

at 25 mm. pressure is collected. The yield of distilled ester averages about 85%.

CONTRIBUTION FROM THE
DEPARTMENT OF BIOCHEMISTRY
UNIVERSITY OF SOUTHERN CALIFORNIA
SCHOOL OF MEDICINE
LOS ANGELES, CALIFORNIA
RECEIVED JUNE 8, 1931
PUBLISHED SEPTEMBER 5, 1931

PAUL W. JEWEL
JOSEPH S. BUTTS

COMMUNICATIONS TO THE EDITOR

THE BROMINE-SENSITIZED OXIDATION OF UNSATURATED HYDROCARBONS

Sir:

If one absorbs a pure unsaturated hydrocarbon (C_2H_4 , C_3H_6 or C_4H_8) in the presence of pure oxygen by means of bromine water, more gas is absorbed than corresponds to the hydrocarbon present. This extra decrease in volume is not accounted for by the solubility of oxygen in bromine water, for the same results were obtained when the bromine water was presaturated with oxygen.

Thus a bromine-sensitized formation of carbon dioxide and water, both of which would be dissolved in aqueous solution, was suspected. In order to test this assumption in a simple experiment, one side of a 300-cc. sphere was connected to a high vacuum pump through a stopcock and a liquid air trap, the other side communicated, through an ordinary stopcock, a capillary, and a three-way stopcock, with a mercury manometer and a mercury Toepler pump. A tube containing some bromine was also attached to the bulb. The two stopcocks adjacent to the sphere were lubricated with Stephens' stopcock grease [H. N. Stephens, *THIS JOURNAL*, **52**, 635 (1930)]. The system was evacuated, the bromine evaporated and frozen out again with liquid air. The procedure was repeated and the sphere filled with bromine corresponding to its vapor pressure at about 30° (about 100 cc., N. T. P.). The bromine tube and the pumping line were sealed off between sphere and stopcock. The bromine was again frozen out and a mixture of specially purified ethylene (56.7 cc., N. T. P.) and oxygen (55.2 cc.) was filled in on top of the frozen bromine. The manometer was then opened and read. The two stopcocks were closed, leaving some oxygen in the manometer, and the capillary between the stopcocks was cut in two. The sphere was exposed to direct sunlight, then the liquid air removed and the sphere gently rotated¹ to distribute the bromine. The bromination took place immediately. After two hours of exposure the sphere was immersed to exactly the same point in liquid air and again sealed on the system. The

¹ This seemed to be of great importance.

gas pressure was less than before, showing that some oxygen had disappeared. The oxygen was pumped off; less was recovered than was put in (53.1 cc.) [analysis according to Franzen, *Ber.*, **39**, 2069 (1906)]. The sphere was then heated to -79° , whereupon the pressure increased. Some gas was pumped off and analyzed with barium hydroxide for carbon dioxide. The precipitate showed the presence of carbon dioxide (1.4 cc.).

The new effect may be considered analogous to the chlor-sensitized carbon-dioxide formation from carbon monoxide which has been studied by Bodenstein and co-workers. The effect is in interesting contrast to that reported in a brief note recently published by R. Livingston [*J. Phys. Chem.*, **34**, 2121 (1930)]. If his data are correct, one must assume that carbo-oxides (CO) are not oxidized in a bromine-sensitized reaction, whereas carbo-hydrides (C_2H_4) are oxidized to a slight extent. An energy chain propagated by the heat of formation of the water formed may account for this difference. Incidentally, the bromination of the hydrocarbon and its heat effects must be taken into account.

The bearing of this new type of reaction upon the use of the bromine pipet will be reported in a paper soon to appear.

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA

GEORG R. SCHULTZE

RECEIVED JULY 25, 1931
PUBLISHED SEPTEMBER 5, 1931

THE ALLEGED SELENIUM TRIOXIDE OF WORSLEY AND BAKER

Sir:

The method reported by Worsley and Baker¹ for the preparation of selenium trioxide has failed to yield that substance when carried out by Meyer and Pawletta,² and more recently Hoffman and Lenher³ have shown that the product is selenium dioxide contaminated with water and selenium oxychloride.

In 1927-1928 the Worsley and Baker experiment was repeated in this Laboratory. Selenium oxychloride was prepared by the dehydration of selenium hydroxychloride⁴ and redistilled twice under diminished pressure. This material melted at 9.4° and showed also by the test with cobalt carbonate⁵ that it contained traces of water. Highly purified selenium was dissolved in this solvent and oxidized with ozone (18 g. of O_3 per cu. meter of O_2). The precipitate obtained after thirty hours was examined. It contained traces of chlorides which could not be removed

¹ Worsley and Baker, *J. Chem. Soc.*, **123**, 2870 (1923).

² Meyer and Pawletta, *Ber.*, **60**, 985 (1927).

³ Hoffman and Lenher, *THIS JOURNAL*, **51**, 3177 (1929).

⁴ Muehlberger and Lenher, *ibid.*, **47**, 1842 (1925).

⁵ Lenher, *ibid.*, **43**, 32 (1921).

by washing with carbon tetrachloride and the selenium content was 61.52 and 61.60%. This substance did not liberate chlorine when boiled with hydrochloric acid⁶ and a precipitate was not formed when barium chloride was added to an aqueous solution of the material. Moreover, during the oxidation, the selenium oxychloride was dehydrated, as it no longer gave the characteristic reaction with cobalt carbonate. From these facts the authors conclude that the product formed by the ozone oxidation of Se-SeOCl₂ solution is not SeO₃ but SeO₂ contaminated with chlorides and water. This work was nearly completed before the authors were aware that a similar but more elaborate investigation had been carried out by Professor Lenher and his students. Announcement has been withheld until an account of the Wisconsin experiment has been published.⁷

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
POLYTECHNIC INSTITUTE OF BROOKLYN
BROOKLYN, N. Y.

G. B. L. SMITH
C. L. MEHLTRETTER

RECEIVED JULY 13, 1931
PUBLISHED SEPTEMBER 5, 1931

ACID-BASE REACTIONS IN PYRIDINE SOLUTION

Sir:

A preliminary study of the behavior of acids and bases in pyridine solutions has been made by us using a Hellige comparator and indicator solutions prepared by dissolving the solid dyes directly in pure pyridine.

In what follows the term apparent " P_H " referred to a pyridine solution simply means that a given indicator in the pyridine solution gives a color identical with that given by the same indicator in a water solution of that P_H , without implying that the acidity in pyridine is identical with that in aqueous solution.

In the first series of experiments, dilution curves for pyridine were obtained by making such indicator comparisons for the acids and bases under investigation for concentrations ranging from 0.00001 to 1.0 M . The results for trichloroacetic acid and diethylamine are shown in Fig. 1.

Since the change in apparent P_H with concentration is independent of the indicators used, it is obvious that the specific changes reside primarily in the activity coefficients of the acid and base studied.

In the second series we investigated the behavior of this acid and of this base in mixtures of water and pyridine. For this purpose indicator comparisons are reported in Fig. 2 for solutions containing a constant amount of acid or of base but with varying proportions of pyridine and water.

⁶ Gooch and Evans, *Am. J. Sci.*, [3] 50, 400 (1895).

⁷ For further details, see thesis submitted by C. L. Mehlretter in partial fulfillment of the requirement for the degree of Bachelor of Science in Chemistry at the Polytechnic Institute of Brooklyn in June, 1928.

The rapid decrease in apparent P_H on addition of pyridine to aqueous 0.1 M diethylamine suggests very strongly that pyridine has some acid proper-

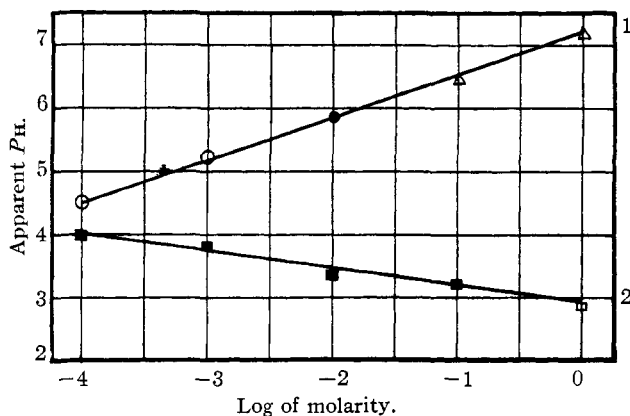


Fig. 1.—Dilution curves for acid and base in pyridine: 1, diethylamine; 2, trichloroacetic acid. \square , Thymol blue; \blacksquare , brom phenol blue; \circ , brom cresol green; \bullet , brom cresol purple; \triangle , brom thymol blue.

ties. Pyridine is therefore amphiprotic in character but much less so than water in view of its smaller power of differentiating acids and bases of

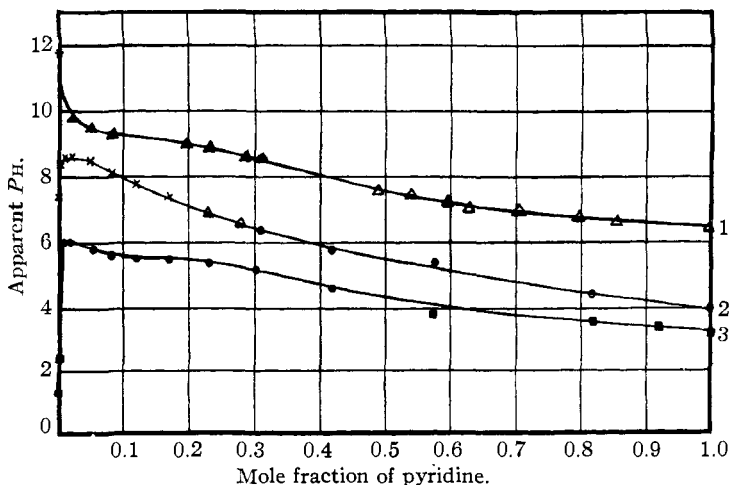


Fig. 2.—Effect of changing solvent on apparent P_H of dissolved acid or base: 1, 0.1 N diethylamine in pyridine-water; 2, pure pyridine and water; 3, 0.1 N trichloroacetic acid in pyridine-water; \square , thymol blue; \blacksquare , brom phenol blue; \circ , brom cresol green; \bullet , brom cresol purple; \triangle , brom thymol blue; \times , cresol red; \blacktriangle , phenolphthalein; $*$, sulfo orange (Lamotte).

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

It is also found that the change in apparent P_H 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.

LAWRENCE E. KROHN
VICTOR K. LA MER

RECEIVED AUGUST 11, 1931
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THE LOW-TEMPERATURE EXPLOSION OF MIXTURES OF OZONE AND HYDROGEN BROMIDE

Sir:

In an attempt to discover the nature of the reaction chain carriers in the thermal decomposition and explosion of ozone sensitized by bromine vapor¹ by seeking appropriate chemical compounds capable of reacting exclusively with oxygen atoms in the presence of ozone, hydrogen bromide was investigated.²

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°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.

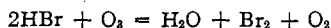
The difference in lag periods in different vessels, the effect of coating the walls with a uniform solid layer of the products of decomposition (bromine and ice at -104°), the effect of packing a vessel with glass tubes, and the effect of vessels of different sizes on the slow reaction below the explosion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

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

² P. Harteck and U. Kopsch, *Z. physik. Chem.*, 12B, 327 (1931).

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

At -104° the slow reaction goes to completion in a time ranging from twenty seconds to four minutes in accordance with the following equation



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.

U. S. BUREAU OF MINES
PITTSBURGH EXPERIMENT STATION
PITTSBURGH, PENNSYLVANIA

BERNARD LEWIS
W. FEITKNECHT

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PUBLISHED SEPTEMBER 3, 1931

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 success 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

³ H. Alyea and F. Haber, *ibid.*, 10B, 193, 1930; H. Alyea, *THIS JOURNAL*, 53, 1324 (1931).

⁴ H. W. Thompson, *Z. physik. Chem.*, 10B, 273 (1930).