

Anal. Calcd. for $C_{13}H_{13}O_6N_7 \cdot 1.5H_2O$: C, 48.6; H, 4.7; N, 20.9. Found: C, 48.4; H, 5.0; N, 20.9.

The crystal form, ultraviolet absorption spectrum and paper partition chromatography (R_f , 0 (*n*-butanol); 0.11 (collidine-lutidine, 1:1); 0.22 (acetic acid-*n*-butanol-water, 1:4:1); 0.40 (phenol-water-ammonia solution, 80:18:2))¹² showed the identity of this product with an authentic sample of pteroylglutamic acid.

(12) Kuwada, Mizuno and Masuda read a paper on the paper partition chromatography of folic acid and related compounds at the meeting of the Pharmaceutical Society of Japan in September, 1949.

THE DEPARTMENT OF PHARMACY
FACULTY OF MEDICINE
UNIVERSITY OF KYOTO
KYOTO, JAPAN

RECEIVED MARCH 29, 1950

Adsorption Effects in the Decomposition of Hydrogen Peroxide Vapor

BY MILTON TAMRES AND ARTHUR A. FROST

Adsorption phenomena in studying the kinetics of hydrogen peroxide vapor decomposition were reported by MacKenzie and Ritchie¹ and by Giguère² who investigated extensively the sensitivity of the reaction to surface conditions. The reaction was studied at this Laboratory by a static method employing an oil (Nujol heavy mineral oil) manometer to follow the reaction rate. Results at 45° and room temperature showed a pressure increase during a run in excess of the 50% expected for a homogeneous reaction. This can only be explained by adsorption effects of hydrogen peroxide and water.

For experiments at 21°, a small quantity of liquid hydrogen peroxide of approximately 90% concentration was distilled at room temperature under reduced pressure until a trace of the liquid remained. Decomposition of the resulting vapor at initial pressures of 0.5 to 0.7 mm. and presumably of very high peroxide concentration, was studied in two spherical 500-cc. Pyrex vessels. The observed over-all change in pressure was approximately 62% of the initial pressure for one vessel and 50% for the other although their surfaces were treated identically. That this difference in adsorption was not due to possible slight differences in experimental conditions was shown by employing an experimental technique whereby hydrogen peroxide vapor could be introduced simultaneously into both reaction vessels, equalizing the pressure of vapor between them and following the "differential" rate of reaction with the oil manometer each end of which was connected to one of the vessels. The "differential" rate of reaction showed that initial decomposition proceeded more rapidly in the vessel where adsorption was greater, the difference in extent of adsorption being noted by the difference in final pressures in the reaction vessels. Each run required several days and consequently few were made. The results, however, seemed reproducible.

(1) R. C. MacKenzie and M. Ritchie, *Proc. Roy. Soc. (London)*, **A185**, 207 (1946).

(2) P. A. Giguère, *Can. J. Research*, **25B**, 135 (1947).

Packing the reaction vessel with approximately 5 g. of soft glass wool strikingly demonstrated this effect, approximately three times as much hydrogen peroxide being adsorbed than was present in the vapor phase.

Attempts to minimize surface effects by coating Pyrex glass surfaces with microcrystalline wax (Cerese wax AA) and with silicone (Dri-Film 9987) were unsuccessful. A comparison of the rate of decomposition at 45.0° showed that the wax only slightly decreased the rate as compared with the chromic acid cleaned surface whereas the silicone surface catalyzed the reaction.

For photochemical experiments, the reaction vessel was a cylindrical Pyrex glass cell to which a Vycor window was sealed with Apiezon W. The cell, which was 4 cm. inside diameter and of 250-cc. capacity, was jacketed with a copper coil through which water at 26.2° was circulated. The ultraviolet source was a Hanovia quartz mercury discharge lamp, emitting predominantly 2537 Å. radiation. The rate of the photochemical reaction was much faster than that of the thermal reaction, and was not influenced by the introduction of 0.05 to 8.0 mm. pressure of nitrogen (except as described below), oxygen or water vapor, nor by 0.05 to 1.0 mm. pressure of hydrogen or air. This is in agreement with results reported by Volman.³

The complete photolysis of the vapor from a supply of approximately 95% liquid hydrogen peroxide resulted in a pressure change which was from 49 to 61% of the initial pressure, again indicating adsorption of peroxide. The fact that Volman reported an over-all change in pressure which was less than 50% of the initial pressure, does not eliminate the possibility of adsorption in his experiments since his liquid hydrogen peroxide supply was of lower concentration.

An interesting observation in the photochemical studies should be mentioned. In the initial experiments, when nitrogen was being used as the inert gas, decomposition was very rapid for nitrogen pressures less than 0.1 mm., while at higher nitrogen pressures the rate was decreased noticeably if the nitrogen were admitted first to the cell, but was unaffected by the presence of nitrogen if peroxide were first introduced. A change to oxygen as the foreign gas showed no such pressure dependence and a return to nitrogen no longer produced this effect.

These observations confirm the heterogeneous character of the thermal reaction and indicate that the photochemical reaction also has some heterogeneous characteristics.

Acknowledgment.—This work was supported by a fellowship from the U. S. Rubber Company.

DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

RECEIVED JUNE 23, 1950

(3) D. H. Volman, *J. Chem. Phys.*, **17**, 947 (1949).