## Summary[14]

1. Crotoxin, the crystalline neurotoxin isolated from rattlesnake venom, has been shown to be a homogeneous substance in electrophoresis experiments.

2. Crotoxin solutions do not exhibit the phenomenon of "reversible boundary spreading" to a detectable extent, in contradistinction to all other proteins studied.

3. The isoelectric point of crotoxin has been determined and the $d\mu/dpH_0$ value.

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[14] The authors are indebted to Dr. L. G. Longsworth for his suggestions during the preparation of the manuscript.

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[CONTRIBUTION FROM THE WESTINGHOUSE RESEARCH LABORATORIES]

# Ionization and Dissociation by Electron Impact: Normal Butane, Isobutane, and Ethane

BY D. P. STEVENSON[1] AND J. A. HIPPLE, JR.

## Introduction

Mass spectrometer studies of the dissociation products resulting from electron bombardment of gases at low pressures have provided many interesting and instructive results. In particular, the work on the lower hydrocarbons, methane,[2] ethane,[3] ethylene,[4,5] propane,[6] propylene[6] and allene[6] has yielded considerable data on energies and unimolecular reactions of the ions $CH_4^+$, $C_2H_6^+$, etc., not obtainable in any other way. It was felt that the extension of such studies to one of the simplest isomeric pairs, *n*- and *i*-butane, would be helpful in deciding or at least defining questions of interpretation raised by the work on the simpler molecules. Furthermore, the continually growing interest in the application of the mass spectrometer to problems in the analysis of hydrocarbon mixtures makes necessary a knowledge of the complete mass spectra, so that the limitations of this analytical tool can be discussed. With this latter point in mind we have extended the results of the previously published investigation of ethane.[3]

## Experimental

Inasmuch as the apparatus is to be described in detail by one of the authors (J. A. H.) in a separate publication, we will give but a cursory discussion of the pertinent details here.

The 180° tube (~16 cm. radius) and accessories are supported within a water-cooled spherical solenoid. The strength of the magnetic field used throughout this investigation was ~1000 Oersteds, corresponding to 130 volts accelerating potential to bring $m/e = 100$ into focus. The positive ion accelerating voltage is supplied by a 1200 volt electronic power source. The electrons are obtained from an oxide coated platinum cathode, their accelerating potential being controlled by means of a wire wound drum potentiometer. An electrometer tube amplifier and sensitive galvanometer are used to measure the positive ion current. The resolving power of the tube with the wide slits used is 1:150 as indicated by the extent to which the mercury isotopes are resolved.

The gases are admitted to the ionization chamber through a glass capillary leak. A separate pumping lead to the arm of the tube containing the cathode chamber assures the complete removal of any pyrolysis products formed on the filament.

The samples of the two butanes were obtained from the Gulf Research Laboratories, while the ethane was taken from a sample given to us by the Standard Oil Co. of Indiana.

Preliminary examinations of the mass spectra of the butanes were made using an automatic recorder. The peaks corresponding to the various masses were all quite symmetrical, and were spaced in exact accord with the inverse relationship between $m/e$ and accelerating voltage. No satellites or shoulders were observed for any of the masses. The measurements reported in this paper were all manually recorded. The symmetry of the peaks indicated that the current at the top of the maxima could be taken as a measure of the total current due to the corresponding ion. The linear variations of the positive ion current with the density of the electron beam and with the pressure in the ionization chamber indicate that only the products of primary reactions were observed. The total electron emission from the cathode ran from 5 to 15 $\mu$ amp., while the intensity of the bombarding beams lay between 0.1 and 3 $\mu$ amp.

## Results

The results of this investigation may be divided, for convenience, into two parts: (A) the variation of the mass spectra of the molecules with the electron energy, $V^-$, for $V^-$ large with respect to the critical potentials; and (B) the determination

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(1) Westinghouse Research Fellow.

(2) L. G. Smith, *Phys. Rev.*, **51**, 263 (1937).

(3) J. A. Hipple, *ibid.*, **53**, 530 (1938).

(4) P. Kusch, A. Hustrulid and J. T. Tate, *ibid.*, **52**, 843 (1937).

(5) J. Delfosse and J. A. Hipple, *ibid.*, **54**, 1060 (1938).

(6) J. Delfosse and W. Bleakney, *ibid.*, **56**, 256 (1939).

of the critical potentials for the more abundant ions in the mass spectra.

**A.** The relative abundances of some of the principal ions in the spectrum of ethane are given for round values of $V^-$ in Table I. The dots in this and subsequent tables indicate no measurements were made. The data of Hipple[3] for 100 volt electrons are included for comparison. Since the earlier work was carried out with a tube whose focusing properties are independent of the initial velocity of the ions[7] in contrast to our tube in which the initial velocities of the ions enter into the focusing, the agreement is very satisfactory.

TABLE I

MASS SPECTRUM OF ETHANE

| $m/e$ = <br> $V^-$, e. v. | 30 <br> $C_2H_6^+$ | 29 <br> $C_2H_5^+$ | 28 <br> $C_2H_4^+$ | 27 <br> $C_2H_3^+$ | 26 <br> $C_2H_2^+$ | 25 <br> $C_2H^+$ | 15 <br> $CH_3^+$ |
|---|---|---|---|---|---|---|---|
| 30 | 100 | 72 | 347 | 70 | 29.5 | .. | 7.3 |
| 60 | 132 | 101 | 462 | 147 | 99 | .. | 11.8 |
| 100 | 135 | 106 | 488 | 153 | 101 | 16 | 15.5 |
| 100[a] | (135)[b] | 103 | 486 | 142 | 84 | 16 | 12 |
| 175 | 126 | 99 | 452 | 140 | 88 | .. | 12.5 |

[a] Ref. 3 of the text. [b] This value assumed to fit our scale.

TABLE II

MASS SPECTRUM OF $n$-BUTANE

| $m/e$ = <br> $V^-$ | 58 <br> $C_4H_{10}^+$ | 57 <br> $C_4H_9^+$ | 56 <br> $C_4H_8^+$ | 55 <br> $C_4H_7^+$ | 54 <br> $C_4H_6^+$ | 53 <br> $C_4H_5^+$ | 52 <br> $C_4H_4^+$ | 51 <br> $C_4H_3^+$ | 50 <br> $C_4H_2^+$ | 49 <br> $C_4H^+$ | 48 <br> $C_4^+$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 30 | 100 | 13.5 | 3.4 | 3.5 | ... | ... | ... | ... | ... | ... | ... |
| 50 | 119 | 15.3 | 4.4 | 5.6 | 1.1 | 4.2 | 1.2 | 3.9 | 3.3 | 0.4 | <0.1 |
| 100 | 125 | 16.0 | 4.4 | 5.6 | 1.1 | 4.1 | 1.4 | 5.3 | 7.3 | 2.5 | ... |

| $m/e$ = <br> $V^-$ | 43 <br> $C_3H_7^+$ | 42 <br> $C_3H_6^+$ | 41 <br> $C_3H_5^+$ | 40 <br> $C_3H_4^+$ | 39 <br> $C_3H_3^+$ | 38 <br> $C_3H_2^+$ | 37 <br> $C_3H^+$ | 36 <br> $C_3^+$ |
|---|---|---|---|---|---|---|---|---|
| 30 | 462 | 68 | 105 | ... | 12.1 | ... | ... | ... |
| 50 | 530 | 79 | 140 | 7.3 | 52 | 5.7 | 2.0 | <0.1 |
| 75 | 555 | 82 | 149 | ... | 53 | 7.4 | 3.9 | 0.4 |
| 100 | 580 | 83 | 153 | 7.9 | 52 | 8.1 | 4.6 | 0.7 |

| $m/e$ = <br> $V^-$ | 29 <br> $C_2H_5^+$ | 28 <br> $C_2H_4^+$ | 27.5 <br> $C_4H_7^{++}$ | 27 <br> $C_2H_3^+$ | 26.5 <br> $C_4H_5^{++}$ | 26 <br> $C_2H_2^+$ | 25.5 <br> $C_4H_3^{++}$ | 25 <br> $C_2H^+$ | 15 <br> $CH_3^+$ |
|---|---|---|---|---|---|---|---|---|---|
| 30 | 162 | 125 | .. | 71 | .. | .. | ... | ... | 1.2 |
| 50 | 222 | 164 | .. | 172 | .. | .. | ... | ... | 12.8 |
| 70 | 236 | ... | 0.15 | ... | 0.27 | 27 | 1.9 | 1.7 | .. |
| 100 | 240 | 179 | .. | 184 | .. | 31 | ... | ... | .. |

TABLE III

MASS SPECTRUM OF $i$-BUTANE

| $m/e$ = <br> $V^-$ | 58 <br> $C_4H_{10}^+$ | 57 <br> $C_4H_9^+$ | 56 <br> $C_4H_8^+$ | 55 <br> $C_4H_7^+$ | 54 <br> $C_4H_6^+$ | 53 <br> $C_4H_5^+$ | 52 <br> $C_4H_4^+$ | 51 <br> $C_4H_3^+$ | 50 <br> $C_4H_2^+$ | 49 <br> $C_4H^+$ | 48 <br> $C_4^+$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 30 | 100 | 32 | ... | ... | ... | ... | ... | ... | ... | ... | .. |
| 50 | 117 | 37 | 7.5 | 6.8 | 1.4 | 6.4 | 1.5 | 5.9 | 4.9 | 0.7 | 0.15 |
| 100 | 123 | 39 | 7.7 | 6.9 | 0.9 | 5.5 | 1.5 | 7.6 | 9.7 | 3.2 | 0.79 |

| $m/e$ = <br> $V^-$ | 43 <br> $C_3H_7^+$ | 42 <br> $C_3H_6^+$ | 41 <br> $C_3H_5^+$ | 40 <br> $C_3H_4^+$ | 39 <br> $C_3H_3^+$ | 38 <br> $C_3H_2^+$ | 37 <br> $C_3H^+$ | 36 <br> $C_3^+$ |
|---|---|---|---|---|---|---|---|---|
| 30 | 877 | 292 | 248 | .. | 29 | .. | .. | .. |
| 50 | 1020 | 344 | 352 | 18.7 | 120 | 13.7 | 4.8 | 0.26 |
| 75 | 1070 | 354 | 370 | 19.2 | 128 | 16.7 | 10.1 | 0.74 |
| 100 | 1070 | 361 | 377 | 18.6 | 120 | 20.2 | 11.4 | 1.30 |

| $m/e$ = <br> $V^-$ | 29 <br> $C_2H_5^+$ | 28 <br> $C_2H_4^+$ | 27 <br> $C_2H_3^+$ | 26 <br> $C_2H_2^+$ | 25.5 <br> $C_4H_3^{++}$ | 25 <br> $C_2H^+$ | 15 <br> $CH_3^+$ |
|---|---|---|---|---|---|---|---|
| 30 | 128 | 80 | 126 | .. | ... | ... | 2.0 |
| 50 | 188 | 112 | 279 | 21 | ... | ... | 29 |
| 100 | 196 | 122 | 296 | 32 | 2.8 | 2.7 | 37 |

Tables II and III summarize the behavior of the spectra of the butanes. No corrections were made for the presence of $C^{13}$ in its natural abundance, 1.1%. Thus the spectra as given correspond to the mass numbers ($m/e$), rather than to the formulas. Since the correction is small and the relative currents due to the masses are of analytical interest, the uncorrected values have been tabulated.

Careful comparison of the ratios of the currents due to masses 44 and 43 and masses 30 and 29 showed that the butane samples were free of propane and ethane. The exact correspondence of the ratio 44/43 to that calculated for

$$\left(\frac{C^{13}C_2^{12}H_7^+}{C_3^{12}H_7^+}\right) \text{ and of } \frac{30}{29} \text{ to } \left(\frac{C^{13}C^{12}H_5^+}{C_2^{12}H_5^+}\right)$$

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(7) W. Bleakney and J. A. Hipple, *Phys. Rev.*, **53**, 521 (1938).

indicated that neither of the butanes gives the ions $C_3H_8^+$ or $C_2H_6^+$. This point will be returned to later.

The currents of masses $29^+$ and $28^+$ could conceivably be due in part to $C_4H_{10}^{++}$ and $C_4H_8^{++}$. We searched very carefully, but were unable to find currents due to masses 29.5 or 28.5 ($C^{13}C^{12}_3H_{10}^{++}$ or $C^{13}C^{12}_3H_8^{++}$), hence concluded that the ions $C_4H_{10}^{++}$, $C_4H_9^{++}$ and $C_4H_8^{++}$ are absent from the butane spectra.

**B.** The method used to derive the critical or appearance potential, $A(X^+)$, from the initial portions of the ionization efficiency curves has been discussed by Smith[2] (see below). Argon was used to correct the voltage scale for the contact potential of the cathode. Its ionization potential, $I^Z(A) = 15.69$ e. v. was taken from the tables of Bacher and Goudsmit.[8]

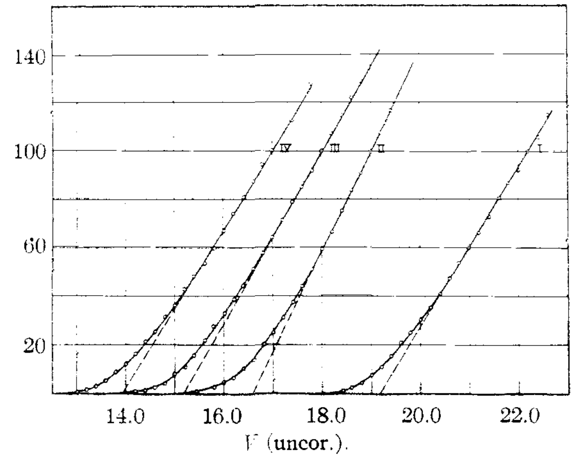

Fig. 1.—Ionization efficiency curves for the processes I, A → $A^+$; II, $C_2H_6 \rightarrow C_2H_5^+$; III, $C_2H_6 \rightarrow C_2H_6^+$ and IV, $i$-$C_4H_{10} \rightarrow C_4H_{10}^+$. Vertical scale is arbitrary and different for each curve.

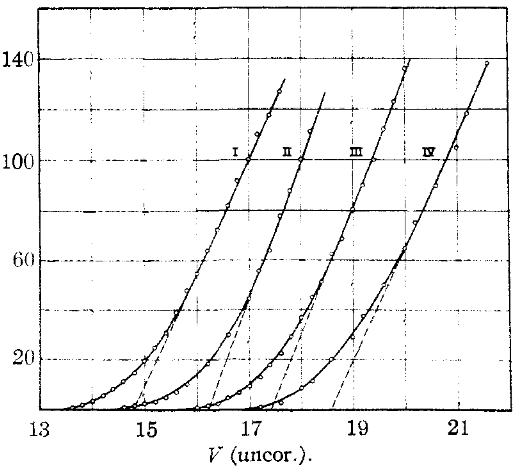

Fig. 2.—Ionization efficiency curves for the processes I, $i$-$C_4H_{10} \rightarrow C_3H_7^+$; II, $n$-$C_4H_{10} \rightarrow C_2H_5^+$; III, $i$-$C_4H_{10} \rightarrow C_3H_5^+$ and IV, $n$-$C_4H_{10} \rightarrow C_2H_3^+$. Vertical scale is arbitrary and different for each curve.

In Table IV the results of our investigation of ethane are compared with the earlier results of Hipple.[3] The agreement between the results given by such very different instruments is excellent.[8a]

TABLE IV

| Ion | $A$ (ion) [This Research], e. v. | $A$ (ion) [Hipple[3]], e. v. |
|---|---|---|
| $C_2H_6^+$ | 11.59 ± 0.1 | 11.6 ± 0.1 |
| $C_2H_5^+$ | 12.84 ± 0.1 | 12.7 ± 0.2 |
| $C_2H_4^+$ | 12.09 ± 0.1 | 12.1 ± 0.1 |
| $C_2H_3^+$ | 15.1 ± 0.2 | 15.2 ± 0.3 |

The appearance potentials of those ions in the spectra of the butanes, which were investigated, are given in Table V. Typical examples of the ionization efficiency curves from which the appearance potentials were determined are given in Figs. 1 and 2.

TABLE V

APPEARANCE POTENTIALS FOR $n$- AND $i$-BUTANE (ELECTRON VOLTS)

| ion = $R^+$ | $A_6(R^+)$ $n$-$C_4H_{10}$ | $A_6(R^+)$ $i$-$C_4H_{10}$ | Probable process |
|---|---|---|---|
| $C_4H_{10}^+$ | 10.34 ± 0.1 | 10.34 ± 0.1 | $C_4H_{10}^+ + \epsilon^-$ |
| $C_4H_9^+$ | 12.0 ± 0.3 | 11.5 ± 0.3 | ${}^xC_4H_9^+ + H + \epsilon^-$ |
| $C_3H_7^+$ | 11.14 ± 0.1 | 10.94 ± 0.1 | $C_3H_7^+ + CH_3 + \epsilon^-$ |
| $C_3H_6^+$ | 10.94 ± 0.1 | 10.74 ± 0.1 | ${}^xC_3H_6 + CH_4 + \epsilon^-$ |
| $C_3H_5^+$ | 13.09 ± 0.1 | 13.54 ± 0.1 | ${}^xC_3H_5^+ + \left\{\begin{array}{l} CH_4 + H \\ CH_3 + H_2 + \epsilon^- \end{array}\right.$ |
| $C_2H_5^+$ | 12.04 ± 0.1 | 12.7 ± 0.2 | $C_2H_5^+ + C_2H_5 + \epsilon^-$ |
| $C_2H_4^+$ | 11.49 ± 0.1 | 12.0 ± 0.2 | ${}^xC_2H_4^+ + C_2H_6 + \epsilon^-$ |
| $C_2H_3^+$ | 14.1 ± 0.3 | 14.6 ± 0.3 | ${}^xC_2H_3^+ + ? + \epsilon^-$ |
| $CH_3^+$ | >20 | 20 ± 2 | $CH_3^+ + C_3H_7^+ + 2\epsilon^-$ |

[x] Ambiguity with respect to the structure of the positive ion; see text.

The method employed in determining the critical potentials given in Tables IV and V is not completely satisfactory. Considerable personal factors may be involved in the choice of the initial break ($V_B^-$) of the ionization efficiency curve, $I^+(V^-)$. Furthermore, greatest weight is given to measurements of least accuracy, that is, those near the appearance potential. For these reasons

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(8) R. F. Bacher and S. Goudsmit, "Atomic Energy States," McGraw-Hill Book Co., New York, N. Y., 1932.

(8a) The reason that our value of $A(C_2H_5^+)$ is higher than Hipple's lies in the fact that we corrected our ionization efficiency curve for mass 29 for the contribution by the ion $C^{13}C^{12}H_4^+$. This correction was suggested by Dr. O. Beeck and Mr. Eltenton of the Shell Development Co. in a letter to one of the authors. The value of $A(29^+)$ derived from the uncorrected ionization efficiency curve is in exact agreement with Hipple's value. It may be noted that the correction is entirely insignificant for similar processes in the butanes.

we examined the curves, $I^+(V^-)$, for various processes in ethane, the butanes, argon and neon very carefully in the hope that some other characteristic, subject to a more objective determination, could be used in estimating the appearance potentials.

The observation that all the ionization efficiency curves, $I^+(V^-)$, are linear over the range $\sim 7\%$ to $\sim 65\%$ of their maximum values, suggested that the intercept of the extrapolated linear portion with the $V^-$ axis ($I^+ = 0$), $V_L^-$, might be used in making estimates of the appearance potentials. It was found that for the process, $R \rightarrow R^+ + \epsilon^-$, in eight atoms or molecules[9] $V_L^- - V_B^- = 1.06_5$ volts. The mean deviation was $\pm$ 0.06 volt and the maximum deviation was 0.12 volt from the average, which are well within the uncertainty of the individual measurements. Thus the linear intercepts, $V_L^-$, can be used in place of the initial breaks, $V_B^-$, in determining the appearance potentials of the parent ions.

For more complex processes, such as those involving the rupture of a C–C or a C–H bond, the difference $V_L^- - V_B^-$ is also constant but greater than for simple ionization. Eleven reactions of the types, $R—CH_3 \rightarrow R^+ + CH_3$ or $R—H \rightarrow R^+ + H$, have $V_L^- - V_B^- = 1.54 \pm 0.09$ volts. In a recent article one of the authors[10] applied differences between the $V_B^-$'s for such reactions to the estimation of C–H and C–C bond strengths. The use of $V_L^-$'s gives the same results. If one wishes to compare the appearance potentials of the reactions $R_1—R_2 \rightarrow R_1—R_2^+ + \epsilon$ and $R_1—R_2 \rightarrow R_1^+ + R_2 + \epsilon^-$, the apparent difference given by the $V_L^-$'s is $\sim$0.5 volt greater than that given by the $V_B^-$'s.

The still more complex processes, such as the formation of $C_2H_3^+$ from ethane, normal or isobutane, have $V_L^- - V_B^- = 2.3 \pm 0.2$ volts. The various phenomena discussed here are illustrated in Figs. 1 and 2.

## Discussion

Ignoring the questions concerning the suitability of the method used to correct the voltage scale, we may associate the appearance potentials of the parent ions, $C_2H_6^+$, $i$-$C_4H_{10}^+$ and $n$-$C_4H_{10}^+$ with their vertical ionization potentials.[11] It has been pointed out by Mulliken[12] that the lowest ionization potential in ethane is probably that of removing an electron from the C–C bonding orbital $[\sigma + \sigma]$ and that $I_{\text{vert}}$ $[\sigma + \sigma]$ is undoubtedly greater than $I_{\text{adiabatic}}$ $[\sigma + \sigma]$. The reason for the inequality $I_{\text{vert}} > I_{\text{ad}}$ lies in the fact that the removal of a bonding electron will cause an increase in the equilibrium separations of the atoms. In ethylene a comparison of the appearance potential of $C_2H_4^+$ (10.8 e. v.)$^{-1}$ with the spectroscopic ionization potential $I_{\text{ad}}(C_2H_4) = 10.41$ e. v.[13] suggests that in ethane the inequality is at least 0.4 e. v. Thus, one might estimate $I_{\text{ad}}(C_2H_6) \leq 11.6 - 0.4 = 11.2$ e. v. The electron removed in ionizing a butane probably comes from the same type of orbital as in ethane. Since the electron deficiency is much less in the ions $C_4H_{10}^+$ than in $C_2H_6^+$ it is likely that $I_{\text{vert}} \sim I_{\text{ad}}$, and thus from Table V, $I_{\text{ad}}(C_4H_{10}) \leq 10.34 \pm 0.1$ e. v.

If we take the strength of the first C–H bond in ethane as 4.2 e. v.[10] and the appearance potential, $A(C_2H_5^+) = 12.7$ e. v. given in Table IV as the heat of the reaction $C_2H_6 \rightarrow C_2H_5^+ + H$, we find $I_{\text{ad}}(C_2H_5) = 8.5$ e. v. If the linear intercepts discussed above were used to estimate the appearance potentials, this value would be increased by 0.5 e. v. to $I_{\text{ad}}(C_2H_5) = 9.0$ e. v. It is clear that a reliable direct measurement of $I_{\text{ad}}(C_2H_5)$ would be extremely valuable in determining the relative merits of the two possible modes of calibrating the voltage scale.

The relative reactivities of C–H bonds are in the order primary < secondary < tertiary. The lower value of $A(C_4H_9^+)$ in isobutane than in $n$-butane is probably due in part to this. The greater number of C–C acceptor bonds for hyper conjugation[14] in the $t$-$C_4H_9^+$ ion (3) than in the $s$-$C_4H_9^+$ ion (2) probably results in greater stability for the former. Thus one might expect $I_{\text{ad}}(t\text{-}C_4H_9) < I_{\text{ad}}(s\text{-}C_4H_9)$. If one guesses that the inequality signs in the reactivity sequence correspond to $\sim$0.1 e. v.[15] and that the strength of a primary C–H bond is 4.2 e. v.,[10] we get

$$D[s\text{-}C_4H_9\text{-}H] = 4.2 - 0.1 = 4.1 \text{ e. v.}$$
$$D[t\text{-}C_4H_9\text{-}H] = 4.2 - 0.2 = 4.0 \text{ e. v.}$$

Combining these estimates with the corresponding appearance potentials from Table V, we find

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(9) Neon, argon, ethane, $n$- and $i$-butane, propane, propylene and isobutene.

(10) D. P. Stevenson, *J. Chem. Phys.*, submitted for publication.

(11) By "vertical transition" we are to understand the transitions favored by the Frank–Condon principle. We will use "adiabatic" to indicate transition from $v' = 0$ to $v'' = 0$, where $v$ is the vibrational quantum no.

(12) R. S. Mulliken, *J. Chem. Phys.*, **3**, 517 (1935).

(13) W. C. Price, *Phys. Rev.*, **47**, 444 (1935).

(14) R. S. Mulliken, C. A. Rieke and W. G. Brown, THIS JOURNAL, **63**, 41 (1941).

(15) J. O. Smith and H. S. Taylor, *J. Chem. Phys.*, **7**, 39 (1939).

$I_{ad}(s\text{-}C_4H_9)$ = 7.9 e. v. and $I_{ad}(t\text{-}C_4H_9)$ = 7.5 e. v. Due to the low precision of the appearance potentials of $C_4H_9^+$ from the butanes great weight cannot be given to these estimates of $I_{ad}(C_4H_9)$.

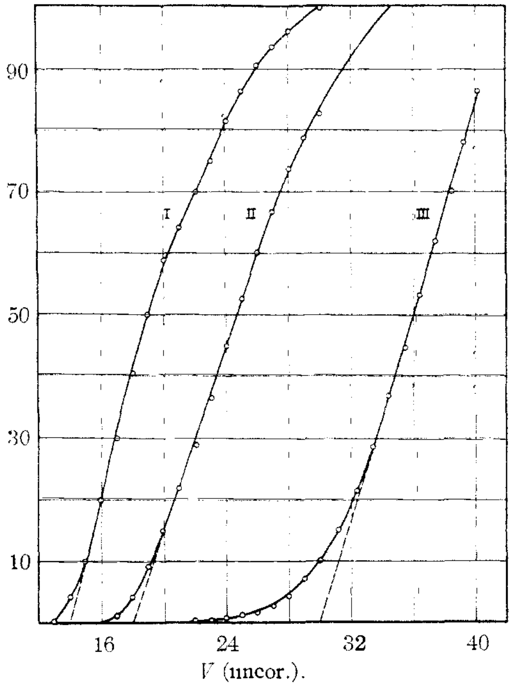

Fig. 3.—Ionization efficiency curves for I, $i\text{-}C_4H_{10} \rightarrow i\text{-}C_4H_{10}^+$; II, $i\text{-}C_4H_{10} \rightarrow C_3H_5^+$; and III, $i\text{-}C_4H_{10} \rightarrow CH_3^+$. Vertical scale is different for each curve. Maximum values are I, 121; II, 123; and III, 180. Compare with Table III.

It seems reasonable to assume that no molecular rearrangement accompanies the formation of $C_3H_7^+$ from either butane. Then, since isobutane is 0.07 e. v.[16] more stable than normal butane one concludes from the values of $A(C_3H_7^+)$ given in Table V that $s\text{-}C_3H_7^+$ is 0.3 e. v. lower in energy than $n\text{-}C_3H_7^+$. If a secondary C–H bond is 0.1 e. v. weaker than a primary C–H bond, we can write, $I_{ad}(s\text{-}C_3H_7) + 0.2$ e. v. = $I_{ad}(n\text{-}C_3H_7)$.

The high value of the appearance potential of $CH_3^+$ in both butanes is probably to be attributed to the simultaneous formation of $C_3H_7^+$. If the vertical ionization of $C_4H_{10}$ to $C_4H_{10}^{++}$ results in the doubly charged ion being formed in a state above the dissociation limit this result is explained. Our failure to observe any $C^{13}C^{12}_3H_{10}^{++}$ ions is in accord with this explanation. The marked second break in $I^+(V^-)$ for the $CH_3^+$ at ~28 volts indicates that a second state of $C_4H_{10}^{++}$ is involved. Since the maxima corresponding to the ions $CH_3^+$ and $C_3H_7^+$ in the mass spectra are quite symmetrical there is no indication that a fraction of these ions is formed with excessive kinetic energy. We may thus conclude that the second reaction giving rise to $CH_3^+$ involves electronic excitation and not simply an antibonding state of $C_3H_7\text{—}CH_3^{++}$. The ionization efficiency curve for $CH_3^+$ is compared with those of $i\text{-}C_4H_{10}^+$ and $s\text{-}C_3H_5^+$ in Fig. 3.

From its structure, one would not expect isobutane to give rise to the ion $C_2H_5^+$. The fact that $C_2H_5^+$ is observed indicates that rearrangements can occur in the ions $C_nH_{2n+2}^+$ in the short time between their formation and dissociation. The value of $A(C_2H_5^+)$ = 12.0 e. v. in isobutane indicates that $C_2H_5$ is the accompanying product, since any other products would require at least 2 volts more energy. The ~0.7 e. v. difference between $A(C_2H_5^+)$ from isobutane and normal butane can probably be associated with the activation energy of the isomerization $i\text{-}C_4H_{10}^+ \rightarrow n\text{-}C_4H_{10}^+$.

The magnitude of the appearance potentials of the ions $C_2H_4^+$ and $C_3H_6^+$ in the spectra of ethane and the butanes indicates that the formation of these ions is accompanied by the formation of stable molecules.[3,6] Two mechanisms are possible for these reactions. The one suggested by Delfosse and Bleakney[6] involves the assumption that the atoms or groups which form the stable un-ionized accompanying product are originally bound to the same carbon atom. This suggests an ethylidine structure for the ions $C_2H_4^+$ and $C_3H_6^+$. The other possible mechanism would involve the groups forming the stable un-ionized molecule coming from adjacent carbon atoms, and suggests that the ions $C_2H_4^+$ and $C_3H_6^+$ are olefinic molecular ions.

One might expect the resonance between the equivalent structures

$$H_2C\text{—}C^+H_2 \qquad H_2C^+\text{—}CH_2$$

in the olefinic molecular ions to stabilize them with respect to the isomeric ethylidene ions by at least 0.5 e. v. If this is true, the appearance potentials given in Tables IV and V for $C_2H_4^+$ and $C_3H_6^+$ indicate that the second mechanism is the more probable one.

From Rossini's review article[16] we can write

$$C_2H_6 = C_2H_4 + H_2 \qquad \Delta H^0_{298\cdot1} = 1.42 \text{ e. v.} \qquad (1)$$

$$n\text{-}C_4H_{10} = C_2H_4 + C_2H_6 \qquad \Delta H^0_{298\cdot1} = 0.96 \text{ e. v.} \qquad (2)$$

$$i\text{-}C_4H_{10} = C_3H_6 + CH_4 \qquad \Delta H^0_{298\cdot1} = 0.80 \text{ e. v.} \qquad (3)$$

$$n\text{-}C_4H_{10} = C_3H_6 + CH_4 \qquad \Delta H^0_{298\cdot1} = 0.73 \text{ e. v.} \qquad (4)$$

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[16] F. D. Rossini, *Chem. Rev.*, **27**, 1 (1940) (1 kcal. = 0.04338 e. v.).

Treating the appearance potentials, $A(C_2H_4^+)$ and $A(C_3H_6^+)$ as heats of reaction, we find

$C_2H_6$: $I_{ad}\ (C_2H_4) = 12.09 - 1.42 = 10.67$ e. v. (1′)
$n$-$C_4H_{10}$: $I_{ad}\ (C_2H_4) = 11.49 - 0.96 = 10.53$ e. v. (2′)
$i$-$C_4H_{10}$: $I_{ad}\ (C_3H_6) = 10.74 - 0.80 = 9.94$ e. v. (3′)
$n$-$C_4H_{10}$: $I_{ad}\ (C_3H_6) = 10.94 - 0.73 = 10.21$ e. v. (4′)

Equations (1′) and (2′) compare very favorably with Price's[13] directly measured $I_{ad}(C_2H_4) =$ 10.41 e. v. Delfosse and Bleakney[6] found $C_3H_6$; $A\ (C_3H_6^+) = 10.0$ e. v.[17] with which Eqs. (3′) and (4′) are to be compared. The essential agreement between the directly observed $I_{ad}(C_2H_4)$ and $I_{ad}(C_3H_6)$ with the indirect calculations (1′ to 4′) suggests that olefinic molecular ions rather than ethylidinic ions are formed in these reactions.

The mechanism suggested by Delfosse and Bleakney was suggested by the observations of Delfosse and Hipple[5] that in the reactions $C_2H_4 \rightarrow H_2^+ + \ldots$ the hydrogens forming the $H_2^+$ are originally attached to the same carbon atom. Kusch, Hustrulid and Tate[4] have shown that this reaction of ethylene is considerably more complex than the reactions like $C_2H_6 \rightarrow C_2H_4^+ + H_2$. In this connection it will be noted that the reactions $C_4H_{10} \rightarrow C_3H_8^+$ or $C_2H_6^+$ do not occur.

The ~0.7 e. v. difference between $A(C_2H_4^+)$ in normal butane and in isobutane may be attributed to an activation energy of isomerization as was done in the discussion of the formation of $C_2H_5^+$ from isobutane. On the other hand, it might be that the "same atom mechanism" operates in the dissociation of isobutane and the 0.7 e. v. is the difference in energy between the ethylene and the ethylidene ions.

Attempts to interpret the appearance potentials of the ions $C_3H_5^+$ and $C_2H_3^+$ from the butanes are impeded not only by the ambiguity with respect to the structures of these ions but also by the fact that several sets of un-ionized products of roughly the same energy are possible. The magnitudes of the appearance potentials are indicative of a minimum decrease in the number of bonds.

If we combine Eq. 2 given above with $A(C_2H_3^+)$ in ethane, Table IV, we get

$$n\text{-}C_4H_{10} = C_2H_3^+ + C_2H_4 + H_2 + H \quad A \sim 16.1 \text{ e. v.} \quad (5)$$

Kusch, Hustrulid and Tate[4] found $A(C_2H_3^+)$ in ethylene to be 14.1 e. v., thus we can write

$$n\text{-}C_4H_{10} = C_2H_6 + C_2H_3^+ + H \quad A \sim 15.1 \text{ e. v.} \quad (5')$$

These values are considerably greater than our observed $n$-$C_4H_{10}$; $A(C_2H_3^+) = 14.1$ e. v. Similar difficulties exist in attempted interpretations of the observed values of $A(C_3H_5^+)$.

The ionization efficiency curves for the ion $C_2H_3^+$ from both butanes indicate a second break ~4–4.5 e. v. above the initial break. Since this is just the order of the strength of C–C and C–H bonds, one can infer that the accompanying un-ionized products are more dissociated for electron energies greater than 18 e. v. than for electrons with energies between 14–18 e. v.

An examination of the distribution of the ions in the mass spectra of the two butanes (Tables II and III) immediately reveals certain limitations to the applicability of the mass spectrometer to hydrocarbon analysis. The excessively large fragmentation to ions in the $C_3$ and $C_2$ mass regions will reduce considerably the accuracy with which $C_3$ and $C_2$ hydrocarbons can be determined in the presence of butanes. Although this is particularly true with respect to $C_3$ and $C_2$ unsaturates, it is also true for propane and ethane. The large relative abundances of the ions $C_3H_7^+$ and $C_2H_5^+$ give rise to considerable quantities of masses 44 and 30 through the ions $C^{13}C^{12}_2H_7^+$ and $C^{13}C^{12}H_5^+$. Since the natural abundance of $C^{13}$ is 1.1%, the relative current of mass 44 will be ~3.3% of mass 43 and of mass 30 will be 2.2% of mass 29. For concentrations of propane and ethane of the order of 2–3% or less, the corrections will be of the order of the quantity to be measured which is always unsatisfactory. In contrast to this less pleasant aspect it should be noted that extremely small traces of the butanes can be determined with ease in the presence of large concentrations of lower hydrocarbons. This is possible because at the low pressures involved there is no building up of heavier ions by recombination.

The relatively small abundances of the ions $C_4H_8^+$—$C_4^+$ to which the butanes give rise, will make possible the determination of $C_4$ unsaturates with reasonable precision.

It is interesting to note that a definite similarity exists between the unimolecular dissociation reactions of the ions $C_nH_{2n+2}^+$ and the thermal reactions of the hydrocarbons. The carbon–carbon bond in the ethane ion shows but little tendency to break; less than 10% of its spectrum lies in the $C_1$ region. The butanes on the other hand have only ~10% of their spectra in the parent $C_4$ region. A direct comparison of the ions in the mass spectra with the pyrolysis products

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[17] One of the authors (D. P. S.) has found, $C_3H_6$; $A(C_3H_6^+) =$ 9.7 e. v.

of hydrocarbons or hydrocarbon free radicals[18] cannot be made because none of the ions in the mass spectra result from collisions after the initial ionization. Thus the characteristic chain reactions are absent.

## Summary

The variation of the relative abundances of the ionic dissociation products formed by electron impact in ethane, normal and isobutane are reported as a function of the energy of the bombarding electrons. The critical potentials of a number of the processes have been measured, and their significance is discussed. Certain limitations of the mass spectrometer as an analytical tool are also discussed.

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[18] F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, Md., 1935.

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# The Mechanism of the Catalytic Conversion of Para-hydrogen on Nickel, Platinum and Palladium

BY A. FARKAS AND L. FARKAS

The catalytic conversion of para-hydrogen on metals was explained by the dissociation of the hydrogen molecules on the surface of the catalyst.[1] This mechanism was later extended to the ortho–para conversion of deuterium and to the reaction $H_2 + D_2 = 2HD$.[2]

It seemed to receive confirmation when it was found that the rate of ortho–para conversion on palladium was very nearly equal to the rate of the diffusion of hydrogen through palladium.[3] From these experiments the conclusion was drawn that in the conversion and in the diffusion process the rate determining step is the dissociation of the hydrogen molecules on the surface of the catalyst.

Roberts questioned the correctness of the suggested mechanism[4] on the basis of his own experiments.[5] In these he was able to show that a clean tungsten surface will take up hydrogen molecules with great speed, that the molecules will be dissociated and that the atoms form a very stable layer on the surface of the tungsten. As this layer will give off atoms or molecules only at a very high temperature it was suggested that it is more reasonable to assume that the ortho–para conversion of hydrogen involves a reaction between the atomic layer and the molecules adsorbed or impinging on this layer. A direct proof for this view was brought forward by Eley and Rideal,[6] who showed that on an evaporated tungsten layer which has been in contact with hydrogen, the rate of the para-hydrogen conversion and the rate of exchange of atoms between molecular deuterium and the hydrogen in the tungsten layer are about equal.

The object of the present paper was the examination of the mechanism of the para-hydrogen conversion on typical hydrogenation catalysts such as nickel, palladium and platinum.

## Experimental

The reaction vessel was either a bulb or a cylindrical vessel having a volume of 700 to 1100 cc. The pressure in the reaction system was measured by a Pirani gage. The entrance of vapors of grease or mercury into the reaction vessel or into the Pirani gage was prevented by traps cooled by liquid air. The gases were introduced into the reaction vessel by means of locks having a volume of 0.1 to 0.2 cc.

The reaction vessel was equipped with an electrically heated wire. The catalyst was prepared by heating the wire to a temperature at which the evaporation of the metal begins and thus an invisible layer of high activity is formed on the inner surface of the reaction vessel. The active layer thus prepared was, on the average, not more than one or two atoms deep, since the whole of the wire when completely evaporated would have formed a layer about one hundred atoms deep and actually only a small fraction of the wire, certainly not more than one per cent., was evaporated.

The concentration of para-hydrogen and of deuterium was determined according to the micro-thermal conductivity method.[2,7]

**Nickel.**—In the first series of experiments a reaction vessel of 730 cc. volume and having an inner surface of 390 sq. cm. was used. This vessel was provided with a nickel wire 11 cm. long, 0.1 mm. in diameter.

Table I shows the dependence of the half-life time of the para-hydrogen conversion on pressure in the presence of an evaporated nickel film.

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(1) Bonhoeffer and Farkas, *Z. physik. Chem.*, **B12**, 231 (1935); Bonhoeffer, Farkas and Rummel, *ibid.*, **B21**, 225 (1933).

(2) Farkas and Farkas, *Proc. Roy. Soc.* (London), **A144**, 467 (1934).

(3) Farkas, *Trans. Faraday Soc.*, **32**, 1667 (1936).

(4) Roberts, *ibid.*, **35**, 941, 944 (1939).

(5) Roberts, *Proc. Roy. Soc.* (London), **A152**, 452 (1935).

(6) Eley and Rideal, *Nature*, **146**, 401 (1940); Eley, *Proc. Roy. Soc.* (London), **A178**, 452 (1941).

(7) Farkas, *Z. physik. Chem.*, **B22**, 344 (1933).