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Studies of Reactions Induced by the Photoactivation of the Water Molecule. I

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(Received April 22, 1936)

Unbuffered gas free solutions of methyl alcohol have been irradiated with ultraviolet light in the wave-length range longer than 1850Å and it is found that reactions involving the methyl alcohol occur, induced by the photoactivation of the water molecule. Gas free water itself is not changed by the irradiation. Products initially obtained in the water-photosensitized reaction are hydrogen as the

only gas and a small amount of formaldehyde accounting for 10 to 20 percent of the hydrogen produced. The direct photoactivation of the methyl alcohol leads to its decomposition according to $\text{CH}_3\text{OH} + (h\nu) = \text{CH}_2\text{:O} + \text{H}_2$. The spectral limit for the water-photosensitized reaction is in the neighborhood of 2000Å.

A MARKED increase in the absorption of light by water takes place below 2000Å. The present communication is concerned with an investigation of reactions, in aqueous solution, induced by the activation of the water molecule with wave-lengths in this region. Our studies have included transformations of carbon monoxide, methyl and ethyl alcohols, formic acid, acetaldehyde, acetone, and diethyl ether, irradiated in gas free solutions. Gas free water, if sufficiently purified, is not itself changed by the irradiations used.

The irradiations have been carried out employing a quartz mercury arc and condensed sparks. The sparks were operated in air or hydrogen by means of a kenotron rectified transformer (20 kv, 50 to 100 ma) and with a 0.02-microfarad condenser in parallel with the spark. The constancy of the irradiations was controlled by a cadmium photoelectric cell connected to a string electrometer. The irradiated solutions were contained in thin walled fused quartz cells and in some experiments in Pyrex cells with windows of crystalline quartz and fluorite.

The reactions were studied by an analysis of the gases produced and by other specific tests. The gas analyses were carried out in a van Slyke gas apparatus. The entire contents of the irradiation cells (usually about 20 cc) were transferred into a 50-cc extraction chamber and the analysis performed in the usual manner. Potassium permanganate was used to liberate oxygen from hydrogen peroxide, sodium hydroxide for the absorption of carbon dioxide, sodium hydrosulfite for the absorption of oxygen, and ammoniacal cuprous chloride for the absorption of

carbon monoxide. The composition of the residual gas could be determined by a combustion analysis. Kahlbaum, Merck and Baker's best chemicals used without further purification gave identical results in the irradiations.

For the purification of the water used in preparing the irradiated solutions, distilled water from a Barnstead still was refluxed for extended periods successively in potassium hydroxide-potassium permanganate and in sulfuric acid-potassium dichromate mixtures and the vapor, mixed with oxygen, finally passed through a quartz tube heated to 900°C. This vapor was then condensed in a Pyrex reservoir from which it could be directly transferred into the chamber for filling the cells. The water thus obtained still contains traces of organic impurities as revealed when the water (gas free) is irradiated with ultraviolet light, the decomposition of these impurities taking place with the production of hydrogen and carbon dioxide. With the type of purification described, these gases are reduced to a few micromoles per 1000 cc of water. The water from the Barnstead still gave, under similar treatment, as much as 10 to 20 micromoles of these gases (Fig. 1). The water can be further purified by irradiation with x-rays and this procedure was used in the work with the most dilute solutions.

The purified water was transferred directly to a Pyrex evacuation chamber into which the irradiation cells fitted through ground joints. The chemicals were added, connection made to a water pump, and the dissolved gases removed by the simultaneous warming and shaking of the solution. The solution was then rapidly forced into the irradiation cells by slightly increasing

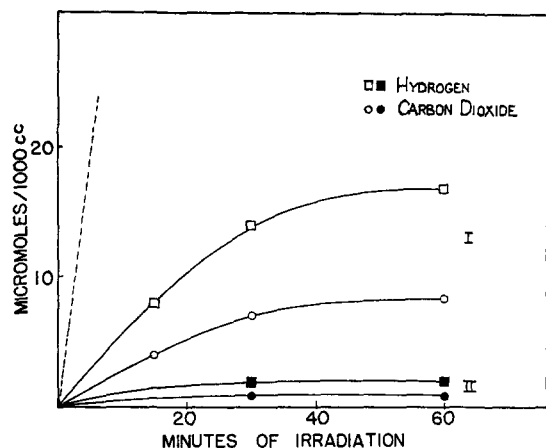


FIG. 1. Water-photosensitized decomposition of organic impurities in water (gas free) by irradiation with ultra-violet light. I: water from tin still; II: water purified as described in text. For comparison, the dotted line shows hydrogen production obtained by irradiating 1 millimolar methyl alcohol. Light source: aluminum spark.

the pressure (with air) on the surface of the liquid. Solutions prepared in this manner yield less than 1 micromole of dissolved gases per 1000 cc of solution. Before being filled, the cells and evacuation chamber could be heated to 500°C for the purpose of removing possible traces of organic material.

We shall begin by describing certain experiments carried out with solutions of methyl alcohol. The water-photosensitized transformation of organic molecules generally is a function of the hydrogen ion concentration, but the present experiments were carried out in unbuffered solution. Besides analyses of the gases produced, supplementary analyses were made for formaldehyde by Hehner's method,¹ the amounts being estimated quantitatively by the use of proper blanks. With this method, the amount of formaldehyde could be estimated to an accuracy of 10 micromoles per liter. The light source was an aluminum spark, the light from which was filtered through 1.4 cm of water. The irradiated solutions were contained in a cylindrical fused quartz cell also 1.4 cm deep and placed 5.4 cm from the spark, and the concentration range 0.001 to 1.0 molar methyl alcohol was studied. Under these conditions, in the initial reactions, the gas produced is essentially hydrogen. (The

analyses are not accurate enough to exclude the possibility of the production of small amounts of hydrocarbons.) At the highest concentrations of methyl alcohol there appears to be a trace of carbon monoxide. Formaldehyde is obtained, but at the lower concentrations of methyl alcohol it amounts to only a small fraction of the hydrogen produced. The production of hydrogen and formaldehyde as functions of the methyl alcohol concentration is given in Fig. 2. The values shown are the initial amounts produced per 1000 cc of solution and per minute of irradiation. The reaction time curves remain linear over appreciable ranges in the production of these products. In Fig. 3 is shown the hydrogen production as a function of the time of irradiation for 1 millimolar methyl alcohol.

An estimation of the percentage energy of the chemically active rays absorbed by the irradiated solutions was obtained by interposing, between the light source and the reaction vessel, a similar vessel filled with solutions of methyl alcohol and determining the resulting decrease in the hydrogen produced. These measurements were carried out with 1 millimolar and with 1 molar methyl alcohol in the reaction vessel. The values obtained for the absorption at the lower concentrations of methyl alcohol are not greatly different whether the light intensity is recorded by the effect on 1 millimolar or on 1 molar methyl alcohol and the absorption curve in Fig. 2 was obtained with 1 millimolar methyl

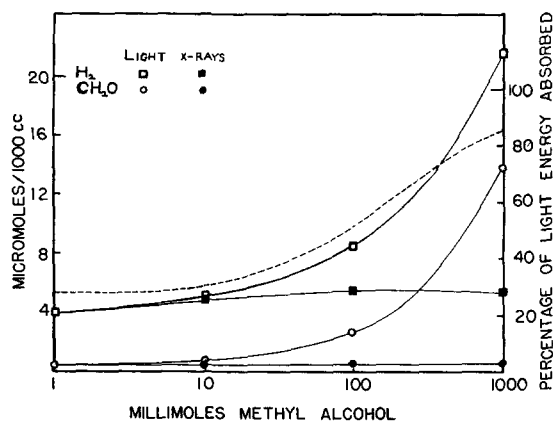


FIG. 2. The production of hydrogen and formaldehyde by the irradiation of solutions of methyl alcohol with light and x-rays. The dotted line represents percentage of effective light energy absorbed in the irradiated solution.

¹ Fulton, C. C., J. Ind. and Eng. Analyt. Ed. Chem. **3**, 199 (1931).

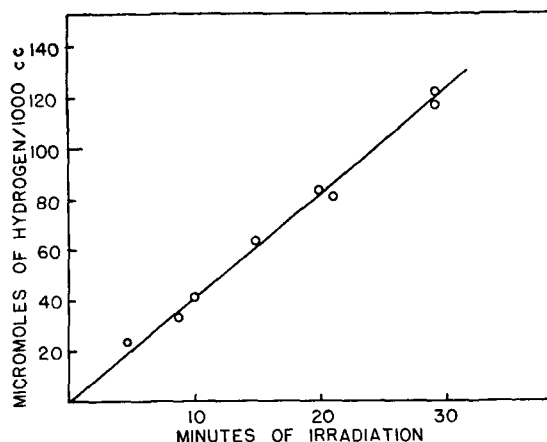


FIG. 3. Production of hydrogen as a function of time of irradiation for 1 millimolar methyl alcohol.

alcohol. The absorption is constant at the lower concentrations of methyl alcohol. Since the absorption is far from complete, it is concluded that this constant absorption represents the absorption of the solvent, while the absorption of the methyl alcohol itself at these concentrations must be comparatively small.

From these results we are led to the conclusion that the reactions occurring at the low concentrations of methyl alcohol cannot be due to the direct photoactivation of methyl alcohol, but are to be attributed to the absorption of the light by the solvent with the subsequent transfer of the absorbed energy to the methyl alcohol. This inference is based in part on the manner in which the hydrogen production varies with the methyl alcohol concentration. From the absorption measurements it follows that the absorption of the chemically active rays by the methyl alcohol itself decreases nearly as the concentration at the low values of concentration used. However, no indication of this decrease in absorbed energy is seen in the hydrogen production, which, on the contrary, at the low concentrations is nearly constant, and has a value which corresponds approximately to the absorption of the light in the water. This view as regards the reaction mechanism is confirmed by a consideration of the qualitative nature of the reactions. The chemical transformations resulting from the photoactivation of the methyl alcohol molecule with wave-lengths within the

range here used, were studied by Patat² in the vapor phase, and it was found that the initial reaction was essentially the decomposition of the methyl alcohol into hydrogen and formaldehyde. In the present irradiations, at low concentrations of methyl alcohol, the formaldehyde accounts for only a small fraction of the hydrogen produced. At around 10 millimolar methyl alcohol the hydrogen and formaldehyde production both rise rapidly and at approximately equal rates, which is consistent with the observations on methyl alcohol vapor if this rise is considered as representing the direct photodecomposition of the methyl alcohol.

It will be noticed (Fig. 2) that the hydrogen production continues to decrease as the methyl alcohol concentration decreases, even after the point has been reached where the direct photodecomposition should be negligible. A similar decrease is shown by the water-photosensitized decomposition of methyl alcohol for irradiation with x-rays.

The water-photosensitized reactions induced by x-rays have already been the subject of considerable study.^{3a-h} A much greater variety of reactions is obtained than with light, but so far as one can judge from the types of analysis used, the reactions occurring are the same in the two cases (light and x-rays) for methyl alcohol. The only gas produced by x-rays is hydrogen, and there is a production of formaldehyde which accounts for the same percentage of the hydrogen as in the case of light. In Fig. 2 are given the quantities of these two molecules obtained per unit of x-ray dosage, chosen arbitrarily so that the hydrogen production agrees with that for light at 1 millimolar methyl alcohol. The curves for light and x-rays agree at the lower concentrations, and deviate where the direct photodecomposition by light becomes appreciable. For x-rays, direct photodecomposition is negligible over the entire range of methyl alcohol concentrations used.

The following experiments were carried out to

² F. Patat, *Zeits. f. Elektrochemie* **41**, 494 (1935).

³ (a) Fricke H. and S. Morse, *Phil. Mag.* **7**, 129 (1929); (b) H. Fricke and E. R. Browncombe, *J. Am. Chem. Soc.* **55**, 2358 (1933); (c) *ibid.*, *Phys. Rev.* **44**, 240 (1933); (d) H. Fricke, *J. Chem. Phys.* **2**, 556 (1934); (e) H. Fricke and E. J. Hart, *J. Chem. Phys.* **2**, 824 (1934); (f) *ibid.* **3**, 60 (1935); (g) H. Fricke, *J. Chem. Phys.* **3**, 364 (1935); (h) H. Fricke and E. J. Hart, *J. Chem. Phys.* **3**, 596 (1935).

obtain an approximate idea of the spectral limit for the water-photosensitized decomposition of methyl alcohol. The aluminum spark was used as before, and the irradiations made with different concentrations (2.5 to 30 millimolar) of potassium sulfate added to the water in the filter cell; the hydrogen production only was recorded. Although the direct photodecomposition becomes more pronounced at higher sulfate concentrations, still at one millimolar methyl alcohol it remains negligible in comparison with the photosensitized reaction at all concentrations of potassium sulfate used. In Fig. 4 is given the hydrogen obtained at this concentration of methyl alcohol in unit time, plotted logarithmically against the sulfate concentration. The aluminum lines effective in these experiments are those at 1860A, 1934A, and 1990A, and the transmissions of these wave-lengths through the 1.4 cm of potassium sulfate are shown as calculated from the absorption coefficients given by Ley and Arends.⁴ As the sulfate concentration is increased, the rate of change of the hydrogen production with sulfate concentration continues to decrease, and at the highest sulfate concentration is smaller than that which follows from the transmission of 1934A. The limit of the water-photosensitized reaction is therefore at a wave-length longer than this value. For comparison,

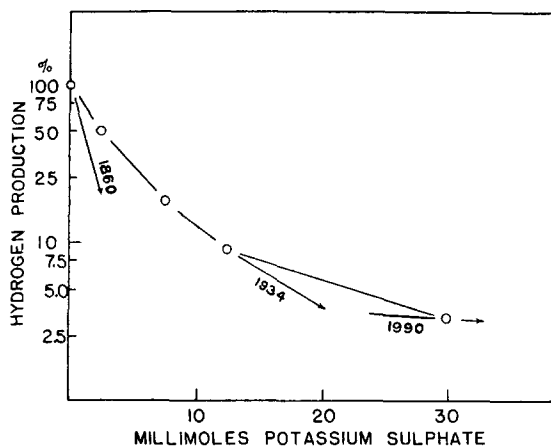


FIG. 4. Hydrogen production as a function of the concentration of potassium sulfate in filter cell. Light source: aluminum spark. The transmissions of certain of the aluminum lines are shown.

⁴ H. Ley and B. Arends, *Zeits. f. physik. Chemie* **15**, 311 (1931).

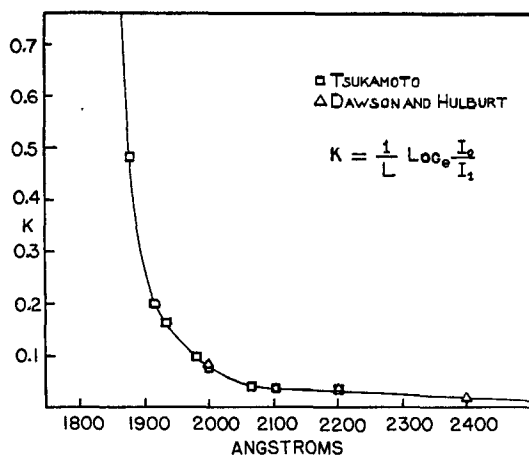


FIG. 5. Absorption spectrum of water.

in Fig. 5 is given a graph of the absorption coefficients of water in this region.^{5,6} For sulfate concentrations greater than 10 millimolar, the influence of 1860A is negligible. If we assume that the hydrogen produced at the higher sulfate concentrations is due to the aluminum lines at 1934A and 1990A, and that the same number of quanta are emitted by the spark at these two wave-lengths, a calculation shows that the quantum efficiency of the water-photosensitized reaction at 1990A is of the order of 1/10 of the quantum efficiency at 1934A. Below 1934A the quantum efficiency appears to be of the same order as that of the direct photodecomposition of the methyl alcohol. (Compare Fig. 2.) For methyl alcohol in the vapor phase, this quantum efficiency was found by Patat² to be of the order of unity.

At wave-lengths longer than shown in the graph of Fig. 5, the absorption of water decreases continuously,⁶ but over the whole spectrum remains much greater than one would expect, on theoretical grounds, from scattering. As determined by the action on methyl alcohol, the photochemical activity of water appears to stop in the neighborhood of 2000A. This does not necessarily mean that the photochemical activity of water has an absolute limit at this wave-length. Studies of the action on molecules other than methyl alcohol appear to show that

⁵ K. Tsukamoto, *Rev. d'optique* **7**, 89 (1928).

⁶ L. H. Dawson and E. O. Hulburt, *J. Opt. Soc. Am.* **24**, 175 (1934).

the photochemical activity extends still further out. Unfortunately, because of the low absorption of water at these long wave-lengths, the chemical effects are small and it is a matter of considerable difficulty to eliminate or correct for direct photodecomposition.

We have remarked that water is not decomposed under the conditions of irradiation used in the present experiments (Fig. 1). This is what one would expect, in view of the fact that no decomposition is obtained even upon irradiation with x-rays.^{3c} Several investigators⁷⁻¹¹ have claimed decomposition occurs under conditions

⁷ M. Kernbaum, *Comptes rendus* **149**, 273 (1909).

⁸ Thiele, *Zeits. f. angew. Chemie* **22**, 2472 (1909).

⁹ A. Coehn, *Ber. chem. Ges.* **43**, 880 (1910).

¹⁰ D. Bertelot and H. Gaudechon, *Comptes rendus* **150**, 1690 (1910).

¹¹ Tian, *Ann. de physique* [9] **5**, 248 (1916).

of irradiation which would appear to supply considerably less energy in the region below 2000Å, than has been used in the present experiments. In some of these experiments the decomposition of organic and other impurities (compare above) in the irradiated water may have been misinterpreted as a decomposition of the water. One other possibility should also be kept in mind: Water may be decomposed in the presence of certain impurities acting catalytically. This has been found to be the case for x-rays. We recently reported^{3b} that traces of the iodide or bromide ion were effective with x-rays in this respect. These particular ions, however, have no action in the case of light.

We wish to thank Mr. D. M. Gallagher for his assistance in this work.

Spectroscopic Studies of the Simpler Porphyrins

I. The Absorption Spectra of Porphin, *ms*-Methyl Porphin, *ms*-Ethyl Porphin, *ms*-Propyl Porphin and *ms*-Phenyl Porphin*

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(Received March 19, 1936)

The molecular absorption coefficients of porphin and four *ms*-substituted porphins have been measured throughout the visible region and the curves showing absorption coefficient as a function of wave-length are shown. All of the substances have a very strong absorption band at the violet end of the visible region. The rest of the spectrum, while similar in pattern for all of the substances, shows some characteristic differences.

INTRODUCTION

IN previous papers,^{1, 2} the fluorescence spectra and photodecomposition of the chlorophylls and some of their derivatives were discussed. It was found that the fluorescence spectra of all of the substances studied showed a similar pattern. Because of this, it seemed desirable to make similar studies on simpler chlorophyll derivatives. An ideal series of substances for this

purpose is now available since Dr. Paul Rothemund,^{3, 4} at this laboratory, has succeeded in synthesizing porphins from substances of aldehydic function and pyrrole. The formula for porphin, which is formed from pyrrole and formaldehyde, is shown in Fig. 1. This substance is of considerable interest, as it is the simplest form of the ring system of the two biologically important pigments, haemin and chlorophyll. It is apparent from Fig. 1 that two isomeric forms of this substance are possible, one with the

* This work was done with the experimental cooperation of Mr. Alex Horvath on a special scholarship arrangement.

¹ V. M. Albers and H. V. Knorr, *Cold Spring Harbor Symposia on Quantitative Biology* **3**, 87-97 (1935).

² Reference 1, pp. 98-107.

³ Paul Rothemund, *J. Am. Chem. Soc.* **57**, 2010 (1935).

⁴ Paul Rothemund, *J. Am. Chem. Soc.* **58**, 625-627 (1936).