different strengths. Thus in water we have 0.1 N trichloroacetic acid  $P_{\rm H} = 1.4, 0.1 N$  diethylamine  $P_{\rm H} = 11.8$ , a difference of 10.4 units; whereas in pyridine we found " $P_{\rm H}$ " of 0.1 N trichloroacetic acid = 3.2; " $P_{\rm H}$ " of 0.1 N diethylamine = 7.4, a difference of only 4.1 units.

It is also found that the change in apparent PH of an acid or base as the solvent is progressively changed from water to pyridine follows a smooth curve from mole fraction pyridine = 0.2 to 1.0. The most marked change occurs before the mole fraction of pyridine has reached 0.2 and the irregularity of the curves in this region is obviously due to pyridine behaving as a base in dilute water solution.

CONTRIBUTION NO. 670 DEPARTMENT OF CHEMISTRY COLUMBIA UNIVERSITY NEW YORK, N. Y. RECEIVED AUGUST 11, 1931 PUBLISHED SEPTEMBER 5, 1931 LAWRENCE E. KROHN VICTOR K. LA MER

## THE LOW-TEMPERATURE EXPLOSION OF MIXTURES OF OZONE AND HYDROGEN BROMIDE

Sir:

Sept., 1931

In an attempt to discover the nature of the reaction chain carriers in the thermal decomposition and explosion of ozone sensitized by bromine vapor<sup>1</sup> by seeking appropriate chemical compounds capable of reacting exclusively with oxygen atoms in the presence of ozone, hydrogen bromide was investigated.<sup>2</sup>

It was found that hydrogen bromide reacted with pure ozone practically instantaneously at room temperatures. Above a certain definite limiting pressure of the gases an explosion takes place. The reaction can be measured conveniently at the temperature of boiling ethylene  $(-104^{\circ}C)$ . Explosions are observed even at this low temperature at a pressure only a little greater than at room temperature. As the initial pressure is increased, the slow reaction increases in velocity and goes over to an inflammation at the explosion limit and finally to a detonation at several millimeters above the limit. The explosion limit is of the order of 20 to 30 mm. for an equimolar gas mixture.

The difference in lag periods in different vessels, the effect of coating the walls with a uniform solid layer of the products of decomposition (bromine and ice at  $-104^{\circ}$ ), the effect of packing a vessel with glass tubes, and the effect of vessels of different sizes on the slow reaction below the explosion limit and on the limit itself indicate that the reaction takes place through

<sup>1</sup> Bernard Lewis and W. Feitknecht, Z. physik. Chem., Bodenstein Festband, 113 (1931); THIS JOURNAL, 53, 2911 (1931).

<sup>2</sup> P. Harteck and U. Kopsch, Z. physik. Chem., 12B, 327 (1931).

the medium of chains which require a surface for their initiation.<sup>1,3,4</sup> A glass surface was found to be much less efficient for starting chains than a solid bromine-ice surface.

At  $-104^{\circ}$  the slow reaction goes to completion in a time ranging from twenty seconds to four minutes in accordance with the following equation

 $2HBr + O_3 = H_2O + Br_2 + O_2$ 

If ozone is added in excess the reaction stops when all the hydrogen bromide has disappeared. Under the conditions of an explosion, however, any amount of excess ozone is completely decomposed. In a detonation some of the hydrogen bromide remains undecomposed due to the equilibrium established at the high instantaneous temperature developed.

The kinetics of the reaction is being studied in detail.

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## NEW BOOKS

Annual Survey of American Chemistry. Vol. V, 1930. Edited by CLARENCE J. WEST, Director Research Information Service, National Research Council. Published for National Research Council by The Chemical Catalog Company, Inc., 419 Fourth Ave., New York, N. Y., 1931. 629 pp. 14 × 21.5 cm. Price, \$5.00.

Volume V (1930), "Annual Survey of American Chemistry," edited by Clarence J. West, with a brief foreword by Harry A. Curtis, presents in 630 pages a comprehensive survey of the work done in all branches of Chemistry in this country during 1930.

The subject matter covered is divided into forty chapters, each contributed by a specialist in the particular field covered. The individual contributors are to be congratulated on the successs which they have had in so arranging the material comprised within the separate chapters that the work as a whole has continuity.

An admirable author and subject index adds greatly to the usefulness of the book. The list of authors in fine print, three columns to a page, requires nineteen pages and shows better than words can describe the great strides which chemical research has made in this country. The usefulness of the volume is greatly increased also by the careful attention which the Chemical Catalog Company gave to the printing and binding.

Although the reviewer did not examine the text critically for errors, there appear to be surprisingly few, considering the nature of the task

<sup>8</sup> H. Alyea and F. Haber, *ibid.*, **10B**, 193, 1930; H. Alyea, THIS JOURNAL, **53**, 1324 (1931).

<sup>4</sup> H. W. Thompson, Z. physik. Chem., 10B, 273 (1930).