Thus the mechanism of the slow combustion of methane at relatively low temperatures may be more complex than considered previously[5].

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Quantitative Determination of Bilirubin and other Tetrapyrrols

A REAGENT, 3-methyl-2-benzothiazolon-hydrazono hydrochloride (MBTH, supplied by Aldrich Chemicals Co., Inc., Wisconsin), synthesized in 1910 has recently been introduced in quantitative photometry for the determination of aliphatic aldehydes[1], and also for aromatic amines, imino-heteroaromatic compounds, certain azodyes, carbazoles, stilbenes, Schiff bases and pyrrole derivatives[2].

Only the steps involved in the reaction between MBTH and formaldehyde have been settled[1]. First, formaldehyde condenses with MBTH, and secondly, excess MBTH is oxidized by ferric-chloride to a reactive cation which afterwards condenses with the formaldehyde–MBTH complex to a strongly coloured cationic pigment.

Because MBTH reacts with certain pyrrole derivatives, investigations have been carried out to see if this reagent forms highly chromophoric bonds also with bilirubin and other tetrapyrrols. Three different reactions between 'bilirubin' and MBTH have been studied.

(*A*) MBTH reacts with purified bilirubin to give a pigment with a broad maximum at 635 mμ and an extinction coefficient (moles/l./cm.) of 119,000 compared with 60,500 for bilirubin dissolved in chloroform read at 454 mμ, and to 81,000 for bilirubin coupled with diazotized sulphanilic acid read in a strong acid solution at the 570 mμ maximum.

(*B*) Bilirubin is split into two dipyrrols when the tetrapyrrole reacts with diazotized sulphanilic acid. Theoretically, formaldehyde is released when the second dipyrrole couples. However, the excess diazo-reagent necessary to get a complete coupling seems to interfere and formaldehyde could not be detected with MBTH in the distillate.

(*C*) The azo-pigments of bilirubin separated from the reagents by adsorption to alumina oxide react with MBTH to give pigments which have their maximum absorption at 615 mμ with extinction coefficients near 80,000 moles/l./cm.

Oxidation products of bilirubin (biliverdin, urobilin) also react with MBTH to form strongly coloured products. The fraction of oxidized bilirubin present in a solution may, consequently, be determined because bilirubin and its oxidation products react with MBTH, while only bilirubin and mesobilirubin couple with diazotized sulphanilic acid.

Procedure for reaction A. A reaction mixture containing 0·5 ml. of bilirubin in chloroform, 4 ml. of isopropyl-alcohol and 1 ml. of 0·4 per cent MBTH in water is allowed to stand for 5 min. at room temperature. The colour turns to blue-green when 1 ml.

of 1·3 per cent of ferric chloride in 0·25 N hydrochloric acid is added. After 1 hr. the mixture is read in a spectrophotometer at 635 mμ against a blank without bilirubin.

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π-Charge-Transfer Complexes of Hexamethylborazole

BORAZOLE has been described as inorganic benzene. It might be expected[1] that appropriately substituted borazoles would form complexes similar to the well-known π-molecular complexes of benzene and its derivatives[2]. Recently it has been observed[3] that mixtures of hexamethylborazole and tetracyanoethylene in chloroform show a broad featureless absorption band ($\lambda_{max} = 561$ mμ) not possessed by either component alone. It was suggested that hexamethylborazole, acting as an electron donor, forms a π-π-charge-transfer complex with the electron acceptor tetracyanoethylene. Other electron acceptors should also form such complexes with hexamethylborazole. Unfortunately complexes with hexamethylborazole are relatively weak: the association constant (K) for the tetracyanoethylene complex is 0·7 l.mole^{-1} in chloroform at 21°, compared with $K = 27\cdot6$ l.mole^{-1} for the corresponding hexamethylbenzene complex. The only other similar interaction which was reported was with the electron acceptor chloranil. In this case, instability of the complex, and the position of the charge-transfer band which overlapped a transition of chloranil itself, made the definite determination of the charge-transfer band impossible.

We have now observed a broad absorption band in mixtures of hexamethylborazole with 2,3-dicyano-p-benzoquinone in chloroform ($\lambda_{max} = 460$ mμ); similar mixtures with 2,3-dicyano-5,6-dichloro-p-benzoquinone give an absorption with $\lambda_{max} = 487$ mμ.

Several workers have demonstrated the empirical linear relationship between the ionization potential (I_p) of the donor molecules and the frequencies of the charge-transfer bands of complexes of electron donors with a given electron acceptor[4]. This result is not immediately apparent from theoretical arguments[5]. Nevertheless the relationship has been shown to give consistent values of I_p for donors from the positions of the absorption maxima of complexes with several different acceptors[6]. Application of such a relationship to a series of complexes of donors of known ionization potential with 2,3-dicyano-p-benzoquinone gives $I_p = 8\cdot6$ eV. for hexamethylborazole; similarly from corresponding complexes of 2,3-dicyano-5,6-dichloro-p-benzoquinone, $I_p = 8\cdot6$ eV. The earlier work with the tetracyanoethylene complex yielded a value of $I_p = 8\cdot5$ eV.

Although it is not claimed that this method gives accurate values of the vertical ionization potential for hexamethylborazole, the consistency of I_p interpolated from λ_{max} for these three complexes of hexamethylborazole at least suggests that the