{neo-C}_5\text{H}_{12} = \text{iso-C}_4\text{H}_8 + \text{CH}_4$, $\Delta H_{298}^{\circ} = 0.80 \text{ eV}$. For 2 : 2-dimethylbutane, 2 : 2 : 3-trimethylbutane and 2 : 2 : 3 : 3-tetramethylbutane, the appearance potential of C_4H_8^+ is essentially equal to the ionization potential of *isobutylene*. Hence, here, too, pyrolysis and back diffusion must occur.*

It does not seem likely that these pyrolytic reactions can lead to products that would cause error in the measurements of the appearance potentials of the alkyl ions. This belief is based on the observation that

* It should be noted that these appearance potentials of C_4H_8^+ strongly support Honig's determination of the ionization potential of *isobutylene* and his conclusion that the value found by Stevenson and Hipple (*J. Amer. Chem. Soc.*, 1942, **64**, 2769), 8.9 eV, is in error.

with decreasing molecular weight the appearance potentials of alkyl ions increase. The low pressures obtaining in the mass spectrometer preclude association reactions that could lead to higher molecular weight substances which might cause low apparent appearance potentials. Furthermore, such substances would have been detected in the recordings of the complete mass spectra. If the pyrolyses lead to appreciable quantities of alkyl radicals C_3H_7 and C_4H_9 , and these are sufficiently long lived to diffuse through the four slits that separate the cathode from the ionization chamber, it is conceivable that the appearance potentials of $C_3H_7^+$ and $C_4H_9^+$ given in Table II are low in the cases other than *isobutane* and *neopentane*. However, the internal consistency of the appearance potentials indicates such effect, if any, must be less than the experimental error.

It is to be noted that the pyrolysis and back diffusion is not unique to the Westinghouse Type L.V. mass spectrometer. Koffel and Lad,¹⁴ using a spectrometer of quite different construction, have reported for *isopentane*, $A(C_3H_8^+) = A(C_3H_7^+) - 0.9$ eV; for 2:3-dimethylbutane, $A(C_3H_8^+) = A(C_3H_7^+) - 1.7$ eV; for 2:2-dimethylbutane, $A(C_4H_9^+) = A(C_4H_8^+) - 1.0$ eV; and for 2:2:3-trimethylbutane, $A(C_4H_9^+) = A(C_4H_8^+) - 1.1$ eV. These differences are quite like those reported in Table II, and thus we conclude their mass spectrometer also suffers from insufficient differential pumping between the cathode chamber and the ionization chamber.

In view of the above, it is apparent that the reported intensities of such ions as $C_3H_8^+$, $C_4H_9^+$ and the like in the mass spectra of branched alkanes, the A.P.I. 44 Catalog of Mass Spectra, are of no real significance as far as indicating the probability of the formation of such ions by electron impact induced dissociations.

The fact that the appearance potentials of the propylene and butylene ions in the mass spectra of *isobutane* and *neopentane*, respectively, are essentially equal to the sum of the heat of the reaction; alkane = olefin plus methane and the ionization potential of the olefin indicates the absence of significant activation energy for the reverse reaction, olefin ion plus methane equals alkane ion. The absence of activation energy for this reaction indicates there may well be no activation energy for a reaction of the type, *n*-alkane ion \rightarrow *sec.*-alkyl ion plus *sec.*-alkyl radical. Thus it seems likely that the electron impact method is inapplicable to the evaluation of energies of formation and ionization potentials of C_3 and higher normal alkyls. Incomplete interpretation of data on the appearance potentials of $C_3H_7^+$ and $C_4H_9^+$ in the mass spectra of *n*-pentane, *n*-hexane, *n*-heptane and *n*-octane appears to substantiate this conclusion.¹⁵

The author wishes to express his deep appreciation of the late Dr. Otto Beeck's continued encouragement in the here-described and other research.

Shell Development Company,
Emeryville,
California.

¹⁴ Koffel and Lad, *J. Chem. Physics*, 1948, **16**, 420. These authors made an extensive investigation of electron impact induced processes in the C_1 - C_7 alkanes. However, their use of linear intercepts as measures of appearance potentials renders their data non-comparable with the present work. Further, it has been shown that (*Physic. Rev.*, 1943, **63**, 121; *J. Chem. Physics*, 1950, **18**, 1347) appearance potentials deduced in this manner (linear intercepts) are not the minimum energies for dissociation processes. However, the linear intercepts do provide an approximate measure of the difference between appearance potentials.

¹⁵ That such ambiguity as this might arise in the interpretation of alkyl ion appearance potentials has been suggested to the author by Prof. S. Winstein, private communication.