interatomic distances given here are all for a value of

$$a = 4.605 \times 10^8 \text{ cm.}^{-1} \qquad (14)$$

This choice has the advantage of yielding the simple relationship

$$r_{AB} = r^*_A + r^*_B - {}^1/_2 \log D_{AB} \qquad (15)$$

when the values of r_{AB}, r^*_A and r^*_B are in Å. and those of D_{AB} are in kcal./mole.

Comparison with Experiment

With the aid of this equation, the constant energy radii listed in Table I have been obtained. These, in turn, have been used to compute the values of r_{AB} (calcd.) listed and compared with the corresponding experimental values in Table II.

Calculations have been made both from the experimental bond energies and from bond energies computed from electronegativities and non-polar bond-energy contributions. Both of these are given in the preceding paper.[17]

The average differences between the observed and computed distances are about 0.019 Å. for the figures from experimental bond energies and about 0.024 Å. for those from computed bond energies. These averages would be reduced somewhat if one omitted those cases in which, from other considerations, there is reason to believe that the experimental values of the bond energy (*e.g.*, H–As) or the bond length (*e.g.*, H–Se or Te–Te) are quite inaccurate.

In order to obtain even rough agreement for the hydrogen compounds, it was found necessary to use several different values of r^*_H, depending on the row of the Periodic Table in which the element to which the hydrogen is bonded belongs. This is probably a result of the fact, already noted,[15] that these bonds do not obey the assumed energy–distance relationship well, at least with the same value of a which is found satisfactory for other bonds. An alternative explanation is that equation (11) does not hold with sufficient accuracy for bonds involving hydrogen, with the same value of E^*_{rep} as is satisfactory for other bonds.

It will be noted that the discrepancies in the cases of such very strong, very polar bonds as Si–O and Si–F have been greatly reduced, but not entirely eliminated. (A different assumption as to the sublimation energy of silicon does not improve the situation appreciably.) It seems likely that here, as with bonds involving hydrogen, the basic assumptions underlying the present treatment no longer hold with sufficient accuracy. One way out of the difficulty would be to add to equation (15) another term, involving either the electronegativity or perhaps the fraction of double-bond character, but this does not seem warranted in the present state of our knowledge.

Instead of using Equation (15), one can obviously compute interatomic distances from the non-polar radii by means of the relation

$$r_{AB} = r_{np.A} + r_{np,B} - {}^1/_2 \log \left(\frac{D_{AB}}{D_{np.A} + D_{np.B}}\right) \qquad (16)$$

making use of the non-polar bond-energy contributions listed in the preceding paper. A set of non-polar radii, consistent with the constant energy radii and the non-polar bond-energy contributions which have been listed, is included in Table I. The differences between these and the corresponding radii given by Schomaker and Stevenson are slight. Differences between interatomic distances calculated by equation (16) and those calculated by equation (15) are only such as result from rounding off of the atomic constants used.

In summary, the results presented show that interatomic distances for single bonds between atoms exhibiting their normal valences can be computed, at least within about 0.02 Å., from experimental or calculated bond energies by means of equation (15) or (16), and the constant energy radii of Table I.

ROCHESTER, N. Y.

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[17] M. L. Huggins, THIS JOURNAL, **75**, 4122 (1953).

[CONTRIBUTION FROM THE MASS SPECTROSCOPY LABORATORY, HOWARD UNIVERSITY]

Electron Impact Studies in CH_4, CH_3Cl, CH_3Br and CH_3I

BY HERMAN BRANSON AND CARTER SMITH

RECEIVED MARCH 27, 1953

Data on the appearance potentials of the positive ions produced on electron impact with CH_4, CH_3Cl, CH_3Br and CH_3I in a 60° Nier type mass spectrometer are used to calculate the heat of sublimation of carbon, $L(C) \leq 5.90$ e.v. Further calculations from the data give $D(C–H) = 3.5$ e.v., $D(C–2H) \leq 7.4$ e.v., $D(C–3H) \geq 11.2$ e.v., $D(CH_3–H) \leq 4.2$ e.v., $D(CH_3–Cl) \leq 3.4$ e.v., $D(CH_3–Br) \leq 3.1$ e.v., and $D(CH_3–I) \leq 2.3$ e.v. The measured ionization potentials are $I(CH_4^+) = 13.1$ e.v., $I(CH_3Cl^+) = 11.3$ e.v., $I(CH_3Br^+) = 10.5$ e.v., and $I(CH_3I^+) = 9.6.$ e.v. The derived $I(CH_2^+)$ is ≤ 12 v.

In the mass spectrometer ions are formed by collisions of electrons with molecules and separated according to their mass to charge ratio, following the relation $m/q = r^2B^2/2V$ where r is the radius of the ion path in meters, B is the magnetic induction in webers per meter^2, V is the ion accelerating voltage in volts, m is the mass of the ion in kilograms, and q is the charge on the ion in coulombs. One can measure in the ion gun the appearance potential or the minimum energy required to produce a particular ion. The appearance potential of undissociated ions often check and supplement spectroscopic data. For many substances the data are unique. The ionization potentials of radicals and the bond energies which may be computed provide valuable knowledge toward the understanding of molecular structure.

Electron impact studies in tri and higher atomic gases are complicated by a lack of information concerning the identities of the fragments produced, as well as the kinetic energies, and the states of the fragments. For an XY_3Z type of molecule, for example, some of the possible products including Z^+ ions are $\rightarrow XY_3 + Z^+ + 2e^-$; $XY_3 + Z^+ + 2e^-$; $XY_3^- + Z^+ + e^-$; $XY_2 + Y + Z^+ + 2e^-$; $XY_2 + Y^- + Z^+ + e^-$; $XY + Y_2 + Z^+ + 2e^-$; $XY + Y_2^- + Z^+ + e^-$; $X + Y_2 + Y^- + Z^+ + e^-$; $X + Y_2^- + Y + Z^+ + e^-$; $X + 2Y^- + Y^+ + Z^+ + e^-$. In order to establish any of these reactions unambiguously, the experiment would have to measure the appearance potential of Z^+, its kinetic energy, its state, and simultaneously detect the other ions or neutral fragments, their kinetic energies, and states. The most refined equipment available at present is that of Hagstrum[1] which measures the appearance potential of the ion under investigation and its kinetic energy by applying a retarding field. It is clear, however, that even when dealing with diatomic molecules in such an apparatus, there is still some question as to the state of the ion being measured and no direct information on the other ion or neutral atom produced in the disintegration. From other data, one may reduce the possibilities of interpretation often to a single reaction with definite limits on the kinetic energy and with specific states allowed for the ion and other fragment. The situation with triatomic and higher atomic molecules is not as neat as for the diatomic since one of the fragments may be a multiatomic unit whose energy states are not known. McDowell and Warren[2] have proposed that measurements of the half-widths can decide when an ion is produced with excess kinetic energy. With this information and with data from other experiments, it is often possible even with multiatomic molecules to argue that one and only one specific decomposition is consistent with all the information. These points of view will be utilized in the interpretation of our data on CH_4, CH_3Cl, CH_3Br and CH_3I.

Methane gas has been analyzed in the mass spectrometer several times.[2-5] The results indicate that the ionization potential of the parent ion (CH_4^+) is 13.1 ± 0.1 e.v. The pyrolytic dissociation experiments of Van Artsdalen and Kistiakowsky[6] together with the appearance potential experiments of Stevenson and Hipple[7,8] have shown that the energy of the first bond, $D(CH_3-H)$, is 4.42 ± 0.04 e.v. (102 kcal./mole) and the ionization potential of CH_3 is 10.1 e.v. (232.9 kcal./mole). The ionization and dissociation energy of the CH radical are known from spectroscopic data.[9] Since electron impact data yield no more than the upper energy limit for the processes, the energies concerned in the production of the methylene radical have not been uniquely determined.

Voge calculated the energy of dissociation of CH_4, CH_3 and CH_2 by an extended Heitler–London–Pauling–Slater method.[10] The parameters appearing in his calculations are related to the energy of the CH bond energy and the heat of sublimation of carbon. From consideration of the plots of force constants and C–C bonds against bond distances for some hydrocarbons, Glockler concluded that $L(C) = 5.89$ e.v. fitted the data better than $L(C) = 7.39$ e.v.[11] More recently, however, he has reported that the higher value concurred in by three recent experimental determinations is more consistent with other information on CC, CN, CO, NO and NN bonds.[12] Since the publication of our initial report on this work,[13] McDowell and Cox[14] have published some of their data on CH_3I. They too find $D(CH_3I)$ as 52.6 kcal. (2.3 e.v.).

Our mass spectral data on methane and the three methyl halides (CH_3Cl, CH_3Br, CH_3I) yield upper limits for the ionization potential of the parent molecule, the energy required to remove the components sequentially from the carbon, and the heat of sublimation of carbon. Our data support some values derived from spectroscopic and certain thermal measurements and are inconsistent with other measurements.

Experimental

The data were taken in a 60° mass spectrometer constructed following Nier's design[15] with major modifications in the electronic components. After several of the suggested methods of determining appearance potentials had been tried, the method of vanishing current with argon as the reference gas was chosen since it proved as reliable as any other. The appearance potential was corrected by comparing the linear portion of the ion efficiency curve with the curve for argon, introduced simultaneously with the gas sample, having the same slope. The difference between the observed appearance potential for argon and the listed value, 15.76 e.v., was then added to or subtracted from the observed appearance potential of the ion under study. Our curves of ion current *vs.* electron accelerating voltage are similar to those reported by Hagstrum[1] and others.

Methane, chloro- and bromomethane were obtained from the Mathieson Company in 7.5-pound cylinders. Liquid iodomethane was obtained from Eastman Kodak. The gases were passed through two cold traps and finally transferred to 15-ml. bulbs at a pressure of 10 mm. The bulbs were attached to the inlet system where the initial pressure was 5–10 μ. After the gas entered, the pressure was adjusted to 200 μ. The gas entered the ionization chamber through a General Electric leak, No. 5141081G1, with a 1-mil hole. The pressure in the spectrometer ranged between 1–5 × 10^{-5} mm. No readings were made above 5 × 10^{-5} mm.

The electrons are accelerated from an oxide coated tungsten filament by a single acceleration slit in the ionization chamber. The electron catcher and the ion ejector were operated at the ionization chamber voltage. Detection of the ions was provided by an FP-54 electrometer tube in a Penick-type circuit.[16] An input resistor of 1 × 10^{11} ohms yielded a sensitivity of approximately 1 × 10^{15} amp./mm. at the galvanometer. This amplifier was replaced by a balanced electrometer circuit utilizing two VX-41A (Victoreen) tubes for some of the later measurements. Sensitivity was reduced to approximately half the value previously obtained.

The energy of the ionizing electrons was measured on a dual scale voltmeter (0–25 volts, 0–50 volts), constructed

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(1) H. D. Hagstrum, *Rev. Modern Phys.*, **23**, 185 (1951).

(2) C. A. McDowell and J. W. Warren, *Disc. Faraday Soc.*, No. 10, 53 (1951).

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

(4) J. A. Hipple and W. Bleakney, *ibid.*, **47**, 802 (1935).

(5) R. E. Honig, *J. Chem. Phys.*, **16**, 105 (1948).

(6) G. B. Kistiakowsky and E. R. Van Artsdalen, *ibid.*, **12**, 469 (1944).

(7) D. P. Stevenson and J. A. Hipple, THIS JOURNAL, **64**, 2766, 2769 (1942).

(8) D. P. Stevenson, *Trans. Faraday Soc.*, No. 10, 40 (1951).

(9) G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1950, pp. 459, 518.

(10) H. H. Voge, *J. Chem. Phys.*, **4**, 581 (1936); **16**, 984 (1948).

(11) G. Glockler, *ibid.*, **16**, 842 (1948).

(12) G. Glockler, *Disc. Faraday Soc.*, **10**, 26 (1951

(13) H. Branson and C. Smith, *J. Chem. Phys.*, **20**, 1047 (1952).

(14) C. A. McDowell and B. G. Cox, *ibid.*, **20**, 1496 (1952).

(15) A. O. Nier, *Rev. Sci. Instruments*, **18**, 398 (1947).

(16) D. B. Penick, *ibid.*, **6**, 115 (1935).

from a large scale 0–50 microammeter using high grade precision resistors. The lower scale could be read to 0.1 volt. The meter was calibrated weekly against a potentiometer and a standard cell.

Results.—The data are reported in Tables I, II, IV, V, VII and IX. The errors are given as the root-mean-square of the deviations from the average of measurements taken over the repeated samples. The thermal velocity distribution of the bombarding electrons introduces an error of ~ 0.2 e.v. in observing the breaks in the curve, hence any computed error less than 0.2 e.v. has been raised to that value.

No attempt was made to find negative ions.

Discussion

A. The Heat of Sublimation of Carbon.—The heat of sublimation of carbon can be calculated from a thermochemical cycle involving the heat of reaction and heat of dissociation of CO. Unfortunately, all quantities have been fixed except the dissociation energy of CO. No obvious dissociation limits are apparent from studies of the band spectra.[17] The analysis in terms of predissociation limits yield values for $D(\mathrm{CO})$ of 9.6 and 11.1 e.v., corresponding to $L(\mathrm{C}) = 5.9$ and 7.4 e.v. The electron impact experiments by Hagstrum[1] upon CO lead to the conclusion that $D(\mathrm{CO}) = 9.6$ e.v. and $L(\mathrm{C}) = 5.9$ e.v.

For carbon to appear as a positive ion as a result of electron bombardment in these experiments one or more of the following disintegrations must occur

$$\begin{aligned} \mathrm{CH_3X} + e^- \longrightarrow\ & \mathrm{C^+ + 3H + X + 2e^-} \\ & \mathrm{C^+ + H_2 + H + X + 2e^-} \\ & \mathrm{C^+ + 2H + HX + 2e^-} \\ & \mathrm{C^+ + H_2 + HX + 2e^-} \end{aligned}$$

The appearance potential equation for the first equation is

$$A(\mathrm{C^+}) \geq D(\mathrm{C\text{-}3H\text{-}X}) + I(\mathrm{C^+})$$

where A is the appearance potential, D is the dissociation energy of the indicated reaction and I is the ionization potential of the ion. The equal sign would obtain if no excitational and kinetic energies were possessed by the fragments.

Stevenson[8] has proposed a necessary condition for the equality sign when the molecule breaks into two fragments. In these discussions even when only two fragments result we shall make use of the greater than sign. The values are so close to those obtained by other methods, however, that the equality sign could be substituted within the experimental error.

The dissociation energy may be calculated from several of the reaction equations and their associated energies

$$\begin{array}{rcll} \mathrm{C(graphite)} + 3/2\mathrm{H_2} + 1/2\mathrm{X_2} & \longrightarrow & \mathrm{CH_3X(gas)} & \Delta Hf^0 \\ \mathrm{3H} & \longrightarrow & 3/2\mathrm{H_2} & -3/2D(\mathrm{H_2}) \\ \mathrm{X(gas)} & \longrightarrow & 1/2\mathrm{X_2(gas)} & -1/2D(\mathrm{X_2}) \\ 1/2\mathrm{X_2(gas)} & \longrightarrow & 1/2\mathrm{X_2(S.S.)} & -1/2V(\mathrm{X_2}) \\ \mathrm{C\ (gas)} & \longrightarrow & \mathrm{C(graphite)} & -L(\mathrm{C}) \\ \mathrm{C(gas)} + 3\mathrm{H} + 1/2\mathrm{X} & \longrightarrow & \mathrm{CH_3X} & -D(\mathrm{C\text{-}3H\text{-}X}) \end{array}$$

Addition of the equations yields for the dissociation energy

$$\mathrm{D(C\text{-}3H\text{-}X)} = -\Delta Hf^0 + 3/2D(\mathrm{H_2}) + 1/2D(\mathrm{X_2}) + 1/2V(\mathrm{X_2}) + L(\mathrm{C})$$

where ΔHf^0 is the heat of formation of the compound from the elements in their standard states (S.S.) at 0°K., and $L(\mathrm{C})$ is the heat of sublimation of carbon.

For the initial appearance of the $\mathrm{C^+}$ ion, we have, with A and I in electron volts

$$A(\mathrm{C^+}) \geq D(\mathrm{C\text{-}3H\text{-}X}) + I(\mathrm{C^+})$$

or

$$L(\mathrm{C}) \leq A(\mathrm{C^+}) - I(\mathrm{C^+}) + \Delta Hf^0 - 3/2D(\mathrm{H_2}) - 1/2D(\mathrm{X_2}) - 1/2V(\mathrm{X_2})$$

The values are tabulated in Table III with[18,19]

$D(\mathrm{H_2}) = 4.48$ e.v., $D(\mathrm{Cl_2}) = 2.48$ e.v., $D(\mathrm{Br_2}) = 1.97$ e.v., $D(\mathrm{I_2}) = 1.54$ e.v., $V(\mathrm{Br_2}) = 0.32$ e.v., $V(\mathrm{I_2}) = 0.65$ e.v., $I(\mathrm{C^+}) = 11.26$ e.v.

The first excited state of carbon is the ^{1}D state.[9] It lies 1.3 e.v. above the ground state (^{3}P). Values $\sim$4.6 e.v. for $L(\mathrm{C})$ are obtained if the carbon atom is assumed to be in the ^{1}D state before it is ionized. The ^{5}S state for carbon seems to play no part in any of these reactions, for the values of $L(\mathrm{C})$ obtained when it is used are consistent with none of the others found by other experiments.

Consideration of the other dissociation processes for methane, ($\mathrm{CH_4 \rightarrow C + 2H + H_2}$) and ($\mathrm{CH_4 \rightarrow C + 2H_2}$) lead to $L(\mathrm{C}) = 10.4$ and 14.9 e.v. These may be discarded, as they are not within the limits of previous experiments. Similar processes for the methyl halides yield random values for $L(\mathrm{C})$ over the range 7–13 e.v. The process $\mathrm{CH_3X \rightarrow C + 3H + X}$, when applied to all, is the only one which limits $L(\mathrm{C})$ to a small range of values.

In order for the appearance potentials of $\mathrm{C^+}$ to show as high a conformity with $L(\mathrm{C}) = 7.4$ e.v. as with $L(\mathrm{C}) = 5.9$ e.v., it will be necessary to reveal a source or sources of consistent error which will raise all of our appearance potential values $\sim$ 1.5 volts. Despite the fact that $\mathrm{C^+}$ ions are produced in low abundance, our sensitivity was sufficient to show that the current vanished over a change in electron accelerating voltage of 0.2 volt. The differences, therefore, must be looked for elsewhere.

Pyrolysis of the molecules on the filament seems incapable of accounting for the difference. If the molecules were broken on the filament into neutral fragments and the fragments drifted back into the chamber through the electron slit where they are ionized, there should be no difference in the $\mathrm{C^+}$ values for the four molecules if the neutral fragment is $\mathrm{CH_3}$, $\mathrm{CH_2}$, CH, or C since the filament current is held constant. $D(\mathrm{C\text{-}X}) < D(\mathrm{C\text{-}H})$ so that the probability is less that the neutral fragment would be $\mathrm{CH_2X}$, CHX, or CX. If pyrolysis produces positive ions, they would be retarded by the electron entrance slit which is positive with respect to the filament. Thus the ion current should decrease with increasing electron accelerating voltage. The ion current increases, so that this process seems to be inoperative. On the other hand, even if pyrolysis were contributing

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[17] A. G. Gaydon, "Dissociation Energies," Dover Publications, New York, N. Y., 1950, p. 169.

[18] C. E. Moore, Atomic Energy Levels, Circular 467, Natl. Bur. Standards, Washington, D. C. (1949).

[19] F. D. Rossini, *et al.*, "Selected Values of Chemical and Thermodynamic Properties," Circular 500, Natl. Bur. Standards, Washington, D. C. (1952).

significantly it would require a most improbable distribution of excitational and kinetic energies to give approximately the same value of $L(\mathrm{C})$ for each of these molecules. As an example suppose that $\mathrm{CH_3}$ radicals are produced, the $L(\mathrm{C})$ equation becomes

$$L(\mathrm{C}) \leq A(\mathrm{C^+}) - I(\mathrm{C^+}) + \Delta Hf^0 - 3/2D(\mathrm{H_2}) - 1/2D(\mathrm{X_2}) - 1/2V(\mathrm{X_2}) + D(\mathrm{CH_3} - \mathrm{X}) - (\mathrm{E.E.}) - (\mathrm{K.E.})$$

If $L(\mathrm{C}) = 7.4$ e.v., then for $\mathrm{CH_4}$

E.E. + K.E. ~2.7 e.v.; for $\mathrm{CH_3Cl}$, ~2.0 e.v.;

for $\mathrm{CH_3Br}$, ~ 1.7 e.v. and for $\mathrm{CH_3I}$ ~ 1 e.v.

TABLE I[a]

COMPARISON OF IONIZATION POTENTIALS OBTAINED BY ELECTRON IMPACT AND SPECTROSCOPIC METHODS

Ion	Spec.[b] v.	Electron impact, v.	This work, v.
$\mathrm{CH_4^+}$		13.1 ± 0.2[2] 13.0 ± .1[4]	13.1 ± 0.2
$\mathrm{CH_3Cl^+}$	11.2	11.46 ± .04[c]	11.3 ± 0.3
$\mathrm{CH_3Br^+}$	10.5	10.73 ± .04[c]	10.5 ± 0.4
$\mathrm{CH_3I^+}$	9.5	9.67 ± .04[c]	9.6 ± 0.2

[a] In converting electron volts to kilocalories, we use 1 electron volt = 23.06 kcal.[9] [b] H. Sponer and E. Teller, *Rev. Modern Phys.*, **13**, 144, 145 (1941). [c] J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952).

TABLE II

THE APPEARANCE POTENTIAL OF METHANE FRAGMENTS (V.)

Ion	Smith[3] cor. for argon	Hipple and Bleakney[4]	McDowell[2] and Warren	This work
$\mathrm{C^+}$	26.7 ± 0.7	27	26.2 ± 0.2	26.9 ± 0.2
$\mathrm{CH^+}$	23.4 ± .6	23	22.4 ± .1	23.0 ± .5
$\mathrm{CH_2^+}$	15.8 ± .5	15.7	15.3 ± .5	15.6 ± .2
$\mathrm{CH_3^+}$	14.5 ± .4	14.7	14.4 ± .02	14.3 ± .2
$\mathrm{CH_4^+}$	13.2 ± .4	13.7	13.1 ± .02	13.1 ± .2

We conclude that the evidence favors the process $\mathrm{CH_3X} \rightarrow \mathrm{C}(^3\mathrm{P}) + 3\mathrm{H}(^2\mathrm{S}) + \mathrm{X}(^2\mathrm{P})$ as the actual dissociation process. $\mathrm{H}(^2\mathrm{S})$ and $\mathrm{X}(^2\mathrm{P})$ are the ground states of hydrogen and the halides, respectively. Excited states of these atoms are eliminated for the same reasons as for the other dissociation processes. Hence, the results may be taken as evidence favoring $L(\mathrm{C}) = 5.9$ e.v. as supported by Hagstrum[1] and Goldfinger.[20] These findings are consistent with the earlier electron impact data of L. Smith.[3] Observation of the $\mathrm{C^+}$, $\mathrm{C^-}$ and $\mathrm{H^+}$ ions from methane lead to $L(\mathrm{C}) \leq 6.0$ e.v.

B. The Dissociation Energy of CH.—Both the ionization potential and the dissociation energy of CH are accurately known from spectral analysis. It is of interest to compare the results obtained in this experiment with the accepted values $D(\mathrm{CH}) = 3.47$ e.v. In order to obtain $\mathrm{CH^+}$, there must occur a reaction of the type

$$\begin{aligned} \mathrm{CH_3X} + e^- \longrightarrow & \ \mathrm{CH^+} + 2\mathrm{H} + \mathrm{X} + 2e^- \\ & \ \mathrm{CH^+} + \mathrm{H_2} + \mathrm{X} + 2e^- \\ & \ \mathrm{CH^+} + \mathrm{H} + \mathrm{HX} + 2e^- \end{aligned}$$

The dissociation energy for the first reaction differs from the dissociation energy of the reaction $\mathrm{CH_3X} \rightarrow \mathrm{C} + 3\mathrm{H} + \mathrm{X}$ by the amount $D(\mathrm{CH})$. Therefore, subtraction of the appearance potential equations for the two reactions would be

TABLE III

HEAT OF SUBLIMATION OF CARBON CALCULATED FROM THE APPEARANCE POTENTIAL OF $\mathrm{C^+}$

Molecule	$A(\mathrm{C^+})$, v.	$D(\mathrm{C{-}3H{-}X})$, ev.	$L(\mathrm{C})$, e.v.
$\mathrm{CH_4}$	26.9 ± 0.2	9.65 + $L(\mathrm{C})$	≤5.99 ± 0.2
$\mathrm{CH_3Cl}$	26.0 ± .3	8.81 + $L(\mathrm{C})$	≤5.93 ± .3
$\mathrm{CH_3Br}$	25.4 ± .4	8.22 + $L(\mathrm{C})$	≤5.90 ± .4
$\mathrm{CH_3I}$	24.9 ± .3	7.60 + $L(\mathrm{C})$	≤6.04 ± .3

$$\begin{array}{l} A(\mathrm{C^+}) \geq D(\mathrm{C} + 3\mathrm{H} + \mathrm{X}) + I(\mathrm{C}) \\ A(\mathrm{CH^+}) \geq D(\mathrm{CH} + 2\mathrm{H} + \mathrm{X}) + I(\mathrm{CH}) \\ \hline A(\mathrm{C^+}) - A(\mathrm{CH^+}) = D(\mathrm{CH}) + 11.26 - I(\mathrm{CH}) \end{array}$$

or

$$D(\mathrm{CH}) = A(\mathrm{C^+}) - A(\mathrm{CH^+}) - 0.16$$

The results are shown in Table IV.

TABLE IV

THE APPEARANCE POTENTIALS OF $\mathrm{C^+}$ AND $\mathrm{CH^+}$ AND THE CALCULATED $D(\mathrm{CH})$

Probable process	Appearance potential, v.	$D(\mathrm{CH})$, e.v.
$\mathrm{CH_3I} \rightarrow \mathrm{C^+} + 3\mathrm{H} + \mathrm{I}$	24.9 ± 0.3	≤3.5 ± 0.8
$\rightarrow \mathrm{CH^+} + 2\mathrm{H} + \mathrm{I}$	21.2 ± .5	
$\mathrm{CH_3Br} \rightarrow \mathrm{C^+} + 3\mathrm{H} + \mathrm{Br}$	25.4 ± .4	≤3.4 ± .8
$\rightarrow \mathrm{CH^+} + 2\mathrm{H} + \mathrm{Br}$	21.8 ± .4	
$\mathrm{CH_3Cl} \rightarrow \mathrm{C^+} + 3\mathrm{H} + \mathrm{Cl}$	26.0 ± .3	≤3.4 ± .5
$\rightarrow \mathrm{CH^+} + 2\mathrm{H} + \mathrm{Cl}$	22.4 ± .2	
$\mathrm{CH_4} \rightarrow \mathrm{C^+} + 4\mathrm{H}$	26.9 ± .2	≤3.7 ± .7
$\rightarrow \mathrm{CH^+} + 3\mathrm{H}$	23.0 ± .5	

C. The Dissociation of $(\mathrm{CH_3{-}X})$.—In order to obtain the $\mathrm{CH_3}$ radical in the mass spectrometer, the molecule can dissociate by two methods to produce positive ions

$$\mathrm{CH_3X} + e^- \longrightarrow \mathrm{CH_3^+} + \mathrm{X} + 2e^-$$

and

$$\mathrm{CH_3X} + e^- \longrightarrow \mathrm{CH_3} + \mathrm{X^+} + 2e^-$$

The appearance potential equations are

$$\begin{aligned} A(\mathrm{CH_3^+}) &= D(\mathrm{CH_3} - \mathrm{X}) + I(\mathrm{CH_3}) \\ A(\mathrm{X^+}) &= D(\mathrm{CH_3} - \mathrm{X}) + I(\mathrm{X}) \end{aligned}$$

The dissociation energy may be computed since the ionization energy of $\mathrm{CH_3}$ is known to be 10.1 e.v.[10,11]

Previous work has shown the energy of the first bond in methane to be 4.42 ± 0.02 e.v. We find 4.2 ± 0.2 e.v. to be the bond energy. In the methyl halides, the bond energy decreases with increasing molecular weight.

The necessary condition for the equality

$$A(\mathrm{R_1^+}) \geq I(\mathrm{R_1}) + D(\mathrm{R_1} - \mathrm{R_2})$$

proposed by Stevenson[8] finds additional substantiation in these data. The condition is that the equal sign obtains if

$$I(\mathrm{R_1}) < I(\mathrm{R_2})$$

otherwise

$$A(\mathrm{R_1^+}) > I(\mathrm{R_1}) + D(\mathrm{R_1} - \mathrm{R_2}).$$

In the data in Table V, $I(\mathrm{X}) > I(\mathrm{CH_3})$ for each compound. Thus $A(\mathrm{X^+})$ would be expected to exceed $A(\mathrm{CH_3^+})$ by an amount greater than the difference in the ionization potential. The value

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(20) Statement by H. D. Hagstrum at American Physical Society meeting, Washington, April, 1952.

of $D(CH_3–X)$ calculated from $A(X^+)$ should have a higher limit than that calculated from $A(CH_3^+)$. This tendency is shown in Table V.

TABLE V

THE APPEARANCE POTENTIALS OF CH_3^+ AND X^+ AND THE CALCULATED $(CH_3–X)$ BOND ENERGY

Probable process	Appearance potential, v.	Ionization potential, v.	$D(CH_3–X)$, e.v.
$CH_3I \rightarrow CH_3 + I^+$	12.9 ± 0.3	10.4	≤2.5 ± 0.3
$\rightarrow CH_3^+ + I$	12.4 ± .2	10.1	≤2.3 ± .2
$CH_3Br \rightarrow CH_3 + Br^+$	15.0 ± .5	11.8	≤3.2 ± .5
$\rightarrow CH_3^+ + Br$	13.2 ± .3	10.1	≤3.1 ± .3
$CH_3Cl \rightarrow CH_3 + Cl^+$	16.6 ± .2	13.0	≤3.6 ± .2
$\rightarrow CH_3^+ + Cl$	13.5 ± .5	10.1	≤3.4 ± .5
$CH_4 \rightarrow CH_3 + H^+$	Not measured		
$\rightarrow CH_3^+ + H$	14.3 ± .2	10.1	≤4.2 ± .2

Bauer and Hogness[21] estimated the energy $D(CH_3–Cl)$ to be approximately 0.9 e.v. less than the same bond in methane. They measured the appearance potential of Cl^+ from CH_3Cl to be 26.5 ± 1.0 e.v. Their value gives an inordinately high upper limit (~ 13.5 e.v.) for the dissociation energy with which our value of 3.4 ± 0.5 e.v. is consistent. Our value is higher than that for C–Cl reported by Pauling,[22] 2.9 e.v. (66.5 kcal./mole) and the result of Doty,[23] 3.2 e.v. (74 kcal./mole).

Baughn[24] reported $D(CH_3–I) = 55$ kcal./mole (2.38 e.v.). The electron impact results agree very closely. This work obtained $D(CH_3–I) \leq 2.3 \pm 0.2$ e.v. and Diebler[25] obtained $D(CH_3–I) \leq 2.5$ e.v. from the appearance potential of the CH_3^+.

Processes such as

$$CH_3X + e^- \longleftarrow CH_3^+ + X^- + e^-$$

where negative ions are formed might be expected to play a role in the production of CH_3^+ and the other positive ions discussed in this paper since the halogens have large electron affinities (~ 3.5 e.v.). If this process did occur, we would have for the first appearance of CH_3^+ ions

$$A(CH_3^+) = D(CH_3–X) + I(CH_3) - Ea(X)$$

where Ea represents the electron affinity. Using X = Cl for our example, we have $D(CH_3–X)$ from other experiments is at most 3.8 e.v., $I(CH_3^+) = 10.1$ e.v., $Ea(Cl) = 3.75$ e.v.[26]; hence $A(CH_3^+)$ would be expected to be near 10.2 e.v. The fact that no ion current is detected until the electron acceleration voltage is about 3 volts higher indicates that the process producing X^- plays an insignificant role.

There remains the possibility that this process may play a significant role if either CH_3^+ or X^- is produced with excitational energy. Cl^- has an excited state lying 4.2 e.v. above the ground state.[26] If excited Cl^- is produced, $A(CH_3^+) \sim 14.0$ e.v. which is slightly higher than our experimental value but on the upper fringe of the given experimental error. There is no information in the excited states of CH_3^+. If the additional energy contributed by the electron affinity is compensated by excitation, there will be little change in our computed values. Similar arguments apply for the other positive ions.

The energy of the first bond is the outstanding difference among the four molecules being investigated. This difference should appear also in the total dissociation energy of the molecule. According to the dissociation energies computed using $L(C) = 5.9$ e.v., the energy of the $(CH_3–X)$ bond should be 0.9 e.v. less than the bond in methane. By this reasoning the bond energy in bromomethane and iodomethane should be 2.9 and 2.3 e.v., respectively. Thus, the results for $D(CH_3–Br) \leq 3.1 \pm 0.3$ should be regarded as an upper limit.

The energy of atomization or the heat of total dissociation (C–3H–X) is equal to the sum of the energies required to strip successive atoms from the carbon. Part of this energy is represented in the dissociation energy of the CH_3 radical. This energy is the same for the four molecules. It is equal to the difference between the heat of atomization and the energy of the first bond

$$D(C–3H) = D(C–3H–X) - D(CH_3–X)$$

Voge[10] has calculated this energy to be 11.1 e.v. This figure is to be compared with our value ≥ 11.2 ± 0.2.

The dissociation energy for the methyl radical may be found by subtracting the energy of the $(CH_3–H)$ bond from the heat of atomization of methane. Thus, the difference between this value $D(C–3H) = 11.3$ e.v. and the heats of atomization of the substituted methanes should be the $D(CH_3–X)$ for each molecule considered. The energy $D(CH_3–X)$ computed in this manner agrees with the previously reported values with the exception of $D(CH_3–Br)$. Szwarc and Sehon[27] computed $D(CH_3–Br) \sim 2.9$ e.v. (67.5 kcal./mole). Applying the procedure outlined above leads to the same result, which is lower by 0.2 e.v. from our measured value. Since it is certain that the $D(C–3H)$ energy is a constant quantity, we conclude that the measurements of the appearance potentials concerned are ~0.1 e.v. too great and constitute an upper limit only. Examination shows that $D(C–3H) = 11.2$ e.v. yields more consistent results.

The experiments check the ionization potentials of the methyl halides as observed by Price.[28] The $D(CH_3–X)$ bond energies of chloro-, bromo- and iodomethane are found to be ≤ 3.4 ± 0.5, ≤ 3.1 ± 0.3 and ≤ 2.3 ± 0.2 e.v., respectively.

D. The Appearance Potentials of Other Fragments.—The interpretation of the appearance potentials of CH_2^+ presents a choice between

$$CH_3X + e^- \longrightarrow CH_2^+ + H + X + 2e^-$$

and

$$CH_3X + e^- \longrightarrow CH_2^+ + HX + 2e^-$$

The second reaction cannot be ruled out since HX^+ are observed and their appearance potentials were consistent with $CH_3X + e^- \rightarrow CH_2 + HX^+$

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[21] S. Bauer and T. R. Hogness, *J. Chem. Phys.*, **3**, 687 (1935).

[22] L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1945, p. 53.

[23] P. M. Doty, *J. Chem. Phys.*, **12**, 399 (1944).

[24] E. C. Baughn, B. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **37**, 377 (1941).

[25] V. H. Diebler in conversation with C. Smith.

[26] H. S. W. Massey, "Negative Ions," Cambridge Univ. Press, 1950, p. 21.

[27] M. Szwarc and A. H. Sehon, *J. Chem. Phys.*, **19**, 656 (1951).

[28] W. C. Price, *ibid.*, **4**, 539 (1936).

TABLE VI

D(C-3H) COMPUTED FROM D(C-3H-X) − D(CH$_3$-X) = D(C-3H)

Molecule	D (C-3H-X), e.v.	D(CH$_3$-X), e.v.	D(C-3H), e.v.
CH_4	15.5	$\leq 4.2 \pm 0.2$	$\geq 11.3 \pm 0.2$
CH_3Cl	14.7	$\leq 3.4 \pm .5$	$\geq 11.3 \pm .5$
CH_3Br	14.1	$\leq 3.1 \pm .3$	$\geq 11.0 \pm .3$
CH_3I	13.5	$\leq 2.3 \pm .2$	$\geq 11.2 \pm .2$

$+ 2e^-$. If the presence of HX^+ implies that CH_2^+ when first observed arises from the second reaction, we get consistency in the value 12.0 v. for $I(CH_2^+)$ as shown in Table VII. If the first reaction is assumed, the ionization potentials are, from CH_4, $I(CH_2) \leq 7.5$ v.; from CH_3Cl, $I(CH_2^+) \leq 7.6$ v.; from CH_3Br, $I(CH_2^+) \leq 8.2$ v.; from CH_3I, $I(CH_2^+) \leq 9.0$ v. These values would limit $I(CH_2^+) \leq 7.5$ v. which seems inordinately low. Because of the consistency and the higher value, we prefer to use the second reaction in our interpretation.

TABLE VII

THE APPEARANCE POTENTIALS OF CH_2^+ AND HX^+ AND THE DEDUCED IONIZATION POTENTIAL OF CH_2

Probable process	Appearance potential, v.	I(HX), v.	$I(CH_2)$,[a] v.
$CH_3I \rightarrow CH_2 + HI^+$	13.2 ± 0.6	10.4	
$\rightarrow CH_2^+ + HI$	$14.8 \pm .4$		12.0 ± 0.4
$CH_3Br \rightarrow CH_2 + HBr^+$	$15.1 \pm .3$	12.1	
$\rightarrow CH_2^+ + HBr$	$15.0 \pm .3$		$12.0 \pm .3$
$CH_3Cl \rightarrow CH_2 + HCl^+$	$16.1 \pm .5$	12.9	
$\rightarrow CH_2^+ + HCl$	$15.3 \pm .5$		$12.1 \pm .5$
$CH_4 \rightarrow CH_2 + H_2^+$	Not measured		
$\rightarrow CH_2^+ + H_2$	15.6 ± 0.2		$12.0 \pm .2$

[a] A. Langer and J. A. Hipple reported 11.9 ± 0.2 v. for $I(CH_2^+)$, *Phys. Rev.*, 69, 691 (1946).

This choice for CH_2^+ immediately casts doubt upon

$$CH_3X + e^- \longrightarrow C^+ + 3H + X + 2e^-$$

and

$$CH_3X + e^- \longrightarrow CH^+ + 2H + X + 2e^-$$

as being the processes responsible for the ions C^+ and CH^+, when first observed. The other processes could occur with no change in our calculated results if the additional energy made available is assumed to go into kinetic energy and excitational energy. If the disruption occurs with no kinetic or excitational energy and with H_2 or HX fragments, the derived values based upon C^+ and CH^+ would have to be increased by $D(H_2)$ or D(HX), respectively. The results raise some values as mentioned ahead so that the electron impact data would be rather insensitive, for example, in deciding a value for L(C).

The values for D(C-2H) may be calculated from

$$D(\text{C-2H}) = D(\text{C-3H-X}) - D(\text{CH}_2\text{-HX}) - D(\text{HX})$$

The values are given in Table VIII along with those calculated for D(CH$_2$-HX) and the accepted values for D(C-3H-X) and D(HX). The average is 7.4 e.v. which gives an average value for the removal of the two hydrogens of 3.7 e.v. each.

TABLE VIII

D(C-2H) DETERMINED FROM THE EQUATION D(C-2H) = D(C-3H-X) − D(CH$_2$-HX) − D(HX)

Molecule	D(C-3H-X), e.v.	D(CH$_2$-HX), e.v.	D(HX), e.v.	D(C-2H), e.v.
CH_4	15.5	3.6 ± 0.2	4.5	7.4 ± 0.2
CH_3Cl	14.7	$3.2 \pm .5$	4.4	$7.1 \pm .5$
CH_3Br	14.1	$3.0 \pm .3$	3.7	$7.4 \pm .3$
CH_3I	13.5	$2.8 \pm .6$	3.1	$7.6 \pm .6$

Since D(CH$_3$-X) + D(CH-2H) = D(CH-2H-X), D(CH-2H) may be found from $A(CH^+)$ and $A(CH_3^+)$ and the ionization potentials. The values are collected in Table IX. These values average $\leq$ 7.9 e.v. which is a high upper limit.

TABLE IX

D(C-2H) COMPUTED FROM APPEARANCE POTENTIALS OF CH_3^+ AND CH^+

Molecule	Ion	App. pot., v.	D(C-2H), e.v.
CH_4	CH^{+a}	23.0 ± 0.5	≤ 7.7
	CH_3^+	$14.3 \pm .2$	
CH_3Cl	CH^+	$22.4 \pm .2$	≤ 7.9
	CH_3^+	$13.5 \pm .5$	
CH_3Br	CH^+	$22.3 \pm .5$	≤ 8.1
	CH_3^+	$13.2 \pm .3$	
CH_3I	CH^+	$21.2 \pm .5$	≤ 7.8
	CH_3^+	$12.4 \pm .2$	

[a] $I(CH^+) = 11.1$ v., ref. 9, p. 459.

The heats of removal of successive hydrogens from methane are compared with Voge's[10] calculated values in Table X. Our values are calculated from

$$D(\text{CH}_3\text{-X}) + D(\text{CH}_2\text{-H}) = D(\text{CH}_2\text{-H-X}).$$

The results are low for CH_3 but high for CH_2.

TABLE X

HEATS OF REMOVAL OF HYDROGEN ATOMS FROM METHANE (e.v.)

Process	Voge[10]	This work
$CH_4 \rightarrow CH_3 + H$	4.47	4.4[a]
$CH_3 \rightarrow CH_2 + H$	4.14	≤ 3.8
$CH_2 \rightarrow CH + H$	3.43	≤ 3.9
$CH \rightarrow C + H$	3.47	3.5[a]
Total	15.51	15.6

[a] Accepted values.

Acknowledgments.—This work has been supported mainly by the Office of Naval Research, N8 ONR-538, with some help from our Atomic Energy Commission Project, AT(30-1)-892. We are greatly indebted to Mr. William N. McIntosh for keeping the mass spectrometer in working order. Mr. Foster Drakeford, Mr. LeRoy B. Garner and Mr. James W. Mayo assisted in taking readings.

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