

## PRODUCTS OF THE PHOTOCHEMICAL OXIDATION OF ACETYLENE

Sir:

In view of the fact that the mechanism of the photochemical oxidation of acetylene has been discussed recently from a purely theoretical viewpoint [Mecke, *Trans. Faraday Soc.*, **27**, 374 (1931)], it seems worth while to present at this time certain preliminary observations on the products of this reaction.

When a mixture of acetylene and oxygen (saturated with water vapor at room temperature) is exposed (in a flow system) to the complete radiation of a "hot" quartz mercury arc, oxalic acid and a trace of an aldehyde are formed. The presence of oxalic acid was detected by microchemical precipitation of calcium oxalate and of barium oxalate; the crystals of these precipitates had the characteristic appearances of "tiny, highly refractive octahedra" and of "bundles of needles," respectively [Chamot, "Elementary Chemical Microscopy," John Wiley and Sons, Inc., New York, 1921, p. 337]. Additional evidence was obtained by comparing the concentration of acid and of reducing agent (as determined by titration with potassium permanganate) in a solution of the product. The average value for the ratio of the equivalent concentration of acid to that of reducing agents was 1.4. While the departure from the theoretical value of unity may indicate the presence of an acid, such as acetic, which is not readily oxidizable, it is quite possible that it is due entirely to experimental error, since the quantities available for titration were small (usually 1 or 2  $\times 10^{-5}$  equivalents). The aldehyde was detected with Schiff's reagent. Blanks, which were performed by either not exposing the gas mixture to the radiation or by irradiating oxygen-free acetylene, always gave negative results. No attempt was made to analyze for gaseous products.

The mechanism of the oxidation as predicted by Mecke consists essentially of the following steps: (1) electronic excitation of an acetylene molecule by absorption of a photon; (2) direct addition of the excited acetylene molecule to a normal oxygen molecule; (3) rearrangement of the addition product to glyoxal; (4) the decomposition of glyoxal to formaldehyde and carbon monoxide. If the very probable assumption is made that at room temperature glyoxal is more readily oxidized than decomposed, the chief product of the reaction would be oxalic acid, which is in agreement with the experimental results. At higher temperatures, the decomposition would presumably become the more important step, and the products of the photochemical reaction would approach those of the thermal reaction [compare Bodenstein, *Trans. Faraday Soc.* **27**, 386 (1931); also Spence and Kistia-kowsky, *THIS JOURNAL*, **52**, 4837 (1930)]. Another possible mechanism of the photochemical reaction would involve the addition of two molecules of oxygen to an excited acetylene molecule with the formation of a double

peroxide. Subsequent rearrangement of the peroxide would yield oxalic acid. This second mechanism was suggested by Professor G. N. Lewis.

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## NEW BOOKS

**Liebig und die Bittersalz- und Salzsäurefabrik zu Salzhausen (1824-1831).** (Liebig and the Magnesium Sulfate and Hydrochloric Acid Factory at Salzhausen.) Edited by Dr. ERNST BERL. Verlag Chemie, G. m. b. H., Corneliustrasse 3, Berlin W 10, Germany, 1931. 65 pp. 17 × 24 cm. Price, M. 3.50.

Justus Liebig was only twenty-one years old when in May, 1824, he was called to a professorship at the University of Giessen. In December of the same year at the request of the Hessian Ministry of Finance he analyzed the waters of the Salzhaus Mineral Springs. On the basis of this analysis Liebig recommended that the mother liquors from these waters after the separation of the sodium chloride be worked up by the government as a source of magnesium sulfate and of hydrochloric acid. This recommendation was adopted and Liebig was commissioned to undertake the development of the process and the erection of the plant. He discharged this task with conspicuous success.

In the present small pamphlet there are reproduced verbatim some twenty reports which Liebig made to the Ministry of Finance during the progress of this work. There is also included a lecture in explanation of them delivered by Dr. Berl at the first annual meeting of the Liebighaus Society in Darmstadt.

It is of interest to point out that it was in the mother liquors from these springs that Liebig found the puzzling substance which he called "sodium hydroiodate" and from which he obtained a substance which he considered to be the chloride of iodine but which he instantly recognized to be bromine when Balard's discovery of that element was announced some months later.

Dr. Berl has already published a notable collection of the letters of Liebig. This present pamphlet makes a valuable supplement to that volume.

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**General Chemistry.** By H. I. SCHLESINGER, Professor of Chemistry, The University of Chicago. Revised edition. Longmans, Green and Company, 55 Fifth Avenue, New York, 1930. xi + 847 pp. Illustrated. 14.5 × 21 cm. Price, \$4.00.

The second edition of this excellent text has been increased by about two hundred pages: The changes and additions consist "first, in an amplifica-