4. Antibodies are not soluble in ether.

5. Antibodies are not precipitated nor affected by a short exposure to 30% sodium chloride solution.

6. Antibodies are not injured by certain dil. alkalies or acids.

7. Antibodies are not affected by temperature up to 60°. Higher temperatures progressively destroy or alter their nature.

We may state, therefore, that antibodies do not belong to that group of proteins usually considered under the head of serum proteins.

It is felt that in the present state of knowledge of protein chemistry the negative information such as we have obtained by indirect methods is of value in narrowing the possible field of investigation.

GLENOLDEN, PA.

[FORTY-SEVENTH CONTRIBUTION FROM THE COLOR LABORATORY OF THE BUREAU OF CHEMISTRY.]

KRYPTOCYANINES. A NEW SERIES OF PHOTOSENSITIZING DYES.

BY ELLIOT Q. ADAMS AND HERBERT L. HALLER.

Received September 23, 1920.

The alkyl halides (or other quaternary addition compounds) of lepidine of sufficient purity give, when treated with alcoholic alkalies in hot, concentrated solution, dyes of the isocyanine type.[1] When the reaction is carried on in very dilute solution, if the radical attached to the nitrogen is *iso*-propyl, or if the reaction is carried on with exclusion of air and the addition of chloroform or formaldehyde, there result dyes of a type not hitherto described, having an absorption maximum near 7000 Å, and a maximum of photosensitizing action near 7400 Å. For these dyes, prepared with the aid of chloroform or formaldehyde[2] we have adopted the name of "kryptocyanines."

The structure of these dyes has not been established, but a comparison of the 6 types of dyes of the cyanine series (see Table I and Fig. 1) suggests that the kryptocyanines and hypocyanines[2] are related to the dicyanines as the pinacyanols and cyanines, respectively, are to the isocyanines. Since the structure of both pinacyanols and dicyanines is still uncertain this does not determine the structure of the kryptocyanines, but the suggestion is made that they result from abimolecular 4,5′-condensation.

[1] E. Q. Adams and H. L. Haller, THIS JOURNAL, 42 2389-91(1920).

[2] Since we have not yet established their identity with the dyes of similar properties formed without formaldehyde, etc., we shall provisionally refer to these latter as "hypocyanines."

TABLE I.

Type of dye.	Condensation of quaternary addition compounds of	Absorption[a] maximum (approx.).	Diff.	Sensitization[a] maximum (approx.).
Isocyanine	quinaldine + quinoline quinaldine lepidine	5600 Å		5800 Å
			400	
Cyanine	lepidine + quinoline lepidine + quinaldine			
Pinacyanol	quinaldine (+formaldehyde) quinaldine + quinoline (+formaldehyde)	6000 Å		6400 Å
Dicyanine	2,4-dimethyl quinoline	6600 Å		7000 Å
			400	
Hypocyanine Kryptocyanine	lepidine lepidine (+ formaldehyde)	7000 Å		7400 Å

[a] W. F. Meggers and F. J. Stimson, *J. Opt. Soc. Am. Pub.*, 4, 91–104 (1920); P. W. Merrill, *Astron. Soc. Pac.*, **32**, (185) frontispiece and p. 69.

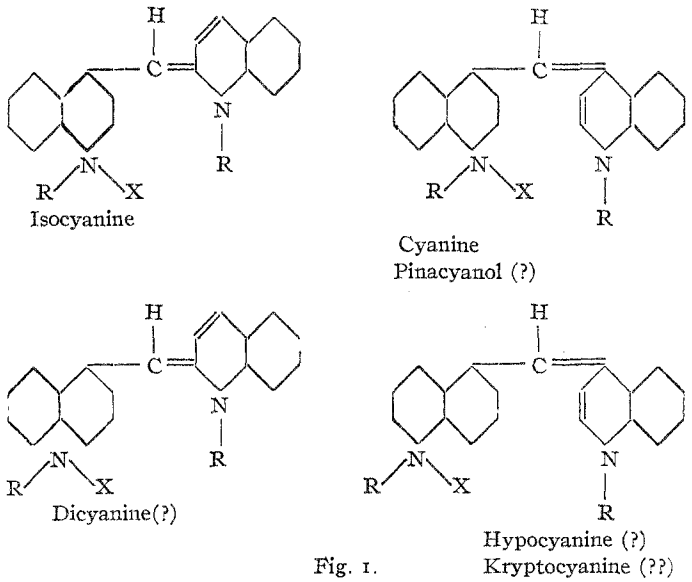

Fig. 1.

Preparation of Kryptocyanine from Lepidine Ethiodide and Formaldehyde (K III).—A solution of 5.98 g. of lepidine ethiodide (0.02 mol) in 100 cc. of 95% ethyl alcohol is heated to boiling under a reflux condenser in a 300-cc. round-bottom flask. After all the air in the flask has been displaced by alcohol vapor, a freshly prepared mixture of 20 cc. of 0.5 *N* sodium ethylate (0.01 mol) and one cc. of 40% formaldehyde solution is slowly added through the condenser. The addition of the alkali-formaldehyde mixture should require about 20 minutes. Boiling is continued for 10 minutes after all the formaldehyde-alkali mixture has been added, the flask stoppered while hot, and allowed to cool slowly. A slimy mass separates, which is filtered off by suction, washed with ice-cold

80% ethyl alcohol, alcohol-ether, and finally with ether alone. The yield is about 0.43 g. of a purplish-black crystalline powder. The mother liquor on standing yields a further crop of dye.

We have prepared kryptocyanines also from tolulepidine ethiodide (with formaldehyde); from lepidine methiodide (with chloroform); from tolulepidine methiodide (with formaldehyde), and from tolulepidine methnitrate (with formaldehyde). The first 2 formed crystals with a characteristic reflection pleochroism; the latter 2 resembled K III in appearance. In no case was the yield as great as with K III, and none of the other dyes equaled K III in sensitizing power.

Summary.

1. A new type of photosensitizing dye having an absorption maximum near 7000 Å and a sensitization maximum near 7400 Å is described.

2. These dyes are formed by the action of alcoholic alkali and formaldehyde (or chloroform) on the alkyl halides (or other quaternary addition compounds) of (sufficiently pure) lepidine and its homologs.

3. Dyes of the same or similar type are produced under some circumstances in the absence of formaldehyde or chloroform.

4. Tentative suggestions are made as to the structure of these dyes.

5. The name "kryptocyanine" is suggested.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE MISSOURI SCHOOL OF MINES.]

METHYL AMINES FROM METHYL ALCOHOL AND AMMONIUM CHLORIDE.[1]

BY W. D. TURNER AND A. M. HOWALD.

Received September 30, 1920.

It has been shown that ammonia can be methylated with methyl alcohol[2] by heating in an autoclave with zinc chloride as a dehydrator. The object of the present work was to determine the conditions of time; temperature, proportion of reagents, etc., best suited for the preparation of methyl amines by this reaction, and the relative importance of each factor.

Experimental Procedure.

Glass bombs were tried as a container but they failed through lack of tensile strength and through attack by the bases. We eventually found steel bombs of extra heavy 10-mm. pipe welded at one end and closed at the other with copper gasket and steel cap to be quite satisfactory. The bombs were weighed before and after charging, then after heating. In this way the loss on heating was known and this could be

[1] An abstract of a thesis submitted by A. M. Howald, in partial fulfilment of the requirements for the degree of Master of Science at the Missouri School of Mines and Metallurgy.

[2] V. Mertz and K. Gaskioroski, *Ber.*, 17, 640 (1884).