

# The Formation of Formaldehyde by the Action of Ultraviolet Light on Carbon Dioxide and Water: An Application of the Allison MagnetoOptic Apparatus

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# The Formation of Formaldehyde by the Action of Ultraviolet Light on Carbon Dioxide and Water: An Application of the Allison Magneto-Optic Apparatus

Since the Allison<sup>1</sup> magneto-optic apparatus gives readings specific for each compound in solution, regardless of others that may be present, and since it will detect concentrations as low as 3 or 4 parts in 1012, it should prove to be a powerful research tool in dealing with many problems in chemistry, physics, and biology. We have recently used this apparatus for the detection and quantitative determination of formaldehyde formed by the action of ultraviolet light on carbon dioxide and water. Formaldehyde gives minima at scale readings 21.83 and 21.92 Allison units. These minima are not found in pure water nor in carbonated water that has not been exposed to ultraviolet light. Upon placing the carbon dioxide saturated water in a quartz flask and irradiating the solution for several hours with the light from a mercury arc lamp, we obtained the light minima characteristic of formaldehyde. We have made ultraviolet light exposures up to 25 hours and find a uniform increase in the formaldehyde concentration with an increase in irradiation period. That this reaction is accompanied with a liberation of oxygen is indicated by the fact we have been able to oxidize (simultaneously with the formaldehyde formation) certain metallic ions from a lower to a higher valence. "Blanks" were run in all experiments to insure the absence of higher valence ions at the start.

This work is being continued and a full account will be published elsewhere upon completion of the investigation.

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October 28, 1933.

<sup>1</sup> Allison and Murphy, J. Am. Chem. Soc. **52**, 3796 (1930); Allison, Ind. Eng. Chem., Anal. Edition **4**, 9 (1932); Allison, J. Chem. Ed. **10**, 71 (1933).

#### Helium Hydride Ion

The existence of helium hydride ion had been predicted on the basis of considerations regarding isoelectronic structures<sup>1</sup> and this ion has actually been found by the methods of mass-spectroscopy by Bainbridge.<sup>2</sup> Similar rare gas hydride ions have been found by Lukanow and Schütze.<sup>3</sup>

The structure of this ion has not yet been considered on the basis of wave mechanics and we thought the appropriate calculation should be made. The problem was considered in two ways:

(1) We supposed that the structure resulted from the interaction of an excited helium atom

$$\psi_1 = ae^{-\alpha r_1}; \qquad \psi_2 = (b + cr_2)e^{-\beta r_2}$$

with a proton. These  $\psi$ -functions for the two electrons of excited helium were found satisfactory when used to

calculate the total energy of the helium atom (2  $^3$ S, 19.77 e.v.) with the values of the parameters  $\alpha$  and  $\beta$ , 2 and 0.7, respectively. However, it was found that at all distances of separation of the atom and the proton repulsive forces predominated.

(2) We next assumed that the structure of helium hydride ion was made up of one helium ion and a hydrogen atom. Applying the method of Rosen<sup>4</sup> for the unsymmetrical system with  $\alpha=2$ ,  $\beta=1$  and m=n=1 which

<sup>&</sup>lt;sup>1</sup> G. Glockler, D. L. Fuller and Charles P. Roe, J. Chem-Phys. 1, 703 (1933).

<sup>&</sup>lt;sup>2</sup> K. T. Bainbridge, Phys. Rev. 44, 59 (1933).

<sup>&</sup>lt;sup>3</sup> H. Lukanow and W. Schütze, Zeits. f. Physik 82, 610 (1933).

<sup>&</sup>lt;sup>4</sup> N. Rosen, Phys. Rev. 38, 255 (1931).

implies that the  $\psi$ -functions used are purely hydrogenic for the normal state, we repeated the calculations. We evaluated all the integrals with exception of  $J_2$  (page 272 of Rosen's paper) and now we find that there is an energy minimum of 8.1 e.v. at a distance of 1.3 Bohr hydrogen radii. The effect of the omitted integral  $J_2$  will be to reduce the value of the energy.

The calculation of the integral  $J_2$  mentioned above appears very laborious and at the present time it is not possible for us to spend the necessary time in its evaluation. However, we believe from physical considerations that its inclusion in the calculation will not change the main result

of our work, i.e., that a minimum exists in the potential energy curve of helium hydride ion and that therefore wave mechanics agrees with experiment in making HeH<sup>+</sup> a stable structure.

It is a pleasure to thank Professor E. L. Hill of the Department of Physics for the advice given and the interest he has shown in these calculations.

GEORGE GLOCKLER D. L. FULLER

University of Minnesota, Minneapolis, Minnesota, November 13, 1933.