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.

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[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).

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The Crystal Structure of Cuprous Chromite

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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-

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[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).

cal-lattice distances corresponding to fourteen unequivocally indexed powder lines. The Bragg angles were measured with a North American Philips X-ray spectrometer. The parameters, with standard errors, are a = 2.9747 ± 0.00014 Å. and c = 17.1015 ± 0.0005 Å. The parameters of the primitive rhombohedral cell are therefore a = 5.9536 ± 0.0002 Å. and α = 28° 56.0′ ± 0.1′. The wave lengths used for Cu Kα radiation are $\lambda\alpha_1$ = 1.54050 Å., and $\lambda\alpha_2$ = 1.54434 Å.

Intensity Measurements.—Intensities were estimated from Weissenberg photographs by the multiple film technique; Mo Kα radiation was used with copper foil between the films to increase the film factor to 4.8.

Structure Determination.—From Weissenberg photographs we observed, as did Stroupe,[1] that the Laue symmetry is apparently D_{6h}. However, the following evidence strongly indicates that the primitive unit cell is rhombohedral and the apparent hexagonal symmetry arises from extensive twinning, the twins being related by a rotation of 60° about the hexagonal c axis.

(1) When the photographs were indexed on a hexagonal cell it was noted that all observed reflections belonged to one of the classes $h - k + l = 3n$ or $h - k - l = 3n$, where n is an integer.

(2) A photograph was obtained in which each reflection belonging to the class $h - k + l = 3n$ was always slightly stronger than the reflection, related to the first by a 60° rotation, for which $h - k - l = 3n$.

(3) The compound $CuFeO_2$ is rhombohedral and the hexagonal cell has dimensions a = 3.028 Å. and c = 17.094 Å.[4] The obvious implication is that the compounds are isomorphous.

In $CuFeO_2$,[4] the copper atom is located at 0, 0, 0, the iron atom at $^1/_2$, $^1/_2$, $^1/_2$, and the oxygen atoms at ± (u, u, u) with u = 0.111 in the rhombohedral cell. We assume that the metal atoms have the same locations in $CuCrO_2$ and the oxygen parameter is approximately the same. To determine the oxygen parameter more precisely we use the relations

$$F_{hkl} = f_{Cu} + f_{Cr} + 2f_0 \cos 2\pi ul \, (l \text{ even}), \text{ and}$$
$$F_{hkl} = f_{Cu} - f_{Cr} + 2f_0 \cos 2\pi ul \, (l \text{ odd})$$

where l is the hexagonal index. It is clear that the reflections for which l is odd are much weaker than those for which l is even and furthermore they are very sensitive to the oxygen parameter. The temperature factor was determined and the experimental structure factors were placed on an absolute scale by comparing those with l even with structure factors calculated with the assumption u = 0.11. A more accurate value of u was then obtained by trial from structure factors with l odd. The pertinent data are given in Table I. The best value of u is 0.108 and we estimate a limit of error of 0.002.

TABLE I

Indices (hexagonal)	Fobsd.	F_0/F_c for different values of u. 0.100	0.107	0.108	0.109	0.120
101	12.31	1.02	1.05	1.05	1.06	1.09
105	4.17	0.84	0.87	0.90	0.93	1.25
107	3.80	3.59	1.14	1.05	0.96	0.52
10.11	4.78	0.71	0.99	1.06	1.14	9.86
201	5.74	0.91	0.93	0.93	0.93	0.97

In this structure, each copper atom has two near oxygen neighbors in a linear array; the Cu–O distance is 1.85 ± 0.04 Å., in good agreement with a distance of 1.84 Å.[5] observed in Cu_2O. Each chromium atom is surrounded by six oxygens at the corners of a distorted octahedron; the Cr–O distance is 1.99 ± 0.02 Å.

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[4] W. Soller and A. J. Thompson, *Phys. Rev.*, **47**, 664 (1935).

[5] R. W. G. Wyckoff, "Crystal Structures," Interscience Publishers, Inc., New York, N. Y., 1948.

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The Heat of Formation of InSb

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In spite of the recent keen interest in the properties of InSb no data have, to the knowledge of the author, been reported for the heat of formation of this compound. In the course of recent work on tin solution calorimetry the author has studied the heats of solution of various pure metals in liquid tin at 450°.[1] Among the metals investigated were indium and antimony, and it therefore became a very simple matter to determine the heat of formation of InSb.

Two different samples of InSb were prepared by melting stoichiometric amounts of indium and antimony in evacuated Pyrex ampoules. After homogenization of the melt for two hours at about 600°, the ampoule was cooled rapidly in an air jet and annealed overnight at 500°. The indium and antimony were of 99.9+% purity, and the total weight of each prepared sample was between 5 and 10 g. A specimen about 1 g. weight was cut from each slug and dissolved in about 100 g. of liquid tin in the calorimeter. The heat of formation of InSb was then obtained from the observed heat of solution of the specimen ($\Delta H_{obs.}$) and the heat effect calculated for formation of the resulting liquid mixture from the elements ($\Delta H_{calc.}$). In this calculation only information relating to the binaries Sn–In and Sn–Sb was used and no attempt was made to correct for the interaction between indium and antimony in liquid tin. This, as well as the uncertainty in the heats of solution of the pure metals in tin, may introduce a systematic error of the order of 1% in the final result. The results obtained in the two runs are given in Table I.

TABLE I

HEAT OF FORMATION OF InSb FROM LIQUID INDIUM AND SOLID ANTIMONY AT 450°

InSb, g. atoms	Tin + InSb, g. atoms	ΔH, joule Obsd.	Calcd.	$-\Delta H^M$, kj./g. atom
0.01406_2	0.9693	358.6	104.2	18.09
$.00669_2$	.8971	169.4	49.5	17.91

Mean: 18.00 ± 0.09 kj.

We may at this point correct for the heat of fusion of indium and refer the heat of formation of the compound to solid indium and solid antimony. If we use the heat of fusion of indium given by Kubaschewski and Evans,[2] 0.78 ± 0.02 kcal./g.

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[1] O. K. Kleppa, to be published.

[2] O. Kubaschewski and E. Ll. Evans, "Metallurgical Thermochemistry," London, 1951.