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 triple 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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RECEIVED APRIL 9, 1934

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 $(C_{16}H_{14})_n$.

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

$$C_2H_2 + h\nu \longrightarrow C_2H_2^* \longrightarrow C_2H + H \qquad (1)$$

$$C_2H + C_2H_2 \longrightarrow C_4H_3 \qquad (2)$$

$$C_4H_3 + C_2H_2 \longrightarrow C_6H_5\text{, etc.} \qquad (3)$$

$$C_nH_{n-1} + C_mH_{m-1} \longrightarrow \text{solid} \qquad (4)$$

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

$$C_8H_7 \longrightarrow C_6H_6 + C_2H \qquad (5)$$

$$C_6H_5 + H \longrightarrow C_6H_6 \qquad (6)$$

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).

ethylene and a hydrogen atom. However, this assumption does not appear to be in agreement with results of Bates and Taylor[1b] on the mercury-sensitized reaction in the presence of hydrogen, or the results of von Wartenberg and Schultze with Wood's hydrogen.[8]

[8] Von Wartenberg and Schultze, *Z. physik. Chem.*, **B2**, 1 (1929).

MINNEAPOLIS, MINN.
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Blue Colored Water Solutions of the Alkali Metals

BY HENRY J. WOLTHORN AND W. CONARD FERNELIUS

Numerous investigators have observed that the alkali and alkaline-earth metals dissolve in liquid ammonia, the alkyl amines[1] and the fused alkali amides[2] to give solutions of an intense blue color. Kraus has clearly demonstrated that the solutions in ammonia contain the ordinary metal cations and ammoniated electrons. Franklin[3] has long thought that the alkali metals would also give similarly colored solutions in water were it not for the fact that the metals react extremely rapidly with this solvent. A few years ago it was demonstrated that sodium dissolves in molten sodium hydroxide (a derivative of water) to give a blue solution.[2] More recently evidence has been obtained in this Laboratory which indicates that the alkali metals are capable of forming very unstable blue solutions in water. A brief résumé of this evidence follows.

By confining potassium in a short length of 6 mm. glass tubing[4] so that the metal is held at the bottom of a beaker of water and the reaction takes place in a confined space, there appear near the metal at irregular intervals transient blue colored patches of about the same intensity of color as that of the alkali metals in other solvents. When lithium is firmly packed into a piece of glass tubing of small diameter and brought into contact with water, a blue line at the reacting interface is frequently visible. Although sodium similarly confined shows no blue coloration, some such coloration is noticed when bits of the metal adhere to the side of a beaker above the water level so that there is a limited amount of water available for reaction. No blue color is obtained by rubbing sodium or potassium on ice. Calcium shows no colorations during its dissolution in water. Potassium gives infrequent and very small colored regions during its reaction with methyl alcohol but gives none with ethyl alcohol. Lithium and sodium give no such coloration with methyl alcohol.

While these observations are not entirely conclusive it is felt that they do indicate that the alkali metals form unstable blue colored solutions in water. The realization that metals are *physically* soluble in water greatly conditions the point of view which one is to adopt toward such processes as reduction by sodium amalgam and solution of metals in acids.[5]

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[1] For bibliography and review see C. A. Kraus, *J. Franklin Inst.*, **212**, 537–62 (1931); W. C. Johnson and W. C. Fernelius, *J. Chem. Ed.*, **6**, 20–35 (1929); W. C. Johnson and A. W. Meyer, *Chem. Reviews*, **8**, 273–301 (1931).

[2] For bibliography see W. C. Fernelius and F. W. Bergstrom, *J. Phys. Chem.*, **35**, 746 fn. (1931).

[3] E. C. Franklin, private communication.

[4] For method of filling these tubes see G. S. Bohart, *J. Phys. Chem.*, **19**, 539 fn. (1915); W. C. Fernelius and I. Schurman, *J. Chem. Ed.*, **6**, 1765-6 (1929).

[5] See for example J. N. Brönsted, THIS JOURNAL, **53**, 3626 fn. (1931).

THE OHIO STATE UNIVERSITY
COLUMBUS, OHIO
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A Note on the Stereochemistry of Four Covalent Palladium, Platinum and Nickel Compounds

BY F. P. DWYER AND D. P. MELLOR

The resolution of four covalent palladium,[1] platinum,[2] and nickel[3] compounds into optically active antipodes, and the separation of *cis-trans* isomers of the type [Pt X_2Y_2], where X = NH_3, $(C_2H_5)_2S$, and Y = Cl, Br, . . ., lead to the conclusion that either (a) planar and tetrahedral configurations of the bonds about the central metal atoms are possible in different complexes, or (b) that the disposition of the bonds is in all cases a pyramidal one, a configuration which would account for both types of isomerism. To establish convincing experimental evidence for (b) it must be shown that a given four covalent complex containing two unsymmetrical chelate groups can exist in *cis* and *trans* forms, the latter only of which is resolvable into optical antipodes. While no completely satisfactory evidence along these lines is yet available, the indications are sufficient to warrant further search. For example, Drew and Head[4] have separated *cis-trans* isomers of bisisobutylenediamine platinous chloride; on the other hand, Reihlen and Hühn[2] have obtained incomplete evidence of optical activity in the cation of

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[1] Rosenheim and Gerb, *Z. anorg. Chem.*, **210**, 289 (1933).

[2] Reihlen and Hühn, *Ann.*, **489**, 42 (1931).

[3] Reihlen and Hühn, *ibid.*, **499**, 144 (1932).

[4] Drew and Head, *J. Chem. Soc.*, 221 (1934); *Nature*, **132**, 210 (1933).

this compound. The observed molecular rotation of the cation was very small, and only one form was obtained.

Additional evidence is afforded by the structure reported for pentlandite,[5] (Ni, Fe)S, which places four S atoms about each Ni atom at the corners of a flat pyramid.

In an attempt to test the possibility of a pyramidal configuration for quadrivalent palladium, we have isolated *cis* and *trans* forms of palladium bisantibenzylmethyldioxime. One form is a pale lemon-yellow color with a melting point of 175°, and the other a deeper yellow with a melting point of 207°. Separation of the isomers was effected by fractional crystallization from benzene-petroleum ether solution. The former isomer is readily changed into the latter by boiling in xylene solution for a few minutes, or allowing the benzene solution to stand for a few days. While sodium salts of both forms of palladium bisantibenzylmethyldioxime may be easily prepared, all efforts to obtain brucine, strychnine, and cinchonine salts, and hence all attempts at resolution, have failed. Several more suitable substances suggest themslves: (a) a dioxime containing a salt-forming group, *viz.*, *p*-carboxybenzylmethyldioxime, (b) benzoylpyruvic acid. The latter readily coordinates with palladium and several fairly stable salts of palladobenzoylpyruvic acid have been prepared. Further details regarding the compounds of palladium with benzylmethyldioxime will be published shortly.

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[5] Alsen, "Strukturbericht," Ewald and Hermann (1913-1928), p. 133.

[CONTRIBUTION FROM SOCONY-VACUUM CORPORATION GENERAL LABORATORIES, RESEARCH AND DEVELOPMENT DIVISION, PAULSBORO, NEW JERSEY]

A Contribution to the Chemistry of Cyclopentadiene. I. The Peroxide Effect[1]

BY GEO. R. SCHULTZE[2]

At the beginning of our investigations upon cyclopentadiene and its dimer, difficulties were found in determining the amount of unsaturation by the ordinary methods of bromination. Staudinger and Rheiner[3] have reported that only one double bond is acted upon when cyclopentadiene is brominated under analytical conditions, while the second one is attacked very slowly. However, in no case were values found of 50% which would correspond to the saturation of one double bond. Results between 60 and 90% were obtained for the monomer, and between 105 and 130% for the dimer.

Influence of Air.—The most important result of the present investigation has been the interesting fact that the addition of bromine is affected by the peroxide content of the material. No quantitative results are found whenever the experimental conditions are such as to permit peroxide formation previous to bromination.

The influence of oxygen upon the halogenation of unsaturates has been known for some time. H. Ingle[4] has pointed out the possibility of autoxidation as one of the reasons for incorrect results, but no application of his suggestion apparently has been made. Verhoogen[5] found a variation in the rate of bromination for different gases in contact with the solution. H. S. Davis and co-workers[6] have reported similar effects when acetylenes are titrated with bromine. Geo. R. Schultze[7] has shown that even a bromine-sensitized oxidation of unsaturated hydrocarbons may complicate the quantitative analysis. M. S. Kharasch and co-workers[8] recently have published two papers on the addition of hydrogen bromide to unsaturated compounds which emphasize the fundamental importance of peroxide formation.

After proper precautions were taken to exclude the influence of oxygen, the bromine water titration worked satisfactorily. However, the disturbing influences which caused variations for the results obtained with bromide-bromate according to the method of H. S. Davis[6] were not wholly

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[1] This work was presented at the Washington, D. C., meeting of the American Chemical Society, March, 1933.

[2] Present Address: Phys. Chem. Inst. Bunsenstr. 1, Berlin, Germany.

[3] Staudinger and Rheiner, *Helv. Chim. Acta*, **7**, 27 (1924); *cf. Ann.*, **447**, 103 (1926).

[4] Ingle, *J. Soc. Chem. Ind.*, **21**, 587 (1902); **23**, 422 (1904); *Chem. Zentr.*, I, 1401 (1902); II, 504 (1904).

[5] Verhoogen, *Bull. soc. chim. Belg.*, **34**, 434 (1925).

[6] Davis, *et al.*, *Ind. Eng. Chem.*, *Anal. Ed.*, **3**, 108 (1931).

[7] Schultze, THIS JOURNAL, **53**, 3561 (1931); *Z. angew. Chem.*, **45**, 574 (1932).

[8] Kharasch *et al.*, THIS JOURNAL, **55**, 2468 and 2531 (1933).