

ART. XLII.—*The Action of Acetylene on the Oxides of Copper*; by F. A. GOOCH and DEFOREST BALDWIN.

[Contributions from the Kent Chemical Laboratory of Yale University—LXXXIX.]

IN a recent paper by Erdmann and Köthner* an account is given of the formation of a peculiar, light-brown, highly voluminous substance by the action of acetylene below 250° C. upon cuprous oxide, or even (though more slowly) upon copper. The product obtained by passing acetylene during eighteen hours over 1 gm. of cuprous oxide (prepared from copper sulphate, grape sugar, and sodium hydroxide) amounted to 7 grms. and filled a space of nearly 300cm^3 . At higher temperatures a black carbonaceous mass is the result, and at red heat (400° – 500° C.) carbon is deposited in graphitic condition. The light-brown fluffy material yielded cuprous chloride to hydrochloric acid, a distillate from its mixture with zinc dust possessing the characteristics of naphthalene or, at higher temperature and under rapid heating, aromatic compounds among which naphthalene and a kresol were indicated. Erdmann and Köthner classify this body as a very complex but non-explosive copper acetylene (acetylen-kupfer), and from their analyses deduce the formula $\text{C}_{44}\text{H}_{84}\text{Cu}_3$. Apart from the unusual constitution of this symbol, its most striking peculiarity is that it implies a loss of carbon, rather than hydrogen, from the acetylene in the reaction with cuprous oxide—a condition of affairs which would be most remarkable in the light of Campbell's experience,† according to which acetylene passed over palladinized copper oxide yielded water at 225° – 230° and carbon dioxide only when the temperature rose to 315° – 320° with the formation of a black deposit. Upon scrutinizing the figures of Erdmann and Köthner with care, however, it appears that the formula given by these investigators rests upon some oversight in calculation: the ratio of carbon atoms to hydrogen atoms proves to be actually, according to the data given, 6.45 : 5.70; which means, of course, that the new product is deficient, as would be expected, in hydrogen (not in carbon) as compared with acetylene.

As to the content of the new substance in copper, the analytical data are unfortunately ambiguous; for we note the weights found of *copper oxide* converted into percentages of *copper* without preliminary reduction. If the fault is typographical and in the analytical data, the calculated percentages of copper being correct, the average percentage of copper amounts to 15.43: if, on the other hand, the analytical data

* Zeitschr. für anorg. Chem., xviii, 49.

† Amer. Chem. Jour., xvii, 690.

are right, the error being in their reduction, the percentage of copper amounts to 12.92. In the one case the summation of the analysis leaves a deficiency of about 1.5 per cent, and in the other of about 4 per cent, which in either case may really represent oxygen in the substance. This condition of matters leaves the "acetylen-kupfer" of Erdmann and Köthner in uncertain standing.

More than thirty years ago it was noticed by Berthelot* that acetylene is polymerized by heat or decomposed partially into carbon and hydrogen, and that such action takes place more readily and at lower temperatures in presence of metallic iron with production of carbon, hydrogen and compounds different from those formed by heat alone.

Moissan and Moureu† have observed the incandescence of acetylene passed over finely divided iron, cobalt, nickel or platinum at the ordinary temperature, with production of carbon, hydrogen, and pyrogenic compounds, and have found the occasion of such behavior in the porosity of the metals employed.

It would seem natural, however, that the presence of oxygen, free or combined, may also play a considerable part in such phenomena, just as appears to be the case in the peculiar action recorded by Gruner‡ of carbon monoxide upon iron reduced by hydrogen, which, as Moissan has shown,§ is produced pure only with the greatest precaution and generally carries a large proportion of ferrous oxide. The fact that the "acetylen-kupfer" of Erdmann and Köthner is produced more easily by the action of cuprous oxide upon acetylene than by the action of metallic copper upon acetylene, suggests that it may be the oxidizing power of the cuprous oxide which gives to this reagent its peculiar activity. The question arises, therefore, as to whether the copper is in reality an essential constituent of the compound of Erdmann and Köthner.

In our experiments upon the action of acetylene upon the oxides of copper (and other elements) we have conducted the gas (made in the ordinary way by the action of water on calcium carbide, and kept over water) over the oxide contained in a porcelain boat placed within a glass tube, 2^{cm} in diameter and 50^{cm} long, which was heated over a small combustion furnace. The glass tube was fitted at each end with a rubber stopper, one carrying a smaller tube for the introduction of the acetylene and a high-temperature thermometer so held that its bulb rested horizontally immediately over the boat containing the oxide, while the other was fitted with a water-trap. In the

* Ann. d. Chim. et d. Phys. [4], ix, 448.

† Compt. Rend., cxvii, 1240.

‡ Ann. d. Chim. et d. Phys. [4], xxvi, 5.

§ Ann. d. Chim. et d. Phys. [5], xxi, 199.

preliminary experiments no attempt was made to purify the acetylene employed other than to keep it over water, or, since water is a product of its action upon oxides, to dry it: in later experiments to secure products for careful analysis it was dried and purified with care.

We found that 225° C. is the temperature most favorable for the formation of the voluminous product obtained by acting with acetylene upon cuprous oxide as described by Erdmann and Köthner. At this temperature the tube is choked rapidly with the fluffy product and water forms, but, as Campbell found in his experiments upon palladinized copper oxide, no appreciable amount of carbon dioxide is produced. The content of the product in copper varies in the sample and in different experiments, our results lying between 1.54 per cent and 24.21 per cent of the substance taken for ignition.

It appeared, also, that the action of acetylene upon cupric oxide is precisely similar to that upon cuprous oxide excepting the evident reduction of the former oxide early in the action. The amount of copper in the product of such action varied in our experiments from 6.53 per cent to 21.30 per cent. In one case the experiment of re-submitting to the action of acetylene a product containing 9.34 per cent of copper was made with the result that a new growth of the substance formed which on analysis yielded 3.87 per cent of copper.

A roll of copper gauze carefully reduced in hydrogen and then oxidized at one end in the outer flame of a Bunsen burner gave, when acted upon by acetylene at 225°–250° C., the characteristic deposit upon the oxidized end only, the unoxidized end being merely discolored.

These results go to show that, while metallic copper may at comparatively high temperatures induce the polymerization of acetylene, it is an oxidizing action which starts at moderately low temperatures the formation of the peculiar derivatives under consideration. Thus we find that ferric oxide heated in acetylene at temperatures varying from 150° to 360°, according to circumstances, darkens, glows, and gathers with evolution of heat a dark carbonaceous deposit. In the products of such action we have found the content of iron varying from 2.80 per cent to 5.86 per cent.

Silver oxide, too, acts upon acetylene: thus, in one experiment, action was evident at the ordinary atmospheric temperature, a violent explosion, which completely shattered the boat and scattered metallic silver upon the sides of the glass tube, following before the temperature reached 100°.

In the locally violent explosion of the last experiment we have evidence of the formation in the early stage of an acetylide which is decomposed later when the temperature of disso-

ciation is reached. In the experiments with the oxides of copper and iron the temperature at which the acetylene begins to act is evidently above the point at which sensitive acetylides would naturally dissociate, and we have in the observed phenomena no evidence of the formation of such compounds of copper and iron under the conditions of experimentation.

In experiments (1) to (3) of the following table are given the results of the analysis of several products obtained by conducting acetylene (purified by passing through a solution of mercuric chloride in hydrochloric acid and dried over caustic potash) over pure cuprous oxide. The temperature was kept in these experiments at 225°, and in the course of a half hour the tube was choked completely by material compacted by the pressure to (1) a spongy mass of light-brown color on the exterior next the walls of the tube, (2) darker within and (3) nearly black in the bottom of the boat, where the cuprous oxide lay originally.

In experiments (4) and (5) the substances analyzed represent the products of the action of acetylene (not specially purified) on cupric oxide.

Weight of substance taken. gm.	Found.			Calculated.			
	CO ₂ gm.	H ₂ O gm.	CuO gm.	C gm.	H gm.	Cu gm.	O by difference gm.
(1) 0.1170	0.3978	0.0673	0.0022	0.1085	0.0075	0.0018	—0.0008
(2) 0.2247	0.7489	0.0979		0.2042	0.0109		
(3) 0.1096	0.3678	0.0488	0.0045	0.1003	0.0054	0.0036	0.0003
(4) 0.1360	0.4116	0.0579	0.0182	0.1123	0.0064	0.0146	0.0027
(5) 0.1188	0.3098	0.0461	0.0317	0.0845	0.0051	0.0253	0.0039

		(1)	(2)	(3)	(4)	(5)
Per cent of carbon		92.74	90.88	91.51	82.57	71.13
“ hydrogen		6.41	4.85	4.93	4.71	4.29
“ copper		1.54		3.29	10.74	21.30
“ oxygen		—		0.27	1.98	3.28
		100.69		100.00	100.00	100.00

The oxygen present in these products is obviously proportional to the amount of copper and is never more than enough to be completely accounted for upon the supposition that some of the original oxide taken still holds its oxygen. So far as the analyses show, the product of lightest color (1) contains very little copper and no oxygen; the darkest product (3) obtained from the cuprous oxide contains oxygen corresponding to a mixture of two parts of copper with three parts of cuprous oxide; the oxygen in the products of (4) and (5)

obtained by acting upon cupric oxide is approximately enough to correspond to a mixture of cuprous and cupric oxides in equal proportions. This fact, taken in connection with the great range of variation in proportion and the minimum to which the copper falls in the product, which would be least likely to include contaminating metal or oxide, suggests very strongly the probability that the oxygen present is in union with copper and that the copper is held mechanically as metal or oxide and is not the essential constituent of an organic compound. Leaving out of consideration, therefore, the copper and copper oxides, and calculating the composition of the products assumed to consist essentially of carbon and hydrogen, we derive the following statement:

	(1)	(2)	(3)	(4)	(5)
Per cent of carbon	93.54	94.93	94.88	94.60	94.31
Per cent of hydrogen . . .	6.46	5.07	5.12	5.40	5.69
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

These figures correspond to symbols varying from $C_{12}H_{10}$ to nearly $C_{16}H_{10}$, with an average approximating $C_{14}H_{10}$, the symbol of anthracene or paranthracene. The analytical data of Erdmann and Köthner point in the average to a product corresponding more nearly to the first of these symbols than to either of the others. The product is doubtless variable with the temperature and the activity of oxidation. Thus, in one experiment in which acetylene was passed over ferric oxide the action began at 365° with incandescence, as described by Moissan and Mouren,* and the analysis of the product (carbon = 91.53, hydrogen = 1.36, Fe = 5.85, O = 1.26) indicates a proportion of carbon to hydrogen about four times as great as that of the average product of action at 225° on the oxides of copper.

Finally, we find no evidence that the product of the action of acetylene on the oxides of copper under the conditions of our experimentation is other than a mixture of a hydrocarbon or hydrocarbons with metallic copper or an oxide of copper, and, probably, in the darker preparations, some free carbon.

* Loc. cit.