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.

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

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

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

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

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]

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

MINNEAPOLIS, MINN. RECEIVED MAY 7, 1934

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).