occur for low values of α and $d\alpha/dx$ where experimental errors are magnified. All of the earlier data gave constants below the upper limit set for K_2 in the present paper. The K_2's obtained from the flowing systems decrease with decreasing x, presumably because the concentration gradient is thereby increased, resulting in more diffusion and consequently greater depression of K_2 from the true value. For the same reason K_2 would be expected to decrease with the total pressure. This is not observed: it may be masked by variation in the amount of atomic hydrogen combining along the tube. It may be concluded from the foregoing discussion that measurements made in flowing systems cannot lead to information on the relative efficiencies of third bodies in effecting combination of hydrogen atoms, unless the processes of diffusion are taken into account, or unless linear rates of flow are used which are much greater than those previously reported.

Summary

1. An apparatus for measuring the rate of recombination of atomic hydrogen in a static system is described.

2. The results obtained show that, after elimination of the wall reaction, the rate of the reaction is proportional to the third power of the concentration of atomic hydrogen, and that the temperature coefficient is small.

3. A lower limit has been set for the ratio

$$\frac{\text{efficiency of atom}}{\text{efficiency of molecule}}$$

in causing combination of a pair of atoms.

4. Some properties of the afterglow accompanying the reaction have been observed and recorded.

5. The results have been discussed in relation to the tnple impact mechanism, and have been compared with those of other authors.

CAMBRIDGE, MASS. RECEIVED MAY 25, 1934

NOTES

Thin Films of Mercury on Glass

BY H. E. BENT

The familiar phenomenon of capillary depression of mercury in a glass tube and the convex surface of the liquid have led to the general conception that mercury does not adhere to glass. It is common knowledge, however, that manometers which have been carefully baked out to remove adsorbed gases exhibit a concave meniscus and that the mercury will "stick" to the top of the tube, as is frequently observed with a McLeod gage when a high vacuum has been obtained.

In order to demonstrate these phenomena before a class in physical chemistry and the accompanying negative pressures which exist in the mercury when the liquid has stuck to the top of the tube, two "U" tubes were prepared and carefully boiled out. Each tube was about seven centimeters high and had an inside diameter of about nine millimeters. The mercury was found to stick so tightly to the top of the tube that frequently a very sharp blow on the desk was necessary to cause the mercury to drop. Sometimes, however, the column would break, leaving a thin film of mercury completely covering the inside surface of the glass. The film would usually last from two to twelve seconds and then disappear with about the suddenness of a bursting soap bubble. By means of a cathetometer the height of the mercury in the other arm of the "U" was measured before and after the film broke. If this change in level is attributed entirely to liquid which has run down from the side of the tube the thickness can be calculated to be 0.008 ± 0.01 mm. After the film has broken the contact angle of the mercury and glass is about 90°. Before the film has broken the contact angle is 0°. Hence the capillary rise of the mercury before the film breaks will be 1.32 mm. Half of this, or 0.66, should be the change in height in one arm of the "U" tube. The observed change varied from 0.45 to 0.79 mm. From these data one may conclude that the film is very thin, probably less than 0.01 mm. There are too many uncontrollable variables such as minute drops remaining on the surface of the glass to permit an accurate determination of the thickness of the film by observations on the position of the meniscus.

These tubes were prepared first in October, 1932, and have retained this property for more than a year and a half. The films are much less stable now than they were a year ago, probably due to gases given off by the glass, and sometimes it is difficult now to demonstrate the thin films although the mercury still sticks readily to the top of the tube.

Apparently mercury adheres to clean glass much more than is ordinarily supposed, the phenomenon being difficult to demonstrate on account of the high surface tension of mercury.

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The Photochemical Polymerization of Acetylene

BY S. C. LIND AND ROBERT LIVINGSTON

Until recently it has been assumed that the only product formed when acetylene is radiated with ultraviolet light is a solid polymer.[1] That benzene is formed, under some conditions, has been reported by Kato,[2] and has been confirmed by Kemula and Mrazek[3] and by Livingston and Schiflett.[4] Kemula and Mrazek also detected traces of other aromatic hydrocarbons. In none of these experiments is there any evidence that benzene can be formed in chemically detectable quantities when acetylene is irradiated at temperatures below 270°.

The formation of appreciable quantities of saturated and ethylenic hydrocarbons has also been reported by Kemula and Mrazek.[3] In one experiment (Table I, reference 3) 17.7% of the acetylene originally present was converted to "cuprene," and 0.64 and 0.71% to "ethylene" and to "ethane," respectively. In a second experiment, the percentages were, respectively, 7.9, 0.05, and 0.27%.[5] Lind and Livingston[1d] in their determination of the quantum yield of this reaction assumed that no condensable gases were formed, and obtained a value of 9.2. If the assumption is made that the same relative amounts of ethylene and ethane were formed in their experiments as have been reported by Kemula and Mrazek,[6] the value of the quantum yield, based upon the disappearance of acetylene, must be increased to 9.7. The difference is not great enough to necessitate any revision of their conclusions.

The difficulty of collecting a reasonable quantity of the photochemical polymer has prevented the determination of its empirical formula by direct analysis. The gas analysis of Kemula and Mrazek[3] makes possible the computation of the empirical formula of their solid product. Their first experiment (Table I, reference 3) leads to the formula $(C_2H_{1.81})_n$ and their second to $(C_2H_{1.86})_n$. These values are consistent with formulas in the range $(C_{10}H_9)_n$ to $(C_{15}H_{14})_n$.

The formula $C_{10}H_9$ lends some support to the following mechanism.

$$C_2H_2 + h\nu \longrightarrow C_2H_2^* \longrightarrow C_2H + H \tag{1}$$
$$C_2H + C_2H_2 \longrightarrow C_4H_3 \tag{2}$$
$$C_4H_3 + C_2H_2 \longrightarrow C_6H_5\text{, etc.} \tag{3}$$
$$C_nH_{n-1} + C_mH_{m-1} \longrightarrow \text{solid} \tag{4}$$

Equation 1 represents either the dissociation of an activated molecule upon collision, or (less likely) a predissociation process.[7] Equation 2 represents the addition of an acetylene molecule to the C_2H radical, which may involve a three-body collision. The radical then adds more acetylene molecules, by a series of direct additions, until it is removed by combination with another radical (equation 4). On the average the sum of the values of m and n is 20, which corresponds to a quantum yield of 10 and to an empirical formula of $C_{10}H_9$. It is quite probable that the product may undergo further slow rearrangements. The formation of benzene and similar compounds can be accounted for by side reactions, such as

$$C_8H_7 \longrightarrow C_6H_6 + C_2H \tag{5}$$
$$C_6H_5 + H \longrightarrow C_6H_6 \tag{6}$$

The absence of hydrogen and the relative amounts of ethylene and ethane, observed in the reaction mixture, may be explained if it is assumed that the addition reaction between a hydrogen atom and acetylene is quite probable but does not occur as readily as the addition reaction between

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(1) (a) Berthelot and Gaudechon, *Compt. rend.*, **150**, 1169 (1910); (b) Bates and Taylor, THIS JOURNAL, **49**, 2438 (1927); (c) Reinike, *Z. angew. Chem.*, **41**, 1144 (1928); (d) Lind and Livingston, THIS JOURNAL, **54**, 94 (1932).

(2) Kato, *Bull. Inst. Phys. Chem. Research* (Tokyo), **10**, 343 (1931).

(3) Kemula and Mrazek, *Z. physik. Chem.*, **B23**, 358 (1933).

(4) Livingston and Schiflett, *J. Phys. Chem.*, **38**, 377 (1934).

(5) These percentages are based upon values of 48.4 and 358.2 mm. for the final total pressures of the first and second reactions, respectively. These values were kindly furnished by Professor W. Kemula, in a private communication.

(6) This assumption while a probable one is by no means necessarily true. The pressure ranges and the wave lengths of the absorbed light were similar in the two sets of experiments, but the maximum temperature reached in the experiments of Kemula and Mrazek was 50° higher than that in the experiments by Lind and Livingston (private communication).

(7) See Herzberg, *Trans. Faraday Soc.*, **27**, 378 (1931). Note, however, that light of λ 1880 Å. was not available under the conditions of the photochemical experiments. For a different opinion see Norrish, *Trans. Faraday Soc.*, **30**, 103 (1934).