

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

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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-

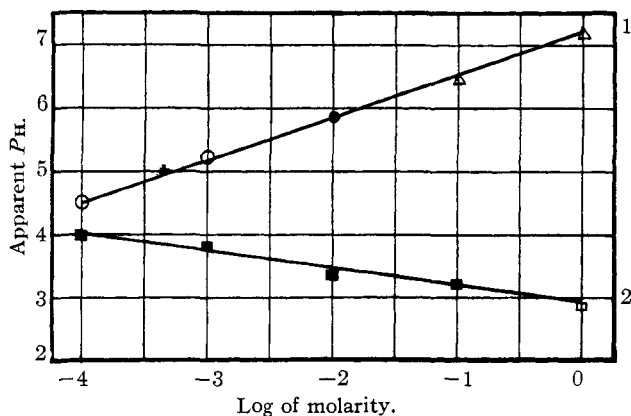


Fig. 1.—Dilution curves for acid and base in pyridine: 1, diethylamine; 2, trichloroacetic acid. \square , Thymol blue; \blacksquare , brom phenol blue; \circ , brom cresol green; \bullet , brom cresol purple; \triangle , brom thymol blue.

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

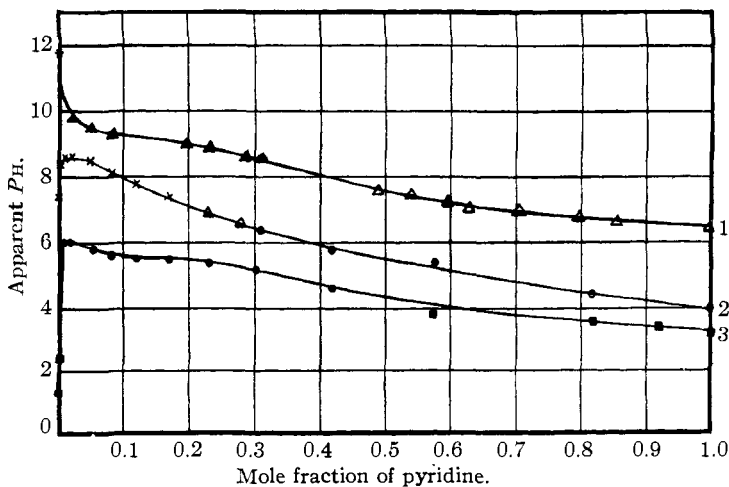


Fig. 2.—Effect of changing solvent on apparent P_H of dissolved acid or base: 1, 0.1 N diethylamine in pyridine-water; 2, pure pyridine and water; 3, 0.1 N trichloroacetic acid in pyridine-water; \square , thymol blue; \blacksquare , brom phenol blue; \circ , brom cresol green; \bullet , brom cresol 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.

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DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK, N. Y.

LAWRENCE E. KROHN
VICTOR K. LA MER

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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).