mation of gaseous perchloryl fluoride at 25°. The precision error was 0.40 kcal., the calibration error was taken as 0.20 kcal., and the accuracy error was estimated as 0.50 kcal. The final value for the standard heat of formation of ClO_3F is then -5.12 ± 0.68 kcal./mole.

Acknowledgments.—The authors wish to acknowledge the aid of Drs. John F. Gall and Gerhard Barth-Wehrenalp of the Pennsylvania Salt Manufacturing Company who furnished the sample of perchloryl fluoride.

MADISON 6, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TEXAS]

Thermodynamic Data from Electron-impact Measurements on Acetylene and Substituted Acetylenes*

BY FRED H. COATS AND ROBBIN C. ANDERSON

RECEIVED AUGUST 20, 1956

Earlier measurements of electron-impact data for propyne and 2-butyne have been extended to other substituted acetylenes: 1-butyne, diacetylene, 1-Br-1-propyne, 1-Cl-1-propyne and phenoxyacetylene. From these the heat of formation of C_2H was determined to be 112 kcal./mole. Bond energies for the carbon–hydrogen and carbon–carbon bonds in acetylene and for certain bonds in the substituted acetylenes can then be evaluated.

Studies of the various dissociation processes for acetylenic compounds by electron-impact techniques furnish a possible source of information on the energies involved in the formation of various free radicals which may be of significance in the thermal decomposition reactions of these compounds. For this reason the appearance potentials for a number of ions from a series of substituted acetylenes have been determined. Experimental data on propyne and 2-butyne have been presented earlier.[1] The determinations of appearance potentials have now been extended to 1-butyne and diacetylene. Since phenoxyacetylene and 1-chloropropyne and 1-bromopropyne all gave evidence of unusual reactivity in decomposition flames of acetylene,[2] they were also included in these determinations.

Experimental

Materials.—The propyne and the butynes were supplied by the Farchan Laboratories of Cleveland. The argon and krypton used as standards were obtained from General Electric Laboratories.

The halopropynes and diacetylene were supplied by Dr. Lewis F. Hatch and his co-workers at the University of Texas. The 1-bromo-1-propyne was prepared by the action of hypobromite on propyne.[3] One sample of 1-chloro-1-propyne was prepared here by dehydrobromination of 1-bromo-1-chloro-1-propene. A second sample was made available through the kindness of Dr. L. C. Leitch.[4] The identity and purity of the halogen-substituted propynes were confirmed by infrared analysis. The phenoxyacetylene was prepared by dehydrobromination of 1-bromo-2-phenoxyethene.[5]

The diacetylene was prepared by dehydrochlorination of 1,4-dichloro-2-butyne.

Preliminary mass scans of each compound were made and compared with mass spectra from the literature.[6] These tests showed no impurities which would interfere with the appearance potential measurements.

Appearance Potentials.—The experimental method for appearance potentials has been described previously.[1] They were measured by the method of vanishing ion currents using a Westinghouse Type LV Mass Spectrometer.

Excess Kinetic Energies.—In these measurements two approaches were used, both of which are based on the fact that the ion-collecting and focussing properties of a sector-type mass spectrometer depend upon the amount of kinetic energy with which an ion is formed. The first of these was originally suggested by Hagstrum and Tate[7] and simply involves comparing the ion accelerating voltage needed to focus the ion under investigation with that calculated from the mass spectrometer focussing equation, mv = constant. As a reference voltage for the calculation, the observed voltage for some ion known to be formed with no kinetic energy is used.

In determining the product of mass and focussing voltage for several thermal ions such as Kr^+, A^+ and Ne^+, it was found that this product is not constant for this instrument. However it was found that over small ranges the change in the mv product per mass unit is constant, and this value for $\Delta mv/\Delta m$ was evaluated by determining the focussing conditions for several ions in the appropriate mass range which are known to be formed with zero kinetic energy.

The second method is that of Berry[8] who has shown that because of discrimination at the collector slit against passage of ions formed with initial kinetic energy, the observed ion current for a particular ion should remain constant as the ion accelerating voltage is decreased to a certain critical value (varying the magnetic field to keep the ion in focus) and should then decrease linearly.

In measuring discrimination effects it was only necessary to measure the observed ion current for a particular ion as a function of the ion accelerating voltage and compare this with similar data for an ion known to involve no appreciable excess kinetic energy. The chief difficulty with this measurement lies in the rather limited range of the ion accelerating voltages available with this particular instrument.

Results

Appearance Potentials.—The experimental results are summarized in Table I. For purposes of comparison and reference the data on acetylene, propyne and 2-butyne which were reported earlier[1] are included here.

The value found here by direct electron impact for the ionization potential of diacetylene is appreciably lower than the figure of 10.9 v. calculated

---

* This research was supported by the Air Force Office of Sci. Res. of the Air Res. and Devel. Command under Contract No AF 18-(600)-430.

[1] F. H. Coats and R. C. Anderson, THIS JOURNAL, **77**, 895 (1955).

[2] M. S. B. Munson and R. C. Anderson, paper presented at Am. Chem. Soc. Meeting, Minneapolis, Minn., Sept., 1955; *cf.* Tech. Note No. 17, Combustion Kinetics Project, Univ. of Texas (Jan., 1955).

[3] F. F. Cleveland and J. M. Murray, *J. Chem. Phys.*, **11**, 450 (1943); *cf.* L. F. Hatch and L. E. Kidwell, THIS JOURNAL, **76**, 289 (1954).

[4] A. T. Morse and L. C. Leitch, *Can. J. Chem.*, **32**, 500 (1954).

[5] T. L. Jacobs, R. Cramer and F. Z. Weiss, THIS JOURNAL, **62**, 1849 (1940); *cf.* L. F. Hatch and H. D. Weiss, *ibid.*, **77**, 1798 (1955).

[6] Catalogue of Mass Spectral Data, American Petroleum Institute, Research Project 44, Carnegie Institute of Technology.

[7] H. D. Hagstrum and J. T. Tate, *Phys. Revs.*, **59**, 354 (1941).

[8] C. E. Berry, *ibid.*, **78**, 597 (1950).

TABLE I

APPEARANCE POTENTIALS

Ion	A_R	Ion	A_R
	H—C≡C—H		
$C_2H_2^+$	11.4 ± 0.1	C_2^+	23.3 ± 0.5
C_2H^+	17.8 ± 0.5		
	CH_3—C≡C—H		
$C_3H_4^+$	10.3 ± 0.1	C_3^+	26.0 ± 1
$C_3H_3^+$	11.8 ± .1	C_2H^+	17.2 ± 0.5
$C_3H_2^+$	14.0 ± .1	CH_3^+	15.4 ± .5
C_3H^+	18.4 ± .3		
	CH_3—C≡C—CH_3		
$C_4H_6^+$	9.9 ± 0.1	$C_4H_2^+$	16.7 ± 0.3
$C_4H_5^+$	12.2 ± .1	$C_3H_3^+$	11.4 ± .2
$C_4H_4^+$	14.0 ± .1	$C_2H_3^+$	14.7 ± .2
$C_4H_3^+$	15.1 ± .2	CH_3^+	17.6 ± .5
	CH_3—CH_2—C≡C—H		
$C_4H_6^+$	10.2 ± 0.1	$C_4H_3^+$	14.6 ± 0.2
$C_4H_5^+$	11.6 ± .1	$C_3H_3^+$	10.8 ± .2
$C_4H_4^+$	10.9 ± .2	$C_2H_5^+$	12.9 ± .1
	H—C≡C—C≡C—H		
$C_4H_2^+$	10.2 ± 0.1	C_2H^+	20.1 ± 0.5
C_4H^+	12.1 ± .3		
	C_6H_5—O—C≡C—H		
$C_6H_5O^+$	9.5 ± 0.1	$C_6H_5^+$	12.2 ± 0.1
	CH_3—C≡C—Br		
$C_3H_3Br^+$	10.1 ± 0.1	Br^+	16.0 ± 0.5
$C_3H_3^+$	11.1 ± .2		
	CH_3—C≡C—Cl		
$C_3H_3Cl^+$	9.9 ± 0.1	Cl^+	18.4 ± 0.5
$C_3H_3^+$	11.0 ± .2		

by Franklin and Field and the spectroscopic value of 10.74 v. reported by Price and Walsh. The former is based on formation of $C_4H_2^+$ from vinylacetylene, so some variation is not surprising, but no reason is immediately apparent for the difference from the spectroscopic value.

Certain of the ions of potential interest were not formed in concentrations sufficiently high to permit the measurement of their appearance potentials. This was true of CH^+ and C^+ from acetylene in particular, and also of CH_3^+ and C_2H^+ from 1-butyne.

Heat of Formation of C_2H.—Where reliable data on the ionization potentials for various fragments are available, dissociation energies have been calculated directly. For the reaction

$$R_1\text{-}R_2 + e^- \longrightarrow R_1^+ + R_2 + 2e^-$$

the well-known relation

$$D(R_1\text{-}R_2) = A(R_1^+) - I(R_1)$$

may be used if it is assumed that R_1^+ and R_2 are formed in their lowest energy states and have only the kinetic energy corresponding to the temperature of the surrounding gas. Stevenson[9] and others have shown that this relation is questionable unless $I_{R_1} \lesssim I_{R_2}$.

For reactions involving C_2H, the above criteria can be met reasonably in the cases of the formation of C_2H^+ from acetylene and diacetylene, CH_3^+ from propyne and $C_2H_5^+$ from 1-butyne. The appearance potentials of C_2H^+ from propyne and 1-butyne involve greater uncertainties in experimental results and these systems do not meet the criterion cited above.

Ionization potentials for methyl and ethyl radicals, 9.96 and 8.67 v., respectively, are now available from direct measurements.[9] Their heats of formation can be determined to be 32 and 26 kcal./mole.[10] Eltenton[11] has determined indirectly $I(C_2H)$ at 11.3 v.

As an example of these calculations consider the process

$$CH_3\text{-}C_2H + e^- \longrightarrow CH_3^+ + C_2H + 2e^- \qquad A(CH_3^+) = 15.4 \text{ e.v.}$$

Since $I(CH_3) = 9.96$ e.v.

$$CH_3\text{-}C_2H \longrightarrow CH_3 + C_2H \qquad \Delta H = 5.4 \text{ e.v.} = 124.5 \text{ kcal/mole}$$

From the heats of formation of propyne[12] and methyl radical

$$\Delta H_f(C_2H) = 124.5 - 32 + 44.3 = 136.8 \text{ kcal.}$$

Similar calculations can be made using C_2H^+ from acetylene and diacetylene and $C_2H_5^+$ from 1-butyne. A comparison of these values along with data from other sources is given in Table II. These show rather marked variations for the different acetylenic compounds.

TABLE II

HEAT OF FORMATION OF C_2H (KCAL./MOLE)

Electron impact: direct calcn.	
C_2H^+ from C_2H_2: 152 ± 15	
	CH_3^+ from CH_3C_2H: 137 ± 12
C_2H^+ from C_4H_2: 153 ± 15	
	$C_2H_5^+$ from $C_2H_5C_2H$: 110 ± 3
Other sources	
Photolysis: 123	D + C_2H_2: 112
Thermochem: 106	CH_3 + C_2H_2: 113

The value of Cherton[13] is the one usually quoted. It is determined from the photochemical threshold for the appearance of diacetylene in the photolysis of acetylene. It should be noted that this value would give $D(H\text{-}C_2H)$ to be 121 kcal./mole whereas Steacie and Le Roy[14] found a threshold for photosensitization which would require that this be < 108 kcal./mole, so it seems likely that Cherton's result is high.

The thermochemical value is the estimate obtained if one takes $D(H\text{-}C_2H)$ to be 104 kcal./mole and uses this for ΔH for the dissociation reaction.

The value for D + C_2H_2 is obtained by assuming this reaction to be slightly endothermic and using the value of Geib and Steacie[15] for the energy of activation as a maximum value for the heat of reaction. A similar calculation can be made using the

---

(9) *Cf.* D. P. Stevenson, Symposium on Mechanisms of Homogeneous and Heterogeneous Hydrocarbon Reactions (Div. of Petrol. Chem., Am. Chem. Soc.) Kansas City, March, 1954, p. 19.

(10) M. Szwarc, *Chem. Revs.*, **47**, 75 (1950).

(11) G. C. Eltenton, *J. Chem. Phys.*, **15**, 455 (1947).

(12) U. S. Bureau of Standards Tables of Selected Thermodynamic Properties.

(13) R. Cherton, *Bull. soc. chim. belg.*, **52**, 26 (1943).

(14) E. W. R. Steacie and D. J. Le Roy, *J. Chem. Phys.*, **12**, 117 (1944).

(15) K. H. Geib and E. W. R. Steacie, *Z. physik. Chem.*, **B29**, 215 (1935).

data of Trotman-Dickenson, Phillips and Steacie[16] on the energy of activation for the reaction of methyl radicals with the butynes and of C_2H with methane.

Indirect calculations may be used in cases where ionization potentials are either questionable or not known. For example consider the steps

$$H_2C\text{–}C_2H \longrightarrow 2C_2H \qquad \Delta H = A_1(C_2H^+) - I(C_2H)$$

$$C_2H_2 \longrightarrow C_2H + H \qquad \Delta H = A_2(C_2H^+) - I(C_2H)$$

Subtracting

$$HC_2\text{–}C_2H + H \longrightarrow C_2H_2 + C_2H$$

$$\Delta H = A_1(C_2H^+) - A_2(C_2H^+) = 2.3 \text{ e.v.} = 53 \text{ kcal.}$$

The heat of formation of diacetylene may be calculated to be 102 kcal./mole from Franklin's[17] parameters, allowing 6 kcal. for resonance stabilization. Using this, one obtains a value of 153 kcal./mole for the heat of formation of C_2H radical.

Similar calculations may be made with propyne and 1-butyne using Deerk and Neuert's[18] value for $A(CH_3^+)$ from methane and Eltenton's[11] value for $A(C_2H_5^+)$ from ethane. These lead to values of 137 and 112 kcal./mole, respectively, for the heat of formation of C_2H radical.

The indirect calculation using data for ethane and 1-butyne involves the most precise of the appearance potentials and it is in agreement with the threshold values. The value of 112 ± 3 kcal./mole may therefore be taken as the best value of the group.

Excess Kinetic Energies in Formation of C_2H or C_2H^+.—The ions of particular interest in this work were C_2H^+ from acetylene, CH_3^+ from propyne and $C_2H_5^+$ from 1-butyne. In the mass range of from 20 to 30, $\Delta mv/\Delta m$ was found to be 45.0 ± 1.0 volt mass units. This value was obtained by measuring the peak shift for the neon isotopes and for the parent peaks from N_2 and C_2H_2.

The shift between peaks corresponding to the $C_2H_2^+$ and C_2H^+ ions from acetylene was found to be 39.0 ± 1.0 volt mass units which would seem to indicate that a number of C_2H^+ ions having excess kinetic energy are formed. No detectable change in this value was observed when the electron beam energy was varied from 25 to 75 electron volts.

The results for the CH_3^+ ion from propyne were inconclusive due to the difficulty in determining a normal shift in this mass range and also to the very low ion currents obtainable.

For the $C_2H_5^+$ ion from 1-butyne a normal value of 45 ± 1 volt mass units was observed which indicates that this ion is formed with little or no excess kinetic energy.

The ion currents observed for $C_2H_2^+$ and C_2H^+ ions from acetylene at various ion accelerating voltages are shown in Fig. 1. The curve obtained for the $C_2H_2^+$ ion is typical of those observed for ions having only thermal energy. However, the absence of a definite break in the curve for C_2H^+ and the non-linearity of the lower portion are characteristic of ions formed with appreciably more than thermal energy.

Qualitatively, these results indicate the C_2H^+ ion is formed from acetylene with excess kinetic energy and thus can explain the observed discrepancies in the calculated values for the heat of formation of C_2H radicals. Quantitatively, the results for C_2H^+ ion from acetylene are not so satisfying. The magnitude of the peak shift indicates that the C_2H^+ ions are formed with approximately 0.24 electron volt excess energy while the differences in the calculated radical heats of formation involve approximately 1.7 electron volts. However, since the range of error in the determination of the appearance potentials and the peak shifts is almost this large in itself, the two are not necessarily inconsistent.

Since it is found that the $C_2H_5^+$ ion is formed with little or no excess energy at ionizing voltages above its appearance potential, it is reasonable to assume that the observed appearance potential for this ion represents the minimum dissociation energy. This would support the conclusion above that the heat of formation of C_2H calculated from this appearance potential is the best of those obtained so far. These results, plus the value of 153 kcal./mole found for formation of C_2H^+ from diacetylene indicate that there also C_2H^+ is formed with excess kinetic energy; but because of the experimental difficulties, it was not practicable to try to determine the excess energy in this case.

Ionization Potential of C_2H.—For the reactions

$$CH_3C_2H + e^- \longrightarrow CH_3 + C_2H^+ + 2e^- \qquad A(C_2H^+) = 17.2 \text{ v.}$$

$$CH_3C_2H \longrightarrow CH_3 + C_2H \qquad \Delta H = 5.4 \text{ e.v.}$$

Direct subtraction would give a value $I(C_2H) = 11.8$ v. which is appreciably higher than the value of 11.3 v. which is based on the data of Hipple.[19] However, the results noted above indicate there is excess energy associated with the particles produced from acetylene, diacetylene and propyne. The calculated ionization potential above would not necessarily be in disagreement with Hipple's value since it probably involves excess energy.

Heat of Formation and Ionization Potential of C_2.—From the appearance potential of C_2^+ from acetylene and the value of 11.5 v. for its ionization potential[20] the heat of formation of C_2 is calculated to be 215 kcal. This may be compared with values of 190–210 kcal.[20,21] from the sublimation of graphite and the Bureau of Standards value of 235 kcal.[12]

Heats of Formation of Certain Ions.—It is interesting to note that the voltage increments for loss of the first hydrogen from propyne and 1-butyne correspond to that for the alkane series, whereas that for 2-butyne corresponds to the increment for alkenes. This raises a question as to the nature of the $C_3H_3^+$ ion from propyne, *i.e.*, whether it is $CH_3\text{–}C{\equiv}C^+$ or $^+CH_2\text{–}C{\equiv}CH$, and also concerning the corresponding ions from the other alkynes.

---

(16) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951); *cf.* E. W. R. Steacie and N. W. R. Phillips, *ibid.*, **4**, 416 (1936).

(17) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949); *J. Chem. Phys.*, **21**, 2029 (1953).

(18) J. Deerk and H. Neuert, *Z. Naturforsch.*, [5a] **50**, 2 (1950).

(19) J. A. Hipple, *Phys. Revs.*, **53**, 530 (1938).

(20) W. A. Chupka and M. G. Inghram, *J. Phys. Chem.*, **59**, 100 (1955).

(21) R. E. Honig, *J. Chem. Phys.*, **22**, 126 (1954).

From the appearance potentials of Table I

$$\mathrm{CH_3{=}C_2H + e^- \longrightarrow C_3H_3^+ + H + 2e^-}$$
$$A(\mathrm{C_3H_3^+}) = 11.8 \text{ e.v.}$$
$$\Delta H_f(\mathrm{C_3H_3^+}) = 264 \text{ kcal./mole}$$
$$\mathrm{CH_3{-}C_2{-}CH_3 + e^- \longrightarrow CH_3{-}C_2^+ + CH_3 + 2e^-}$$
$$A(\mathrm{C_3H_3^+}) = 11.4 \text{ e.v.}$$
$$\Delta H_f(\mathrm{C_3H_3^+}) = 263 \text{ kcal./mole} = \Delta H_f(\mathrm{CH_3{-}C{\equiv}C^+})$$
$$\mathrm{CH_3{-}CH_2{-}C_2H + e^- \longrightarrow CH_2{-}C_2H^+ + CH_3 + 2e^-}$$
$$A(\mathrm{C_3H_3^+}) = 10.8 \text{ e.v.}$$
$$\Delta H_f(\mathrm{C_3H_3^+}) = 254 \text{ kcal./mole} = \Delta H_f(\mathrm{CH_2{-}C{\equiv}CH^+})$$

These values suggest, rather surprisingly, that propyne splits first as

$$\mathrm{e + CH_3{-}C{\equiv}CH \longrightarrow CH_3{-}C{\equiv}C^+ + H}$$

If one considers also the steps

$$\mathrm{CH_3{-}C_2H \longrightarrow CH_3C_2 + H} \qquad \Delta H = A_1(\mathrm{C_3H_3}) - I(\mathrm{C_3H_3})$$
$$\mathrm{CH_3C_2CH_3 \longrightarrow CH_3C_2 + CH_3} \qquad \Delta H = A_2(\mathrm{C_3H_3}) - I(\mathrm{C_3H_3})$$

and subtracting

$$\mathrm{CH_3 + CH_3{-}C_2H \longrightarrow CH_3C_2CH_3 + H}$$
$$\Delta H = A_1(\mathrm{C_3H_3^+}) - A_2(\mathrm{C_3H_3^+})$$

if *both* are $\mathrm{CH_3C{\equiv}C^+}$

$$\Delta H = 0.4 \pm 0.2 \text{ e.v.} = 9 \pm 5 \text{ kcal.}$$

From thermochemical data, $\Delta H = 10.8$ kcal. For a similar calculation assuming $\mathrm{C_3H_3^+}$ from propyne is $\mathrm{^+CH_2C{\equiv}CH}$, the mass spectrographic and thermochemical values differ by 16–50 kcal.

Calculations based on group contributions,[17] however, indicate that only the propargyl ion is a feasible product. $\Delta H_f(\mathrm{C_3H_3^+})$ from propyne is 264 kcal. Using various group contributions, one can calculate heats of formation for various ions as follows: $\mathrm{CH_3CC^+}$, 383 kcal. or 16.6 e.v.; $\mathrm{^+CH_3CC}$, 330 kcal. or 14.3 e.v.; $\mathrm{CH_3CCH^+}$, 351 kcal. or 15.2 e.v.: $\mathrm{^+CH_2CCH}$, 256 kcal. or 11.1 e.v. These calculated values are only approximate. Nonetheless the propargyl ion seems to be the only feasible possibility.

In some very recent experiments, Farmer and Lossing[22] found that the distribution of ions of mass 42 and mass 41 resulting from bombardment of $\mathrm{CD_3CCH}$ by 50 v. electrons indicated that the four hydrogens in the excited ion are equivalent and the loss of hydrogen from either end occurs on a statistical basis. They also measured directly the ionization potential of the propargyl radical and obtained a value of 8.25 ± 0.08 e.v.

These results would also indicate that the $\mathrm{C_3H_3^+}$ formed from an excited molecule-ion, even in the case of 2-butyne, is probably the propargyl ion. It seems, therefore, that on the basis of present available information, one must conclude that only one type of $\mathrm{C_3H_3^+}$ is being observed in the present experiments. Table III shows the heats of formation of propargyl ions and radicals calculated on this basis. There is a discrepancy of 10–12 kcal. in these values, but this is within the range of uncertainty in the calculations.

TABLE III

	$\Delta H_f(\mathrm{C_3H_3^+})$ (kcal./mole)	$\Delta H_f(\mathrm{C_3H_3})$ (kcal./mole)	$\Delta F_f(\mathrm{C_4H_5^+})$ (kcal./mole)	$\Delta H_f(\mathrm{C_4H_5})$ (kcal./mole)
Propyne	264 ± 3	74 ± 5		
1-Butyne	257 ± 5	67 ± 7	256 ± 3	65 ± 5
2-Butyne	269 ± 5	76 ± 7	265 ± 3	74 ± 5

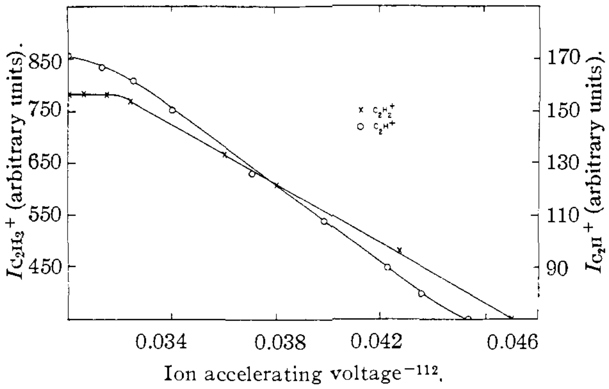

Fig. 1.

Table III also includes heats of formation for the $\mathrm{C_4H_5}$ ions and radicals. The latter were calculated on the basis of assuming that these ions would have almost the same ionization potential as the propargyl group.

Bond Dissociation Energies for Acetylenes.—Using the heat of formation of $\mathrm{C_2H}$ as determined above, the following bond strengths may be determined

$$\mathrm{C_2H_2 \longrightarrow C_2H + H} \qquad \Delta H = D(\mathrm{C_2H{-}H}) = 110 \text{ kcal.}$$
$$\mathrm{CH_3C_2H \longrightarrow CH_3 + C_2H}$$
$$\Delta H = D(\mathrm{CH_3{-}C_2H}) = 100 \text{ kcal.}$$

(116 kcal. was calculated by Cherton[13]).

$$\mathrm{C_2H_5C_2H \longrightarrow C_2H_5 + C_2H}$$
$$\Delta H = D(\mathrm{C_2H_5{-}C_2H}) = 97 \text{ kcal.}$$

The latter two values may also be contrasted with the values of 111.0 and 108.8 kcal., respectively, reported by Roberts and Skinner.[23]

$$\mathrm{HC_2{-}C_2H \longrightarrow 2C_2H} \qquad \Delta H = D(\mathrm{HC_2{-}C_2H}) = 122 \text{ kcal.}$$

(143 kcal. was calculated by Cherton[13]).

On the basis of Farmer and Lossing's data on the propargyl ion, and the assumptions (1) that the $\mathrm{C_3H_3^+}$ is propargyl ion in each case and (2) that $\mathrm{C_4H_5}$ has the same ionization potential as propargyl, the following may be calculated

$$\mathrm{CH_3CCH \longrightarrow H + {\cdot}CH_2CCH} \qquad D(\mathrm{H{-}CH_2CCH}) = 82 \text{ kcal.}$$
$$\mathrm{CH_3CH_2CCH \longrightarrow H + {\cdot}CH_2CH_2CCH}$$
$$D(\mathrm{H{-}CH_2CH_2CCH}) = 77 \text{ kcal.}$$
$$\mathrm{CH_3CCCH_3 \longrightarrow H + {\cdot}CH_2CCCH_3}$$
$$D(\mathrm{H{-}CH_2CCCH_3}) = 91 \text{ kcal.}$$
$$\mathrm{CH_3CH_2CCH \longrightarrow CH_3{\cdot} + {\cdot}CH_2CCH}$$
$$D(\mathrm{CH_3{-}CH_2CCH}) = 59 \text{ kcal.}$$
$$\mathrm{CH_3CCCH_3 \longrightarrow CH_3{\cdot} + {\cdot}CCCH_3}$$
$$D(\mathrm{CH_3{-}CCCH_3}) = 73 \text{ kcal.}$$

Two instances may be noted in which appearance potentials indicate rather surprising values. One of these is $A(\mathrm{C_4H^+}) = 12.1$ v. from diacetylene. Since $I(\mathrm{C_4H})$ might be expected to resemble that for $\mathrm{C_2}$ or $\mathrm{C_2H}$, the indicated value for D(H–C₄H) would be abnormally low unless some factor such as a large resonance energy is involved. A similar situation seems to exist with regard to $A(\mathrm{C_2H_3^+}) = 14.7$ v. from 2-butyne. This seems unusually low for a process which involves splitting of the triple bond.

---

[22] J. B. Farmer and F. P. Lossing, *Can. J. Chem.*, **33**, 861 (1955).

[23] J. S. Roberts and H. A. Skinner, *Trans. Faraday Soc.*, **45**, 339 (1949).

Calculations of other bond strengths of interest might be made from the data of Table I, but these involve reactions in which large amounts of excess energy are probably included. For example, the $A(CH_3^+)$ from propyne would give 5.4 e.v. or 124.5 kcal. for $D(CH_3–C_2H)$. It seems quite evident that this value is too high.

Phenoxyacetylene.—The available data on $C_6H_5^+$ give $I(C_6H_5) = 9.89$ v.[24] Using $A(C_6H_5^+)$ from the phenoxyacetylene, one obtains for the reaction

$$C_6H_5OC_2H \longrightarrow C_6H_5 + OC_2H$$
$$\Delta H = D(C_6H_5–OC_2H) = 53 \text{ kcal.}$$

This somewhat low value is in accord with the unusual reactivity of this compound in acetylene flames, but it is evident that additional data are needed for checking. Measurements of $A(C_6H_5O^+)$ from $CH_3OC_6H_5$ and $C_2H_5OC_6H_5$ should be made for comparison by the indirect method.

It should be noted also that the appearance potential of the $C_6H_5O^+$ seems surprisingly low; but the data available are insufficient for calculation of heats of reaction, etc., for purposes of comparison.

Halopropynes.—Since I(Br) and I(Cl) are larger than $I(C_3H_3)$, direct calculations of heats of reaction using $A(Br^+)$ and $A(Cl^+)$ would apparently not be reliable. Furthermore, the value of $I(C_3H_3)$ is doubtful, as discussed above. Thus there are not sufficient data available at present to permit direct calculations from the electron-impact data. Indirect calculations, using $A(C_3H_3^+)$ from 2-butyne also, give heats of formation of 36 kcal./mole for the bromopropyne and 41 kcal./mole for the chloropropyne. Calculations using $\Delta H_f(CH_3CC^+)$ (see above) give values of 33 and 39 kcal./mole, respectively.

Using heats of formation and ionization potentials as noted above one can calculate

$$CH_3CCBr \longrightarrow CH_3CC\cdot + Br$$
$$\Delta H = D(CH_3CC–Br) = 66 \text{ kcal.}$$
$$CH_3CCCl \longrightarrow CH_3CC\cdot + Cl$$
$$\Delta H = D(CH_3CC–Cl) = 63 \text{ kcal.}$$

Discussion

The fact that the values of the heat of formation of C_2H calculated from the electron impact data for 1-butyne is in agreement with threshold values indicated by the data on free-radical reactions indicates that the value of 112 kcal./mole is better than the earlier figure of 121. One can reasonably explain the variations in the apparent heat of formation of C_2H as obtained from data on other acetylenes on the basis of excess kinetic energy of the ions.

Using the value of the heats of formation and the appropriate appearance potentials, one can calculate for acetylene the bond strengths, etc., shown in Table IV. These are based on the most recent data on heats of formation, as indicated by the footnote references.

TABLE IV

$\Delta H_f(C_2H_2)$	= 54.2 kcal./mole[12]		
		$D(HC_2–H)$	= 110 kcal./mole
$\Delta H_f(C_2H)$	= 112	$D(C_2–H)$	= 130
$\Delta H_f(C_2)$	= 190[20]	$D(HC\equiv CH)$	= 150
$\Delta H_f(CH)$	= 102	$D(C–H)$	= 120
$\Delta H_f(C)$	= 170.4[20]	$D(C–C)$	= 150
$I(C_2H_2)$	= 11.4 v.[1]	$\Delta H_f(C_2H_2^+)$	= 318 kcal./mole
$I(C_2H)$	= 11.3[13]	$\Delta H_f(C_2H^+)$	= 373
$I(C_2)$	= 11.5[20]	$\Delta H_f(C_2^+)$	= 456
$I(CH)$	= 11.1[26]	$\Delta H_f(CH^+)$	= 358
$I(C)$	= 11.26[25]	$\Delta H_f(C^+)$	= 430

The value of $D(HC\equiv CH)$ and from this $\Delta H_f(CH)$ are determined from the heat of atomization of acetylene and the average C–H bond energy of 120 kcal.

Field and Franklin[25] report 360 kcal. as one value for the heat of formation of CH^+ and 11.13 for I(CH). This gives $\Delta H_f(CH) = 103$, $D(HC\equiv CH) = 152$ and $D(C\equiv H) = 119$.

The Bureau of Standards tables list $\Delta H_f(CH) = 142$ kcal./mole, based on the spectroscopic data of Herzberg.[26] This requires that $D(HC\equiv CH)$ be 230 kcal. which seems high. However, it should be noted that D(C–H) would then be 80 kcal., which is in agreement with the spectroscopic value of 83 kcal.[26] Also there is an alternative mechanism for the electron-impact process[25] which would give $\Delta H_f(CH^+) = 395$ kcal. One possibility for reconciling these different values is that the CH observed spectroscopically was produced in an excited state.

Gaydon[27] gives 113 kcal. for the dissociation energy of C_2. This would, however, require that $\Delta H_f(C_2)$ be 227 kcal./mole, which is high in comparison with the experimental observations.[20] Thus the data of Table IV are self-consistent, but it is evident that there are still uncertainties with regard to the fundamental energy relations for the acetylenes.

The data on the phenoxyacetylene and the halopropynes are still incomplete. Nonetheless, the results do indicate that each of these molecules contains at least one bond of low energy which could be expected to break fairly readily. This is consistent with the effectiveness of these compounds in accelerating decomposition flames in acetylene.

AUSTIN 12, TEXAS

---

(24) J. L. Franklin, *J. Chem. Phys.*, **22**, 1895 (1954).

(25) F. H. Field and J. L. Franklin, Electron Impact Phenomena and the Properties of Gaseous Ions (Humble Oil and Refining Company, Research and Development Division, May, 1955).

(26) G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," 2nd ed., D. Van Nostrand Co., New York, N. Y., 1950.

(27) A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, Ltd., London, 1953.