

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).
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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 amines¹ and the fused alkali amides² 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. Franklin⁸ 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 tubing⁴ 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

(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).

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

(5) See for example J. N. Brønsted, *This Journal*, **53**, 3626 fn. (1931).

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A Note on the Stereochemistry of Four Covalent Palladium, Platinum and Nickel Compounds

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The resolution of four covalent palladium,¹ platinum,² and nickel³ compounds into optically active antipodes, and the separation of *cis-trans* isomers of the type $[\text{Pt X}_2\text{Y}_2]$, where X = NH_3 , $(\text{C}_2\text{H}_5)_2\text{S}$, 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 Head⁴ have separated *cis-trans* isomers of bisisobutylenediamine platinumous chloride; on the other hand, Reihlen and Hühn² have obtained incomplete evidence of optical activity in the cation of

(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)₅S₈, 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

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

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

A Contribution to the Chemistry of Cyclopentadiene. I. The Peroxide Effect¹

BY GEO. R. SCHULTZE²

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 Rheiner³ 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.

(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).

The influence of oxygen upon the halogenation of unsaturates has been known for some time. H. Ingle⁴ 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. Verhoogen⁵ found a variation in the rate of bromination for different gases in contact with the solution. H. S. Davis and co-workers⁶ have reported similar effects when acetylenes are titrated with bromine. Geo. R. Schultze⁷ has shown that even a bromine-sensitized oxidation of unsaturated hydrocarbons may complicate the quantitative analysis. M. S. Kharasch and co-workers⁸ 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. Davis⁶ were not wholly

(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).