[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Studies in the Oxidation of Alpha Ray Cuprene[1]

BY S. C. LIND[2] AND C. H. SCHIFLETT[3]

Acetylene under alpha-radiation from radon yields a yellow solid polymer of acetylene, cuprene. The yield per ion pair is approximately twenty molecules.[4] The product is unusually inert to ordinary reagents, and no satisfactory solvent has been found by means of which a molecular weight determination can be made.

Analysis by combustion of the freshly prepared product and of the gas phase indicates the product to be almost an exact polymer. The following is a typical analysis of the solid: C, 90.5%; H, 7.52%; diff., 1.98%; C:H ratio 12.03. The theoretical C:H ratio is 11.80. This 1.98% difference is very probably due to reaction with oxygen of the air, as some ten minutes were required for obtaining and weighing the sample for analysis, during which time the product was open to the air. (It will be shown later that oxidation proceeds rapidly when the product is first exposed to oxygen.) The discrepancy between the experimental and theoretical C:H ratio (for a true polymer) is no doubt due to loss of hydrogen which previously has been shown to accompany the reaction.[5]

In view of the fact that in most instances at any rate the substance under investigation was not the original condensation product but an oxidized product, it was considered worth while to determine whether the freshly prepared unoxidized substance possessed the same indifference toward solvents as had been found for the oxidized substance. Accordingly a sample of the freshly polymerized cuprene was opened in an atmosphere of acetylene and portions treated with the following in the hope of effecting solution for a molecular weight determination: water, ethyl alcohol, ether, acetone, carbon disulfide, carbon tetrachloride, benzene. After a period of twenty-four hours with frequent shaking none had dissolved in any of these liquids.

Many previous attempts[6] have been made to determine the constitution of cuprene (prepared by electrical discharge, or by the catalytic effect of copper), and although it was known that oxygen was absorbed rapidly from the air, apparently many of these investigations were made not only in the presence of air but after the substance had been exposed to air for some time. Losanitsch[7] reported much difficulty in analysis of the polymer due to rapid absorption of oxygen from the air. Jovitschitsch[8] found a 22% deficiency on analysis by combustion and claims to have excluded the possibility of oxidation from the air by working rapidly. He also found no difference in two samples, one analyzed immediately, the other after long standing in the air. However, this is entirely out of agreement with other workers.

From the C:H ratio in the above analysis one calculates that hydrogen is liberated to the extent of approximately 1% of the total acetylene polymerized. By manometric measurements during the course of reaction it was found (*loc. cit.*) that this per cent. ranges from about 0.7% at the beginning to several per cent. at the end, averaging about 2% over the entire course of the polymerization.

It was found that this product oxidizes spontaneously at room temperature, and the present study was undertaken with a view to determine the rate and extent of the oxidation. The oxidation has been followed both manometrically and gravimetrically. The products were analyzed with the results given elsewhere in this paper.

Experiment No. 1.—Cuprene was prepared in a 524-cc. flask from acetylene at a pressure maintained at approximately one atmosphere, by admission of the gas at various intervals. Radon was mixed with the acetylene. After eleven days, when the radon had decayed to approximately 14% of its original amount, the vessel was evacuated thoroughly. Oxygen at 682.3 mm. pressure (S. T.) was then admitted and the pressure was read at intervals. The manometric data are plotted in Fig. 1.

The oxidized product from the above reaction was then

---

(1) This work was supported in part by a grant from the Fluid Research Fund of the Graduate School, University of Minnesota.

(2) Director of the School of Chemistry, University of Minnesota.

(3) Assistant Professor of Chemistry, Macalester College, St. Paul, Minnesota.

(4) Lind and Bardwell, *Science*, **62**, 422 (1925); Mund and Koch, *J. Phys. Chem.*, **30**, 293 (1926).

(5) Lind, "Chemical Effects of Alpha Particles," A. C. S. Monograph, Chemical Catalog Co., New York, 1928.

(6) Walter Herzog, *Kunstoffe*, **21**, 49–53 (1931); Kaufmann and Mohnhaupt, *Ber.*, **56B**, 2533 (1923); Sabatier and Senderens, *Compt. rend.*, **130**, 250 (1900).

(7) S. M. Losanitsch, *Ber.*, **40**, 4656 (1907).

(8) M. Z. Jovitschitsch, *Monatsh.*, **29**, 5–14 (1907).

removed from the reaction vessel, a sample was taken for combustion analysis and the remainder weighed and kept in a desiccator, open to the air. Over a period of eighteen months the product showed no further gain in weight. The analysis of the product was: C, 68.8%; H, 5.90%; diff., 25.3%; C:H ratio 11.69.

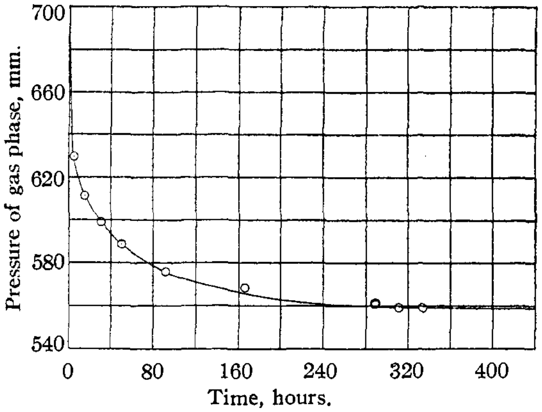

Fig. 1.—Oxidation of cuprene followed manometrically.

In another experiment cuprene was prepared in the same manner as given above and opened to desiccated air for a period of three and one-half months, when it was analyzed with the following results: C, 69.3%; H, 5.91%; diff., 24.75%; C:H ratio 11.65.

Experiment No. 2.—In another experiment, the freshly prepared cuprene was removed from the reaction vessel and weighed as quickly as possible. It was then kept exposed to desiccated air and weighed at intervals. The results are shown in Fig. 2. After six and one-half months this product was analyzed as follows: C, 67.51%; H, 5.59%; diff., 26.9%; C:H ratio 12.08.

Experiment No. 3.—In a 215.15-cc. vessel, 0.1609 g. (0.00619 mole) of acetylene was polymerized in the usual manner and the remainder of the gas was pumped off. Oxygen was then introduced. After eleven days and five and one-half hours, a decrease in pressure, corrected to S. T., of 85.8 mm. was observed. The remaining gas, 273.0 mm. (S. T.), was then pumped out by means of a Toepler pump through two traps, the first surrounded by solid carbon dioxide–acetone and the second by liquid air and then into a receiver for analysis of the gas. Upon removal of the liquid air a pressure rise of 2.3 mm. at 24.8 was observed, less than 1% of the total. Upon removal of the solid carbon dioxide–acetone bath a pressure rise of 2.1 mm. at 24.8 was observed. The average of a series of semi-micro analyses shows the gas remaining after oxidation is complete to consist of traces of carbon dioxide, water vapor, 7.13% carbon monoxide and 92.85% oxygen. Reduced to standard conditions this amounts to 5.4 cc. of carbon monoxide and 71.7 cc. of oxygen. From the total amount of oxygen originally introduced, 101.6 cc., and the amount remaining, 71.7 cc., the amount of oxygen reacting is seen to be 29.9 cc. This is approximately five and one-half times the volume of carbon monoxide formed. The following chemical equation accounts for these results: $(C_2H_2)_{20} + 5^1/_2O_2 \longrightarrow C_{39}H_{40}O_{10} + CO$. The percentage composition of the above formula is: C, 70.1; H, 6.0; O, 23.9; C:H ratio, 11.67. This is in fair agreement with the data obtained by combustion analysis of the oxidized product.

Before the production of carbon monoxide was established definitely it was proposed that this process might consist simply of adsorption, and to clear up this point the oxidized product was heated in an evacuated vessel to 200°, at which temperature charring and decomposition with the distillation of a brown, oily liquid began to occur. Up to approximately 200° no pressure of gas was developed and no obvious change occurred.

Heats of combustion of the unoxidized and the oxidized cuprene, respectively, were determined and found to be as follows:

	Cal./gram	Cal./mole
Unoxidized cuprene	10,203.7	265,296.2
Oxidized cuprene	7,113.5	184,951.0

These values are 85.6 and 59.4%, respectively, of 312,000 cal./mole, which is the value given for the heat of combustion of acetylene in the literature.[10] It was found necessary to pellet these materials with about ten times their weight of sugar for these determinations in order to secure complete combustion. The ignition in the oxygen bomb of cuprene itself and even too rich mixtures of cuprene with sugar resulted in explosion and consequent scattering of the material in the bomb. The value of the heat of combustion of the unoxidized cuprene given above when compared with that of acetylene indicates clearly that the polymerization process is an exothermic one, and is consistent with the conclusions of Heisig.[11] The difference in the heats of combustion of acetylene and of the polymer gives at once the heat of polymerization, *viz.*, ap-

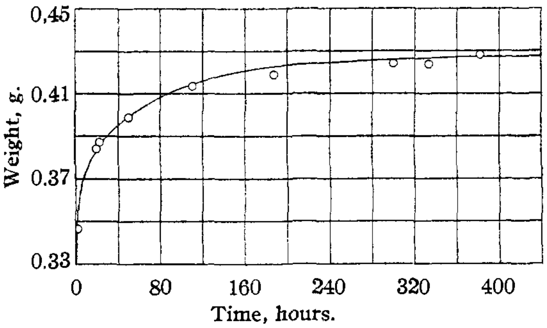

Fig. 2.—Oxidation of cuprene followed gravimetrically.

---

(9) It should be pointed out in connection with the above chemical equation proposed to account for the analysis of solid and gaseous products and the manometric data that other equations will account for the facts almost equally well. For example

$$(C_2H_2)_{24} + 6^1/_2O_2 \longrightarrow C_{47}H_{48}O_{12} + CO$$

would give a net pressure drop only 2 mm. greater than the equation proposed above. The solid would analyze: C, 70.2; N, 6.02; O, 23.78; C:H ratio 11.67, which is nearly as satisfactory as the other. The difference in the gas analysis would also be well within the limits of error. However, it seems quite certain that these equations tell in general the nature of the reaction, *viz.*, that some polymer of acetylene of the order of 20 molecules reacts with oxygen to a definite compound and that in this oxidation carbon is eliminated with the formation of a small amount of carbon monoxide.

(10) I. C. T., McG.-H. Pub. Co., 1929, Vol. V, p. 163.

(11) G. B. Heisig, *J. Phys. Chem.*, **36**, 1000–1005 (1932).

proximately 47 kcal. per molecule of acetylene condensed. Calculating the theoretical heat of polymerization from the values of atomic linkages given by Fajans,[12] on the assumption that in the polymerization one C≡C (161.6 kcal.) is broken and one C═C (122.9 kcal.) and one C—C (73.5 kcal.) are formed per molecule of acetylene, one obtains the value 35 kcal. This is not in too good agreement with the experimental value to be sure, but perhaps as satisfactory as one could expect when it is remembered that the atomic linkages are admittedly only average values.

Acknowledgments.—We wish to thank Dr. F. H. Stodola, to whom we are indebted for the analyses of the solid products, and to acknowledge the kindness of Professor A. E. Stoppel who collaborated with us in determining the heats of combustion.

Summary

Cuprene was prepared by polymerization of acetylene by means of radon mixed with the gas. The solid polymer was then exposed to oxygen and the spontaneous reaction with oxygen at room temperature was followed manometrically. Both the solid and gaseous products were analyzed. The solid product after oxidation (which is nearly complete in twelve or fifteen days) contains approximately 25% oxygen. A little carbon monoxide is formed. The complete analysis shows the following reaction equation to be approximately correct

$$(C_2H_2)_{20} + 5^1/_2O_2 \longrightarrow C_{39}H_{40}O_{10} + CO$$

The spontaneous oxidation was also followed gravimetrically by exposing the freshly prepared cuprene to dry air and weighing at intervals. The results agree with the manometric method and analysis both as to extent and rate of oxidation. The heat of combustion of the oxidized cuprene is approximately 30% less than that of the unoxidized cuprene.

MINNEAPOLIS, MINN. RECEIVED SEPTEMBER 10, 1936

---

[12] Fajans, *Ber.*, **53**, 643 (1920); Taylor, "Treatise on Physical Chemistry," 2d ed., D. Van Nostrand Co., Inc., New York, 1931, p. 323.

[CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, UNIVERSITY OF MINNESOTA]

A Catalytic Method for Determination of Iodine

BY HAROLD P. LUNDGREN[1]

Among the methods used for determination of iodine there are: those determining iodine colorimetrically in a solvent, those titrating iodine using the blue starch–iodine complex as an indicator, those employing a color or precipitation reaction of iodine and those employing the catalytic power of iodine.

It is often necessary to analyze for iodine in concentrations too low to be detected by ordinary colorimetric, volumetric or gravimetric technique. The concentration of iodine may be increased by the Winkler technique until it is within the analytical range. The success of the Winkler method depends on how far the reactions concerned go toward completion. Furthermore, any trace of oxidizing agent left in the solution will cause serious error.

The catalytic methods for determination of iodine are in many cases sensitive to microgram quantities of iodine and are relatively simple and accurate procedures. Bredig and Walton[2] utilized the catalytic activity of iodine in the decomposition of hydrogen peroxide; Bobtelsky and Kaplan[3] utilized the rate of decoloration of permanganate by oxalic acid as catalyzed by iodine. Baines[4] employed the catalytic effect of iodine on the oxidation of thiosulfate by nitrite. Sandell and Kolthoff[5] made use of iodine catalysis in the oxidation of arsenous acid by ceric sulfate in sulfuric acid solution.

It is often necessary to analyze iodine in sulfite solutions since such are commonly used to absorb iodine, especially after combustion technique. In such a solution it would be impossible to apply the previously mentioned catalytic methods since all involve oxidation–reduction reactions and sulfite would interfere.

In a sulfite solution whose hydrogen ion concentration is less than 2 *N*, methylene blue was found to be decolorized more or less rapidly. At an acid concentration of 2 *N*, the reduction of the dye is immeasurably slow; iodide catalyzes the

---

[1] The author wishes to acknowledge with thanks the helpful criticism and suggestions of Professor J. F. McClendon, who has interested him in the field of iodine from the biochemical point of view. Abstracted from part of a thesis included among the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Minnesota.

[2] Bredig and Walton, *Z. Electrochem.*, **9**, 114 (1903).

[3] Bobtelsky and Kaplan, *Z. anorg. Chem.*, **172**, 196 (1928).

[4] Baines, *J. Soc. Chem. Ind. Trans.*, **49**, 481 (1930).

[5] Sandell and Kolthoff, THIS JOURNAL, **56**, 1426 (1934).