pounds as in the homologous series of the long-chain, saturated fatty acids. A molecular arrangement in the crystal which would be in agreement with these observed data can be postulated:

$$\cdots MX\cdot\underbrace{YR\cdot RY\cdot XM\cdot MX}_{\text{repeating unit}}\cdot\underbrace{YR\cdot RY\cdot XM\cdot MX}_{\text{repeating unit}}\cdot YR\cdots$$

Where M is the CH_3 radical, X is the $CONH_2$ group, Y is the COOH group, and R is the long-chain $C_n H_{2n+1}$.

Such an arrangement would result in a 1:1 ratio of acid to amide, both ends would be inactive to further hydrogen bonding, and the repeat pattern of the unit cell would be equal to the sum of the "double spacing" of the "C" form of the acid and the "double spacing" of the acetamide. The values in parentheses in column 2 of Table II are maximum values for this sum. The actual spacing of the 2:2 addition compounds must be somewhat less than this sum since the acetamide must be inclined at some angle to the 001 planes. Hence it cannot make its full contribution to the "double spacing" of the complex. It will be noted that in column 2 the observed 2:2 spacings are less than the calculated spacings (in parentheses) in every case, except for the stearic acid–acetamide compound. Measurements from five different diffraction patterns give values about 8 units higher than expected for this spacing.

In the last column of Table II are given the "short spacings" for each of the molecular compounds. These values, obtained by the usual Pyrex capillary tube "powder" method, are the data required for chemical analyses by the method of Hull[12] as described in detail by Hanawalt, Rinn and Frevel.[13]

Acknowledgments.—The authors acknowledge with thanks the helpful suggestions of Leopold Loeb of this Laboratory and of Merrill E. Jefferson of the Soil and Water Conservation Research Branch of the Agricultural Research Service in the preparation of this manuscript. They are indebted also to Mrs. Elsie F. DuPré for the infrared absorption curves.

---

[12] A. W. Hull, This Journal, **41**, 1168 (1919).

[13] J. D. Hanawalt, H. W. Rinn and L. K. Frevel, *Ind. Eng. Chem., Anal. Ed.*, **10**, 457 (1938).

New Orleans, La.

NOTES

Electron Impact Data on Substituted Acetylenes: Propyne and 2-Butyne[1]

By Fred H. Coats and Robbin C. Anderson

Received August 20, 1954

To obtain further information on energy relations for acetylenic compounds, ionization and appearance potentials of various ions from substituted acetylenes are being determined. Some data on propyne have been reported earlier.[2] The experimental measurements have now been extended to 2-butyne.

Experimental

The instrument used in this work was a Westinghouse type LV mass spectrometer which employs a conventional 90° momentum filter. Its resolution is at least 1 mass unit in 120. Focussing is accomplished by adjusting the magnetic field to encompass the desired mass range and varying the accelerating electric field by means of a decade potentiometer.

The general procedure used in the appearance potential measurements was to determine, simultaneously, the ionization probability curves for the ionic fragment to be studied and for a reference ion, such as that of argon, the ionization potential of which has been accurately measured. The curves are compared by the method of vanishing ion currents[3] in which the lower non-linear portion of each of the curves is extrapolated to zero ion current. Tailing of the curves at very low ion currents gives rise to considerable uncertainty in the extrapolation. To reduce this effect, an intermediate electrode in the electron gun was maintained at a small constant negative potential with respect to the filament. The general problems arising from the energy spread of the electron, and corrective modifications, have been discussed by Fox, Hickam, Kjeldaas and Grove.[4]

The acetylene was commercial product purified from acetone by treatment with concentrated sulfuric acid. The propyne and 2-butyne were obtained from Farchan Laboratories. Preliminary checks in the mass spectrometer gave no indication of peaks from impurities which would interfere with the determination of appearance potentials.

Results

The appearance potentials for ions from acetylene were measured to furnish a check of the method and apparatus. The experimental values in each case were in agreement with those of Kusch, Hustrulid and Tate[5] and with ionization potentials reported by Price[6] and Franklin and Field.[7] These data are compared in Table I.

Table I

Appearance Potentials for Ions from Acetylene

Ion	*A*R (These exp.), v.	*A*R (lit.), v.
$C_2H_2^+$	11.4 ± 0.1	11.2 ± 0.1[a] 11.40[b] 11.46 ± .01[c]
C_2H^+	17.8 ± .5	17.8 ± .2[a]
C_2^+	23.3 ± .5	23.8 ± .3[a]

[a] Kusch, Hustrulid and Tate, electron impact. [b] Price, spectroscopic. [c] Franklin and Field, electron impact.

---

[1] This research was supported by the United States Air Force, through the Office of Scientific Research of the Air Research and Development Command.

[2] F. H. Coats and R. C. Anderson, paper presented at Southwestern–Southeastern Regional Meeting of Am. Chem. Soc., New Orleans, Dec., 1953.

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

[4] R. E. Fox, W. M. Hickam, T. Kjeldaas and D. J. Grove, *ibid.*, **84**, 859 (1951).

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

[6] W. C. Price, *ibid.*, **47**, 444 (1935).

[7] J. L. Franklin and F. H. Field, This Journal, **76**, 1994 (1954).

TABLE II

SUBSTITUTED ACETYLENES

Propyne		2-Butyne	
Ion	A_R, v.	Ion	A_R, v.
$C_3H_4^+$	10.3 ± 0.1	$C_4H_6^+$	9.9 ± 0.1
$C_3H_3^+$	11.8 ± .1	$C_4H_5^+$	12.2 ± .1
$C_3H_2^+$	14.0 ± .1	$C_4H_4^+$	14.0 ± .1
C_3H^+	18.4 ± .3	$C_4H_3^+$	15.1 ± .2
C_3^+	26 ± 1	$C_4H_2^+$	16.7 ± .3
		$C_3H_3^+$	11.4 ± .2
		$C_2H_3^+$	14.7 ± .2

The appearance potentials for the propyne and 2-butyne dissociation series are given in Table II. The ionization potentials for acetylene, propyne and 2-butyne show a general trend similar to those which Honig observed for the alkane and alkene series.[8]

The ionization potentials of propyne and 2-butyne are also in reasonable agreement with the values of 10.48 and 9.85 e.v., respectively, recently reported by Franklin and Field.[7] The value for propyne differs markedly from that of 11.30 e.v. given by Price and Walsh[9] on the basis of spectroscopic evidence. Franklin and Field[7] have already discussed this variation.

Calculations of energy relations based on these data will be published later, after additional experimental data have been compiled, since calculations from the data available at present bring out certain rather marked inconsistencies still to be resolved. These can be illustrated by two simple calculations shown below.

The heat of reaction for the process $C_2H_2 + e^- \rightarrow C_2H^+ + 2e^-$ as given by the appearance potential for the C_2H^+ ion is 17.8 e.v. The energy involved in the process $C_2H \rightarrow C_2H^+$ may be obtained from Eltenton's[10] value of 11.3 e.v. for the ionization potential of the C_2H radical.

Assuming negligible excitation and kinetic energies for the electrons and the products of the electron bombardment process, we have

$$D(HC_2 - H) = A(C_2H^+) - I(C_2H) = 6.5 \text{ e.v. or } 150 \text{ kcal./mole.}$$

An alternative calculation may be based on Honig's value of 210 kcal. for the heat of formation of C_2.[11] For the electron bombardment process

$$C_2H_2 + e^- = C_2^+ + 2H + 2e^-$$

$$\Delta H_{RX} = A(C_2^+) = 23.3 \text{ e.v. or } 537.1 \text{ kcal./mole}$$

Taking $\Delta H_f(C_2H_2) = 54.2$ kcal./mole and $\Delta H_f(H) = 52.1$ kcal./mole, we have $\Delta H_f(C_2^+) = 487.1$ kcal./mole. Then $I(C_2) = 487 - 210 = 277$ kcal./mole or 12.0 e.v. If we assume then that $I(C_2H) = I(C_2)$, we have

$$D(HC_2 - H) = A(C_2H^+) - I(C_2H) = 133 \text{ kcal./mole}$$

It is interesting to note that the value obtained by this method for $I(C_2)$ is consistent also with Eltenton's value of 12 ± 2 e.v.[10]

The value of 133 kcal./mole would seem more reasonable in comparison with the value of 123 kcal./mole for the heat of formation of C_2H reported by Roberts and Skinner[12] but this involves a serious question in the assumption that $I(C_2H) = I(C_2)$, which is not confirmed by the available data on ionization potentials.

It is planned to check these results by obtaining further experimental data on substituted acetylenes such as 1-bromo-1-propyne and 1-chloro-1-propyne. The indirect method of calculation of Schissler and Stevenson[13] may then be applied.

The present data also do not show conclusively whether the first molecular fragment from propyne is formed by splitting off hydrogen from the acetylenic or the methyl carbon. For further evidence on this an investigation of deuteropropyne is planned.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF TEXAS
AUSTIN, TEXAS

---

[8] R. E. Honig, *J. Chem. Phys.*, **16**, 105 (1948).

[9] W. C. Price and A. D. Walsh, *Trans. Faraday Soc.*, **41**, 381 (1945).

[10] G. C. Eltenton, *J. Chem. Phys.*, **15**, 455 (1947).

[11] R. E. Honig, *ibid.*, **22**, 126 (1954); *cf.* also G. Glockler, *ibid.*, **22**, 159 (1954).

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

[13] D. O. Schissler and D. P. Stevenson, *J. Chem. Phys.*, **22**, 151 (1954).

The Crystal Structure of Cuprous Chromite

BY WALTER DANNHAUSER AND PHILIP A. VAUGHAN

RECEIVED AUGUST 23, 1954

In a description of his investigation of copper–chromium oxide catalyst, Stroupe[1] presented some crystallographic data pertaining to $CuCrO_2$ and some related compounds. From powder and single-crystal data he concluded that this compound is hexagonal with cell dimensions of a = 2.975 Å. and c = 17.096 Å. and there are four $CuCrO_2$ units per cell. We have found that, although these unit-cell parameters are correct, the primitive cell is rhombohedral and contains one $CuCrO_2$ unit; the hexagonal cell contains three $CuCrO_2$ units. The disagreement arises from the density of 7.0 reported by Stroupe. We have found the density to be 5.49 g./ml., which is close to the value of 5.609 g./cc. computed on the basis of 3 $CuCrO_2$ units per hexagonal unit cell.

Experimental

Preparation of Cuprous Chromite.—The "normal" hydrogenation catalyst was first prepared by the method recommended by Adkins and Connor.[2] This compound was mixed with excess cuprous oxide and, following the directions of Stroupe,[1] was heated for several hours in air at about 1000°. This procedure gave good yields of the desired compound but we were unable to find in the resulting mass any single crystals large enough for X-ray examination. Gröger's method,[3] in which basic cupric chromate is heated for about six hours at 1000°, gave good crystal specimens although yields were smaller.

Density Determination.—Attempts to determine the density of $CuCrO_2$ by displacement in carbon tetrachloride and carbon tetrabromide gave low and very erratic results. We therefore concluded that these liquids do not wet this compound. The results of three density determinations by displacement in an aqueous solution of aerosol O.T. are 5.53, 5.58 and 5.36 g./cc., the average value being 5.49 g./cc.

Unit-cell Parameters.—As mentioned by Stroupe,[1] powder photographs of this compound could be successfully indexed on a hexagonal lattice. Accurate unit-cell dimensions were obtained by a least-squares treatment of recipro-

---

[1] J. D. Stroupe, THIS JOURNAL, **71**, 569 (1949).

[2] H. Adkins and R. A. Connor, *ibid.*, **53**, 1091 (1931).

[3] M. Gröger, *Z. anorg. Chem.*, **76**, 30 (1912).