PHYSICAL REVIEW VOLUME 63, NUMBERS 3 AND 4 FEBRUARY 1 AND 15, 1943

Ionization and Dissociation by Electron Impact: The Methyl and Ethyl Radicals*

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(Received December 5, 1942)

The lead tetra-alkyls, $Pb(CH_3)_4$ and $Pb(C_2H_5)_4$, were decomposed to yield free methyl and ethyl radicals in a specially designed furnace built into the ionization chamber of a 180° mass spectrometer tube. From the initial breaks of the ionization efficiency curves of the ions, CH_3^+ and $C_2H_5^+$, we have found the ionization potentials of the methyl and ethyl radicals to be $I_{\mathrm{vert}}(CH_3)=10.0_0\pm0.1$ ev and $I_{\mathrm{vert}}(C_2H_5)=8.6_0\pm0.1$ ev. These values are in excellent agreement with those found by indirect calculations from other electron impact data on hydrocarbons. Some of the implications of these results are briefly discussed.

INTRODUCTION

BESIDES their importance to the formulation of the theory of the thermal decomposition of hydrocarbons,[1] the energies of the methyl and ethyl free radicals have considerable theoretical significance. The calculation of the relative energies of CH_4, CH_3+H, CH_2+2H, $CH+3H$, and $C+4H$ is a very suitable test of any quantum mechanical theory of valence.[2] Thus accurate values of these energies are desirable for checking the calculations or for the evaluation of parameters in the theoretical equations. A knowledge of the ionization potentials of the various radicals is important for the same reasons.

In the recent past a considerable body of information has been built up pertaining to the ionization and dissociation of various hydrocarbons by electron impact. In order to interpret these data in an unambiguous fashion and to check those interpretations which have been made, the energetic quantities mentioned above were needed.

Several years ago Fraser and Jewitt[3] reported values for the ionization potentials of the methyl and ethyl radicals, determined by the molecular beam technique. Their well conceived experiments suggested to us the desirability of repeating this work with the mass spectrometer as a detector of the ionization. The repetition seemed particularly desirable, inasmuch as a great deal of the more recently obtained data were very difficult to reconcile with the ionization potentials reported by Fraser and Jewitt.

EXPERIMENTAL

The mass spectrometer used in this research is to be described by one of the authors (J. A. H.) in a separate publication, hence only pertinent details will be reported here.

The electrons are obtained from an oxide-coated platinum cathode, their accelerating potential being controlled by means of a wire wound drum potentiometer. The accelerating voltage is read with an accuracy of ±0.1 percent on a calibrated voltmeter. A separate pumping

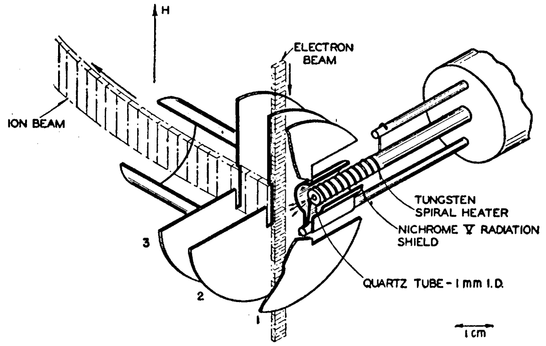

FIG. 1. The furnace and ion source assemblage. The lead alkyls were admitted to the tube through the quartz tube—the end of which is heated by the tungsten spiral. Emerging from the quartz tube, some of the molecules and free radicals are ionized by the electron beam. The ions are drawn to 2 by a small field between 1 and 2; passing through 2, they are accelerated through the slit in 3 by a difference of potential of about 500 volts between 2 and 3, entering the analyzer region where the magnetic field (H) sorts out the ions of different masses (180°-analyzer).

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* Presented at the Physical Society Meeting at State College, Pennsylvania, June, 1942.

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[1] F. O. Rice and K. K. Rice, *The Aliphatic Free Radicals* (Johns Hopkins Press, Baltimore, 1935).

[2] H. H. Voge, J. Chem. Phys. **4**, 584 (1936). The most elaborate quantal calculation.

[3] R. G. J. Fraser and T. N. Jewitt, Phys. Rev. **50**, 1091 (1936); Proc. Roy. Soc. **A160**, 563 (1937).

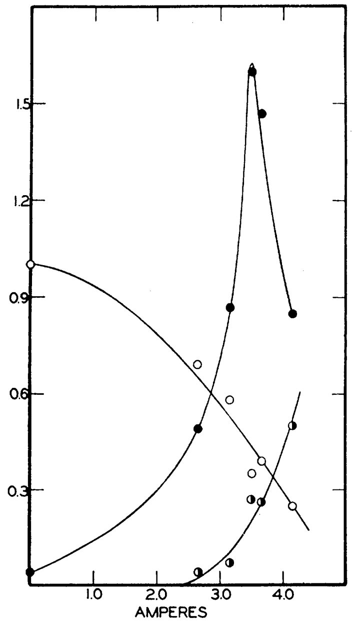

FIG. 2. The effect of furnace temperature on the relative abundance of the ions $Pb(CH_3)^+$ (open circles), CH_3^+ (closed circles) and CH_4^+ (half closed circles) in the spectrum obtained from $Pb(CH_3)_4$.

lead to the arm of the tube, containing the cathode chamber, assures the complete removal of any pyrolysis products formed on the filament itself and on the adjacent parts of the tube heated by radiation from the filament. Argon admitted simultaneously with the substance being studied serves to calibrate the electron accelerating voltage scale.

An isometric view of the ion source and the furnace in which the lead alkyls were thermally dissociated is shown in Fig. 1. The furnace consists of a quartz capillary tube (I.D. ~1 mm) closely wound with 20-mil tungsten wire for the last 1.5 cm of its length. The wound zone is surrounded by a nichrome V radiation shield. This radiation shield, welded to one of the tungsten heater leads (80 mil) is connected to the high voltage electrode 1. The heater current is controlled by a variac, isolated from the high voltage electrodes by means of an insulating transformer. We have no means of measuring the temperature in the present arrangement, but five amperes bring the furnace to incipient red heat (~500°C). The end of the quartz tube is about 5 mm from the electron beam, which is indicated in the figure.

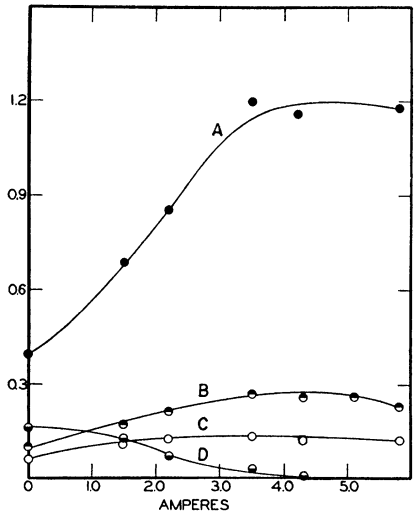

FIG. 3. The variation of the relative abundance of the ions $C_2H_4^+$ (A), $C_2H_5^+$ (B), $Pb(C_2H_5)_3^+$ (C), and $C_2H_6^+$ (D) in the spectrum of $Pb(C_2H_5)_4$ with furnace temperature.

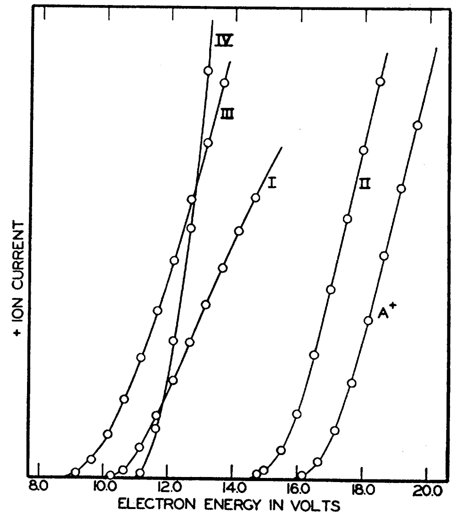

FIG. 4. Ionization efficiency curves: I and II are CH_3^+, III, $C_2H_5^+$, and IV, $C_2H_4^+$. See text, Table I.

The lead alkyls were admitted at low pressure to the lead connecting to the furnace by means of a fine capillary leak, the pressure in back of the leak being adjusted by fixing the temperature of the liquid ($Pb(CH_3)_4 \sim -10°C \cdot Pb(C_2H_5)_4 \sim +30°C$). The argon was admitted simultaneously through a parallel leak. The vapor (and argon) flow through the quartz furnace into the path of the electron beam where the ionization takes place. The products of the thermal dissociation in the furnace can then be studied with the mass spectrometer.

The specially purified samples of the lead alkyls were kindly supplied to us by the Ethyl Gasoline Corporation. In Fig. 2 the relative currents of the positive ions $Pb(CH_3)_3^+$, CH_4^+, and CH_3^+ produced from $Pb(CH_3)_4$ with 20-volt electrons are shown as a function of the heating current. The $Pb(CH_3)_3^+$ is used as an indicator of the completeness of the thermal decomposition because the parent ion is absent. The striking feature of these curves is the sharp resonance found for the production of the methyl radicals as a function of the temperature. It should be noted that, as the temperature is increased beyond that shown in the figure, the CH_3^+ current passes through a minimum and then increases at the same rate as the CH_4^+ current; this indicates that in the higher temperature range the CH_3^+ observed is the product of the dissociation of methane by electron impact. In addition to the ions mentioned above, there is a very large current at mass 28, increasing with temperature, which can be attributed to ethylene with confidence.

At first it was hoped that a sufficient number of free radicals would be formed by dissociation of the lead compounds on a filament close to the electron beam. The failure to observe any free radical formation by this technique with either tungsten or platinum filaments was explained by the sharp maximum for the CH_3^+ current as obtained with the final arrangement.

As may be seen from Fig. 3, the behavior of lead tetraethyl is similar to that of lead tetramethyl except for the lack of a pronounced resonance maximum in the current of the radical ion.

From the observations reported in the preceding paragraphs and the fact that the pressure of the lead alkyls in the furnace was very low (about 10^{-5} mm) it is clear that these compounds decompose on a hot quartz or tungsten surface to give primarily stable hydrocarbons, e.g., methane, ethylene, ethane, etc., at all temperatures. At first sight this result may seem to contradict the results of Paneth type experiments on the preparation and properties of free radicals.[1] The latter experiments are carried out at much higher pressures and the decompositions are probably homogeneous thermal gas reactions. Our results are those of purely heterogeneous dissociation of the lead alkyls, and may well depend on the past history of the quartz or tungsten surfaces involved.

RESULTS

I. The Methyl Radical

Curves *I* and *II* of Fig. 4 are the ionization efficiency curves for mass 15 (CH_3^+) obtained with 3.5 and 5.5 amperes through the furnace. Comparison with the curves of Fig. 2 indicates the following assignment of reactions to these ionization efficiency curves:

$$I.\ CH_3 \rightarrow CH_3^+ + \epsilon^- \qquad A_I(CH_3^+) = 10.0_0 \pm 0.1\ \text{ev}^4$$
$$II.\ CH_4 \rightarrow CH_3^+ + H + \epsilon^- \qquad A_{II}(CH_3^+) = 14.4_4 \pm 0.1\ \text{ev}.$$

The numerical values of the appearance potentials are based on the value $I^z(A) = 15.69$ ev for the ionization potential of argon.[5] This value is dependent on the old value of the conversion factor relating cm^{-1} to ev. If the new value,[6] 1 ev $= 8066\ cm^{-1}$, is accepted $I^z(A) = 15.76$ ev and the appearance potentials should be increased 0.07 ev. Since the dissociation energies which we deduce from electron impact data involve differences between appearance potentials, the error in the absolute voltage scale cancels. The appearance potentials were taken from the initial breaks of the curves.[7] The appearance potential A_I is to be associated with the vertical ionization potential of the methyl

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[4] The uncertainties indicated for the appearance potentials in this paper are meant to show the reproducibility and the accuracy of differences. The range of voltages within which the absolute values of the appearance potentials lie is probably about twice as great as the indicated uncertainty, e.g., $A_I(CH_3^+) = 10.0 \pm 0.2$ ev on an absolute scale.

[5] R. F. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill, New York, 1932).

[6] G. Herzberg, *Molecular Spectra I* (Prentice-Hall, New York, 1939).

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

TABLE I. Summary of results.

Source	Furnace current	Fig. 4	Ion	$A(X^+)$	Reaction
$Pb(CH_3)_4$	3.5 amp.	I	CH_3^+	$10.0_0 \pm 0.1$ ev	$CH_3 \rightarrow CH_3^+ + \epsilon^-$
$Pb(CH_3)_4$	5.5 amp.	II	CH_3^+	$14.4_4 \pm 0.1$	$CH_4 \rightarrow CH_3^+ + H + \epsilon^-$
$Pb(C_2H_5)_4$	4.0 amp.	III	$C_2H_5^+$	$8.6_0 \pm 0.1$	$C_2H_5 \rightarrow C_2H_5^+ + \epsilon^-$
$Pb(C_2H_5)_4$	4.0 amp.	IV	$C_2H_4^+$	$10.8_4 \pm 0.1$	$C_2H_4 \rightarrow C_2H_4^+ + \epsilon^-$

radical. A_{II} agrees exactly with the value reported by Smith[8] for the appearance potential of CH_3^+ in the mass spectrum of methane.

Provided there is no activation energy for the formation of a bond between a methyl ion and a hydrogen atom, the difference, $A_{II} - A_I = 4.4_4 \pm 0.2$ ev, is equal to the strength of the first carbon-hydrogen bond of methane. This value of $D(CH_3 - H)$ is in much better agreement with the recent indirect estimate,[9] $4.3_8 \pm 0.2$ ev,[9] than the estimated uncertainty would lead us to expect.

The reason that the value reported by Fraser and Jewitt[2] for the ionization potential of the methyl radical, $I(CH_3) = 11.2 \pm 0.8$ ev, is so much higher than our value probably lies in the inability of their molecular beam technique to distinguish between the various thermal dissociation products of the lead tetramethyl. As there was no evidence to the contrary, they assumed the predominate product of the thermal decomposition to be the methyl radical. We found that under all conditions the yield of ethylene far exceeded that of methyl radicals, even at the very low pressure of lead tetramethyl we employed, as has been discussed above. Thus their ionization efficiency curve was probably a composite one representing the sum of ionization efficiency curves for the various ions arising from ionization and dissociation of ethylene, methane and the methyl radical.

Some rough measurements on the relative abundances of the lead-methyl ions, made with the furnace cold, showed the trimethyl lead ion to be about fifty times as abundant as the tetramethyl lead ion for 15-volt electrons. For this reason the ionization potential assigned to lead tetramethyl by Fraser and Jewitt should probably be associated with the appearance potential of $Pb(CH_3)_3^+$ in the $Pb(CH_3)_4$ spectrum. This absence of the parent ion from the mass spectrum has also been noted for tertiary butyl chloride.[10]

II. The Ethyl Radical

The furnace temperature was not as critical for the formation of ethyl radicals as for methyl radicals. Curves *III* and *IV* of Fig. 4 were taken with 4 amperes through the furnace. From their initial breaks we deduce

$$\begin{aligned} &III.\ C_2H_5 \rightarrow C_2H_5^+ + \epsilon^- \quad A_{III}(C_2H_5^+) = 8.6_0 \pm 0.1 \text{ ev} \\ &IV.\ C_2H_4 \rightarrow C_2H_4^+ + \epsilon^- \quad A_{IV}(C_2H_4^+) = 10.8_4 \pm 0.1 \text{ ev.} \end{aligned}$$

Thus we have 8.6_0 ev for the vertical ionization potential of the ethyl radical. Equation *IV* was assigned to the appearance potential of $C_2H_4^+$ on the basis of the agreement of the value, $A_{IV}(C_2H_4^+) = 10.8_4$ ev, with that reported by Kusch, Hustrulid and Tate[11] for the appearance potential of this ion in the spectrum of ethylene.

Since Fig. 3 indicates that the $C_2H_4^+$ ion far exceeds the $C_2H_5^+$ ion in the spectrum obtained from the decomposition products of $Pb(C_2H_5)_4$, it is likely that Fraser and Jewitt were actually measuring the ionization potential of ethylene by their molecular beam technique rather than that of the ethyl radical. This is the most reasonable explanation of their value, 10.6 ± 0.8 ev.

As is the case with lead tetramethyl, the abundance of the parent ion in the $Pb(C_2H_5)_4$ spectrum

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[8] L. G. Smith, Phys. Rev. **51**, 263 (1937).

[9] D. P. Stevenson, J. Chem. Phys. **10**, 291 (1942).

[10] D. P. Stevenson and J. A. Hipple, J. Am. Chem. Soc. **64**, 2766 (1942).

[11] P. Kusch, A. Hustrulid, and J. T. Tate, Phys. Rev. **52**, 843 (1937).

is almost unmeasurably small. Thus the value given by Fraser and Jewitt for the ionization potential of $Pb(C_2H_5)_4$ should probably be associated with the appearance potential of $Pb(C_2H_5)_3^+$.

From data on the appearance potentials of the ethyl ion in the spectra of ethane and *n*-butane, we deduce $8.6_8 \pm 0.2$ ev[7] for $I_{\text{vert}}(C_2H_5)$. The direct and indirect determinations are in excellent agreement.

The results described in this section, and the conditions under which they were obtained are summarized in Table I.

DISCUSSION

The indirect method[9] of determining dissociation energies, $D(\ \ )$, from electron impact data involves taking differences between appearance potentials of similar processes. Formally we have

$$\mathrm{R-R'} \rightarrow \mathrm{R^+ + R' + \epsilon^-}; \quad A_1(\mathrm{R^+}) \geqq \Delta E_1, \tag{1}$$

$$\mathrm{R-H} \rightarrow \mathrm{R^+ + H + \epsilon^-}; \quad A_2(\mathrm{R^+}) \geqq \Delta E_2, \tag{2}$$

$$\mathrm{R'-R+2H} \rightarrow \mathrm{(R'-H)+(R-H)}; \quad \Delta E_3, \tag{3}$$

$$\mathrm{R'-H = R'+H}; \quad D(\mathrm{R'-H}) = \Delta E_1 - \Delta E_2 - \Delta E_3 \lesseqgtr A_1 - A_2 - \Delta E_3, \tag{4}$$

where the ΔE's are the minimum energies for the various processes. The equality sign in Eq. (4) for $D(\mathrm{R'-H})$ holds for two conditions: (1) The equalities $A_1 = \Delta E_1$ and $A_2 = \Delta E_2$, or (2) the appearance potentials A_1 and A_2 exceed ΔE_1 and ΔE_2 by the same amount.

The direct method of determining $D(\ \ )$'s from electron impact data is based on the equations

$$\mathrm{(R'-H)} \rightarrow \mathrm{R'^+ + H + \epsilon^-}; \quad A_5(\mathrm{R'^+}) \geqq \Delta E_5, \tag{5}$$

$$\mathrm{R'} \rightarrow \mathrm{R'^+ + \epsilon^-}; \quad A_6(\mathrm{R'^+}) \geqq I^z(\mathrm{R'}), \tag{6}$$

$$\mathrm{(R'-H) = R'+H}; \quad D(\mathrm{R'-H}) = \Delta E_5 - I^z(\mathrm{R'}) \lesseqgtr A_5 - A_6. \tag{7}$$

Because process (6) involves the removal of a non-bonding electron from a radical R′ it seems reasonable to assume the equality of A_6 and I^z. Thus the direct method should give an upper limit for $D(\mathrm{R'-H})$. If R of Eq. (2) and R′ of (5) are similar, e.g., aliphatic radicals, one would expect A_2 and A_5 to deviate from ΔE_2 and ΔE_5 by the same amount. Under these conditions the only way $D(\mathrm{R'-H})$ calculated by Eq. (4) can agree with that calculated by Eq. (7) is for equality signs to hold for Eqs. (1), (2), and (5) and thus for (4) and (7). The excellent agreement found to obtain between the direct and indirect estimates of $D(CH_3-H)$ and $D(C_2H_5-H)$, indicated above, offers strong evidence for the absence of an activation energy in such reactions as

$$\mathrm{R^+ + H} \rightarrow \mathrm{RH^+}, \tag{8}$$

$$\mathrm{R^+ + CH_3} \rightarrow \mathrm{RCH_3^+}, \tag{9}$$

where R^+ is an aliphatic radical ion.

The datum of Cummings and Bleakney[12] on the appearance potential of CH_3^+ in the methyl alcohol provides another check on the direct method of calculation.

$$\mathrm{CH_4 + H_2O = CH_3OH + H} \qquad \Delta E^0 = 5.65 \text{ ev}, \tag{10}$$

$$\mathrm{CH_3OH} \rightarrow \mathrm{CH_3^+ + OH + \epsilon^-} \quad A(\mathrm{CH_3^+}) = 14.0 \pm 0.4 \text{ ev}, \tag{11}$$

$$\mathrm{H + OH = H_2O} \qquad \Delta E^0 = -5.17 \text{ ev}, \tag{12}$$

$$\mathrm{CH_3} \rightarrow \mathrm{CH_3^+ + \epsilon^-} \qquad A(\mathrm{CH_3^+}) = 10.0_0 \pm 0.1 \text{ ev}, \tag{13}$$

$$\mathrm{CH_4 = CH_3 + H}; \quad D(\mathrm{CH_3-H}) = 5.65 + 14.0 - 5.17 - 10.0 = 4.4_8 \pm 0.4 \text{ ev}. \tag{14}$$

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[12] C. S. Cummings and W. Bleakney, Phys. Rev. **58**, 787 (1940).

Hipple's[13] datum on $A(CH_3^+)$ in the ethane spectrum does not lead to quite as good agreement.

$$2CH_4 = C_2H_6 + 2H \qquad \Delta E^0 = 5.18, \tag{15}$$

$$C_2H_6 \rightarrow CH_3^+ + CH_3 + \epsilon^- \qquad A(CH_3^+) = 14.2 \pm 0.4, \tag{16}$$

$$CH_3 \rightarrow CH_3^+ + \epsilon^- \qquad A(CH_3^+) = 10.0_0 \pm 0.1, \tag{13}$$

$$CH_4 = CH_3 + H \qquad 2D(CH_3-H) = 5.18 + 14.2 - 10.0 \tag{17}$$

$$D(CH_3-H) = 4.6_9 \pm 0.3 \text{ ev.}$$

The deviation of this value of $D(CH_3-H)$ from that which we accept, namely, $4.4_0 \pm 0.1$,[14] is almost large enough to be real. If the deviation is real, one must assign an activation energy of ~0.3 ev to the reaction $CH_3^+ + CH_3 \rightarrow C_2H_6^+$, but no activation energies to the reactions, $CH_3 + H \rightarrow CH_4^+$, $CH_3^+ + OH \rightarrow CH_3OH^+$, $C_2H_5^+ + CH_3 \rightarrow C_3H_8^+$, etc. It seems more likely that the value of $A(CH_3^+)$ in the ethane spectrum is in error by 0.2 to 0.3 ev.[15]

Data acquired by one of the authors on butene-1, on the other hand, clearly indicate that reactions involving the vinyl and allyl radical ions adding to H, CH_3, or C_2H_5 to form the corresponding olefinic ions require an activation energy of ~0.4 ev. The addition of a vinyl radical to an ethyl ion, however, seems to require no activation energy.

In a recent paper[7] it was pointed out that for exactly similar processes in various molecules, simple ionization for instance, the differences between the initial breaks of the ionization efficiency curves are equal to the differences between the intercepts of the extrapolated linear portions of the ionization efficiency curves. To state this in another manner, for such processes as $M \rightarrow M^+ + \epsilon^-$, the difference $V_L^- - V_B^- = 1.06_5 \pm 0.060$ ev where V_L^- is the linear intercept and V_B^- the initial break of the ionization efficiency curve. For eleven reactions of the type $R-R' \rightarrow R^+ + R' + \epsilon^-$, $V_L^- - V_B^- = 1.54 \pm 0.09$ ev. If the linear intercepts are used, the combination of the appearance potential of $C_2H_5^+$ in the ethane spectrum with $D(C_2H_5-H)$ leads to 9.1_7 ev for $I^z(C_2H_5)$, while the initial break gives 8.6_8. Both methods yield 8.6 ev when applied to the ionization efficiency curve of $C_2H_5^+$ in the ethyl radical spectrum. The fact that the value of $I^z(C_2H_5)$ deduced from the initial break of the ionization efficiency curve of $C_2H_5^+$ in the ethane spectrum agrees with the directly measured value offers further substantiation of our conclusion that the linear intercepts are not applicable to the determination of appearance potentials.[16]

It is interesting to note that the decrease in the vertical ionization potential brought about by the substitution of CH_3 for H in the methyl radical, 10.0 to 8.6 ev is parallel to the difference previously found between methane[8] and ethane,[7] ethylene[11] and propylene,[10] chlorine atom and methyl chloride,[17] and other similar pairs. Price[17] has discussed the reasons for these decreases.

In conclusion, we should like to express our sincere thanks to Dr. H. A. Beatty and his colleagues at the Ethyl Gasoline Corporation Research Laboratories for their generous cooperation in supplying us with the specially purified samples of the lead tetramethyl and lead tetraethyl.

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[13] J. A. Hipple, Phys. Rev. **53**, 530 (1938).

[14] This value $D(CH_3-H) = 4.4_0 \pm 0.1$ seems to be a good representation of the indirect value, 4.3_8 ev (reference 9), the direct value from $I^z(CH_3)$ and $A(CH_3^+)$ in the methane spectrum 4.4_4, and the value recently deduced by Kistiakowsky and co-workers (J. Chem. Phys. **10**, 305 (1942)) from kinetic data, 4.3_6 ev. Similarly we take $D(C_2H_5-H) = 4.2_0 \pm 0.1$ from the indirect value, 4.1_6,[9] the direct value, 4.2_4, and the kinetic value 4.2_2. We have modified the values quoted by Kistiakowsky and co-workers to account for the difference between that which they took for $D(H-Br)$ and that given by Herzberg (reference 6).

[15] It should be noted that on the basis of the conclusions reached in the preceding paragraphs it is no longer possible to reconcile the electron impact values of $D(CH_3-H)$ with the estimate made by Burton (J. Chem. Phys. **6**, 818 (1938)) from photochemical data. See reference 9.

[16] D. P. Stevenson and J. A. Hipple, Phys. Rev. **62**, 237 (1942).

[17] W. C. Price, J. Chem. Phys. **4**, 539 (1936).