2. The apparent solubility of germanium tetrachloride, and of arsenious chloride, in hydrochloric acid of various concentrations, has been determined. Germanium tetrachloride is practically insoluble in concentrated hydrochloric acid.

3. The distribution of arsenious chloride between concentrated hydrochloric acid and germanium tetrachloride has been studied.

4. The chlorides of antimony, tin and titanium may be removed from germanium tetrachloride by a single extraction with concentrated hydrochloric acid.

PHILADELPHIA, PENNSYLVANIA

THE PHOTOLYSIS OF HYDROGEN PEROXIDE IN AQUEOUS SOLUTION

By LAWRENCE JOSEPH HEIDT

Quantum yields of the photolysis of hydrogen peroxide in aqueous solution as reported in the literature vary from 4 to 500. Rice and Kilpatrick[1] have suggested that dust-free solutions from which all surface effects have been eliminated should give a quantum yield of unity. Allmand and Style[2] found that the quantum yield decreases from 500 to 20 as the intensity of light increases.

Investigations of the photolysis prior to 1929 have been reviewed and discussed by Kistiakowsky[3] and by Griffith and McKeown.[4] Kornfeld[5] suggests the dissociation $H_2O_2 \longrightarrow H^+ + OOH^-$ in explaining her results.

Urey, Dawsey and Rice[6] favor the photolysis $H_2O_2 \overset{h\nu}{\longrightarrow} H_2O + (O)$. In the present investigation a quantitative study of the photolysis in monochromatic light was made to ascertain whether secondary effects can be eliminated to such an extent that the photolysis can be further studied profitably from a theoretical standpoint.

Materials.—General Chemical Co. superoxol (Code B, At 1788) was purified by distillation in an all-Pyrex still, at a pressure of 25 mm. in the presence of an excess of c. P., silver sulfate. The receiving flask at 0° was of

[1] Rice and Kilpatrick, *J. Phys. Chem.*, **31**, 1507 (1927).

[2] (a) Allmand and Style, *J. Chem. Soc.*, 596 (1930); (b) *ibid.*, 606 (1930).

[3] Kistiakowsky, "Photochemical Processes," The Chemical Catalog Co., Inc., New York, 1928, pp. 173–177.

[4] Griffith and McKeown, "Photoprocesses in Gaseous and Liquid Systems," Longmans, Green and Co., New York, 1929, pp. 459–461.

[5] Kornfeld, *Z. wiss. Phot.*, **21**, 66 (1921).

[6] Urey, Dawsey and Rice, THIS JOURNAL, **51**, 1371 (1929).

quartz. Conductivity water for dilution was made by redistillation of distilled water first in a tin and then in an all quartz still. Sulfuric acid was made by dissolving in a quartz flask at 0° the white crystals of acid from 30% reagent quality fuming sulfuric acid in conductivity water. Solutions of the above purified materials were kept in covered quartz flasks. Potassium permanganate, c. p., was not subjected to further purification.

Purification of materials and all experiments were carried out in a laboratory comparatively free from dust. It had no windows and was isolated from chemical fumes. The laboratory air was filtered. All cells and glassware were cleaned with chromic acid and thoroughly rinsed with conductivity water.

Experimental Procedure

The light source, monochromator and radiometric procedure have been described.[7]

Absolute energy measurements were determined by reference to U. S. Bureau of Standards lamp C 44. They were checked against determinations of the decomposition of uranyl oxalate in the same cell using the data of Leighton and Forbes.[8]

A two compartment (9 cm. × 1 cm. × 1 cm.) rectangular quartz cell, all seams fused, was used as the reaction vessel. It was placed flush against the exit slit (0.6 mm. × 20.0 mm.) so that all the light from this slit was intercepted by the front windows of either compartment. Special precautions were taken to have the center of the beam pass through the center of the reaction compartment; otherwise results were erratic and gave higher values of the quantum yield, particularly if the beam grazed a side wall. Photolyses were carried out at 313 mμ and 28 ± 2° in only one compartment at a time, thus eliminating corrections for the dark reaction taking place under otherwise identical conditions in the other compartment. The dark reaction, however, was generally negligible.

Analyses were carried out volumetrically using 0.02 N potassium permanganate standardized against sodium oxalate and oxalic acid. An excess of sulfuric acid was always present. Extra care was taken to prevent surfaces in contact with the hydrogen peroxide from rubbing together, and to add the titer always at the same rate; otherwise, analyses were not reproducible.

The "$P\text{H}$" of the solutions was determined by the use of a glass electrode apparatus[9] kindly furnished by Dr. Hazel. The values should be considered only as qualitative until the reliability of the glass electrode for solutions of this type is further established.

[7] (a) Daniels and Heidt, This Journal, **54**, 2381 (1932); (b) Heidt and Daniels, ibid., **54**, 2384 (1932).

[8] Leighton and Forbes, ibid., **52**, 3139 (1930).

[9] Hazel and Sorum, ibid., **53**, 49 (1931).

Data and Discussion

Results of the photolyses are summarized in the table. Concentration of hydrogen peroxide is expressed in moles per liter. Data for one photolysis for each series are shown and check determinations of the quantum yield, Φ, are given in parentheses. The average quantum yield, Φ av., of the series is given in the last column. In series A, where the original peroxide containing an inhibitor was not purified, a strong blue fluorescence was noted throughout the solution.

TABLE I

Series	[H₂O₂]	[H₂SO₄]	"P_H"	I/I_0	Time of photolysis in sec. × 10⁻³	Quanta absorbed × 10⁻¹⁹	Molecules decomposed × 10⁻¹⁹	Φ	Φ av.
A	1.77	0.0	3.0	89	7.2	7.9	14.2	1.8 (1.7 0.9)	1.5
B	2.36	0.0	3.6	91	7.2	7.0	8.0	1.1 (1.1 1.1)	1.1
C	4.20	0.0	2.5	98	7.2	3.5	6.8	2.0 (3.1 2.1)	2.4
D	3.70	1.3	−1.0	96	14.4	8.2	15.6	1.9 (1.9 1.3)	1.7
E	3.72	4.1	−1.8	95	14.4	5.6	11.2	2.0 (1.3 2.1 1.8)	1.8
F	4.48	1.3	−1.5	98	10.8	6.6	6.4	1.0 (1.6 2.0 2.1)	1.7

It is evident from the table that a quantum yield approaching unity has been obtained, substantiating the predictions of Rice and Kilpatrick[1] for dust-free solutions and those of Griffith and McKeown[4] for radiation of high intensity. The intensity per square millimeter was of the order of 1000 times that of Allmand and Style[2b] in their experiments with filters. The data also show, almost within the limits of experimental error, that Φ tends to increase with the concentration of hydrogen peroxide and to decrease with the addition of sulfuric acid. Results obtained a year later independently by Mr. Harrison Holmes and the author are in general agreement with the above.

Calculations based on the data of the table show that the extinction coefficient, $\epsilon(1/cd \log I_0/I$ where c is expressed in moles per liter and d in cm.), tends to decrease with an increase in [H₂O₂] and in [H₂SO₄]. The reaction cell used in these experiments was irregular but the thickness was approximately 1 cm. and relative values of ϵ are accurate to 5%.

Using the method of Forbes, Heidt and Boissonnas[10] for measuring extinction coefficients, the following was obtained. In a given cell for 2.36 molar H₂O₂, $\epsilon_{313 m\mu} = 0.44$; for 2.36 molar H₂O₂ in 2.6 molar H₂SO₄, $\epsilon_{313 m\mu} = 0.41$ and on adding a slight excess of sodium hydroxide to 2.36 molar H₂O₂, $\epsilon_{313 m\mu} = 1.14$. All measurements were taken before any noticeable decomposition had taken place. From this it appears that some chemical individual derived from hydrogen peroxide, possibly the ion OOH⁻, has an extinction coefficient for λ 313 mμ greater than that of the peroxide. To draw definite conclusions, it is planned to make a detailed study of the dependence of ϵ on [H₂O₂] and [H⁺]. In later experiments

[10] Forbes, Heidt and Boissonnas, THIS JOURNAL, **54**, 960 (1932).

with an improved cell $\epsilon_{313\ m\mu}$ was found to be 0.38 for molar hydrogen peroxide.   This is in good agreement with the value 0.39 obtained by Allmand and Style.[2a]

The author desires to express his appreciation to Professor Farrington Daniels for his help and guidance in this investigation, and to the Research Committee of the University of Wisconsin for substantial aid.

Summary

1.   A quantum yield approaching unity as the concentration of hydrogen peroxide is decreased has been obtained for its photolysis in aqueous solution at 28 $\pm$ 2° using light of high intensity at 313 mμ from a monochromator.

MADISON, WISCONSIN

THE OPTICAL CRYSTALLOGRAPHIC DESCRIPTION OF THE PHENYLOSAZONES AND OTHER DERIVATIVES OF CERTAIN SUGARS[1]

BY VINCENT H. MORRIS

Introduction

The identification of sugars which have been isolated from plants or plant products is a constantly recurring problem.   The usual method of attack consists of preparing insoluble derivatives of the sugars in more or less pure crystalline form and identifying these derivatives through their melting points, optical rotation, microscopic observation of crystal form, etc.   Since the presence of very small quantities of impurities is sufficient to make melting points misleading, as well as to influence the crystal form, positive identification through these characteristics is sometimes difficult.   In searching for some other means, that suggested by Wright,[2] based on the optical properties of the crystalline derivatives, seemed to offer promise of being such a valuable tool in the identification of sugars that a study of certain derivatives of some of the more common sugars was undertaken.

Materials.—The sugars investigated were glucose, fructose, mannose, galactose, arabinose, xylose and maltose.   The derivatives used were the phenylosazones of five of these and the following additional compounds:

[1] This study was carried out under the direction of Dr. H. C. Sampson and Dr. W. G. McCaughey, Departments of Botany and Mineralogy, respectively, The Ohio State University, and presented in partial fulfilment of the requirements of the degree of Doctor of Philosophy to the Faculty of the Graduate School of The Ohio State University.   Original manuscript received October 23, 1931.

[2] Wright, THIS JOURNAL, **38**, 1647 (1916).