

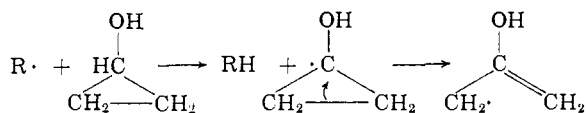
does indeed take this course, it would be without precedent.³

Secondly, the reaction is remarkably solvent dependent, occurring rapidly in carbon tetrachloride and chloroform but not in benzene, methylene chloride, cyclohexane, water or several other solvents. In the third place the reaction is not catalyzed by azobisisobutyronitrile, although several peroxides and hydroperoxides are effective. Finally the complete inhibition of the reaction by di-*t*-butyl-*p*-cresol, an inhibitor which has been demonstrated to be effective against peroxyradicals but never to be effective against alkyl radicals, makes the nature of the chain-carrying radical problematical.

The results so far at hand also permit a mechanism based on the radical catalyzed build up of some electrophilic species which is especially reactive toward cyclopropanols. Kinetic, stereochemical and tracer studies are being made.

We are indebted to the Alfred P. Sloan Foundation for support and to Professor G. A. Russell for helpful discussions. This work was supported in part by the Office of Naval Research. Also, acknowledgement is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society.

(3) It might be pointed out that abstraction of a hydrogen atom from the cyclopropane ring, if it occurred, would be easiest adjacent



to the hydroxyl group. Such abstraction would be expected to lead to acetone, rather than propionaldehyde, as a product.

(4) Ohio Oil Co. Fellow, 1960-61.

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TETRAKIS-(*p*-DIMETHYLAMINOPHENYL)-ETHYLENE DIIODIDE AND ITS FREE RADICAL BEHAVIOR

Sir:

In connection with biological studies of derivatives of tetrakis-(*p*-dimethylaminophenyl)-ethylene (I)¹ we have synthesized the dinitrate (II) and the diiodide (III) of I. Compound I was shaken with silver nitrate in water for 12 hours and afforded II, green crystals from water. *Anal.* Calcd. for C₃₄H₄₀O₆N₆: NO₃⁻, 19.74. Found: NO₃⁻, 19.62, 19.47. In the presence of excess I, the above oxidation conforms to the stoichiometric equation I + 2AgNO₃ → II + 2Ag. Addition of potassium iodide to II in water gave III, brilliant green crystals from water. *Anal.* Calcd. for C₃₄H₄₀N₄I₂·H₂O: I⁻, 32.73; H₂O, 2.33. Found: I⁻, 32.88; H₂O, 2.29. The green diiodide was heated in air at 75° to constant weight. The color changed to black and there was no detectable loss of iodine. *Anal.* Calcd. for C₃₄H₄₀N₄I₂: I, 33.50. Found: I (Carius), 33.34, 33.30. Solutions of II and III in water are purple and their optical spectra are the same.²

(1) R. Willstätter and M. Goldman, *Ber.*, **39**, 3775 (1906).

(2) The ionic character of halogen arylated ethylene complexes has been established and stable carbonium ion structures have been suggested; see R. E. Buckles and N. A. Meinhardt, *J. Am. Chem.*

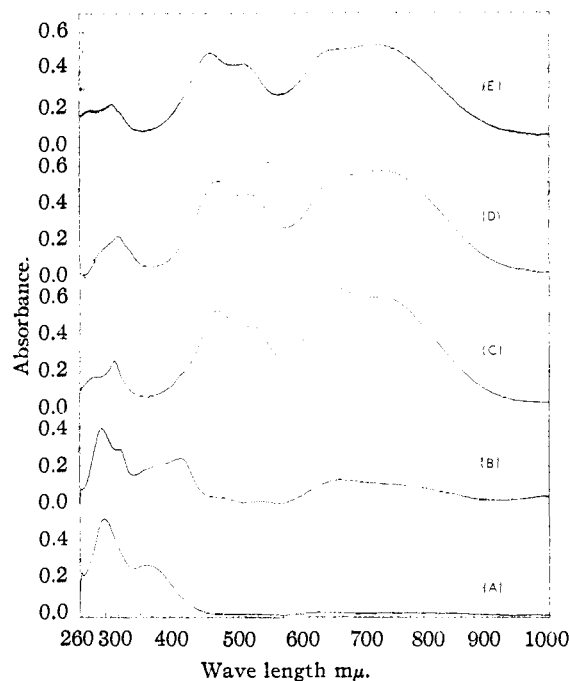
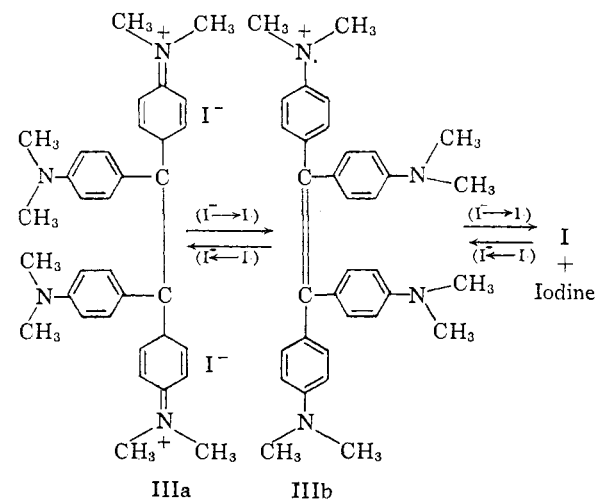


Fig. 1.—Absorption spectra: curve A, compound I, $1.22 \times 10^{-5} M$ in ethylene chloride; curve B, compound III, $1.22 \times 10^{-5} M$ in ethylene chloride; curve C, compound II, $1.12 \times 10^{-5} M$ in ethylene chloride; curve D, compound III, 1.2×10^{-5} in water; curve E, compound II, 1.12×10^{-5} in water

Water solutions of II and III show no e.p.r. signal. However, in ethylene chloride there is a marked difference between the optical and e.p.r. spectra of II and III. Solutions of II are purple and show no radical activity, whereas solutions of III are green and give an intense e.p.r. signal. This cor-

ion-pair (IIIa) \rightleftharpoons cation⁻
radical (IIIb) (Wurster salts)³ \rightleftharpoons compound I + iodine⁴



Soc., **74**, 1171 (1952), and R. Wizinger and J. Fontaine, *Ber.*, **60**, 1377 (1927). Because the dimethylamino group is capable of assuming a positive charge, II and III are envisioned as having cationic structures which are largely *p*-quinoidal.

(3) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3267 (1958).

(4) The detailed nature of the iodine moiety has been omitted from the discussion. It was realized that the equilibrium $2I + I^- \rightleftharpoons I_3^-$ might be involved and this has been pointed out by the referee.

responds to at least 20% of the material being a free radical, when checked against DPPH. Moreover, the optical and e.p.r. spectra are the same whether III is dissolved in ethylene chloride or iodine is added to I in ethylene chloride.

The marked contrast between the iodide ion, which is a good donor of electronic charge, and the nitrate ion which is not, and also the contrast between the non-polar ethylene chloride and the polar water, suggests the mechanism shown in the Chart. It is reasonable that an equilibrium favoring ionic species in polar solvents should shift in the direction favoring less charged forms in less polar solvents. This favorable effect, coupled with the favorable donor iodide ion and the favorable acceptor quinoindal dication, E_0 (polarographic pH 5 in water) + 0.075 v. vs. S.C.E., would facilitate the simple one electron transfer to give IIIb or the two electron transfer to give I. Our studies in this area are continuing and a report on the free radical behavior of the green and the black diiodide in the solid state, will be made later.

Acknowledgment.—We are very grateful to Dr. Nelson J. Leonard, who suggested a free radical study of the compounds.

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ESTIMATION OF BASE PAIRING IN NUCLEIC ACIDS FROM HYPOCHROMISM

Sir:

Hypochromism in nucleic acids occurs as a low extinction coefficient of the native form relative to denatured forms in the absorption band whose maximum is at 260 m μ .¹ The extinction coefficient

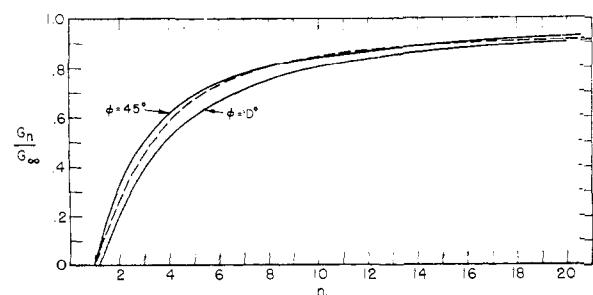


Fig. 1.—Relative hypochromism in DNA as a function sequence length. Solid curves are from Rich and Tinoco⁴ for two orientations (ϕ) of the transition dipole moment relative to the radial direction. Dashed curve represents equation (2).

has therefore been used to estimate the extent of base pairing,² which appears to be the main structural feature lost on denaturation. The calculation usually is based on the assumption that the

(1) R. Thomas, *Biochim. et Biophys. Acta*, **14**, 231 (1954).
(2) P. Doty, H. Boedtker, J. R. Fresco, R. Haselkorn and M. Litt, *Proc. Nat. Acad. Sci. U. S.*, **45**, 482 (1959).

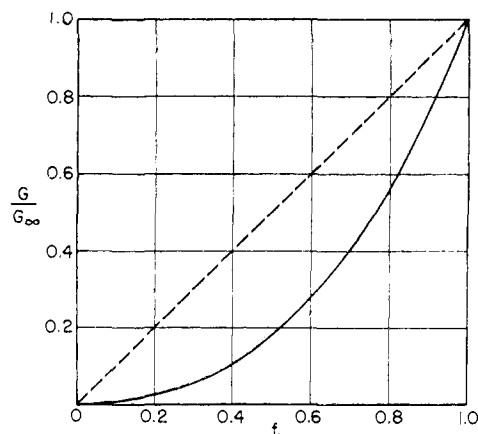


Fig. 2.—Relative hypochromism as a function of fraction of bases paired. Solid curve is from equation (3). Dashed line is for the case $G/G_\infty = f$.

hypochromism is a linear function of the number of base pairs. Since it has been shown by Tinoco³ that the observed hypochromism may be accounted for by interactions between neighboring base pairs along the nucleic acid chain, it appears that this assumption is not justified when the neighborhood of any base pair varies with the extent of pairing. Rich and Tinoco⁴ have shown on experimental and theoretical grounds that the hypochromism of a sequence of base pairs is a sensitive function of the length of the sequence, as shown in Fig. 1. From this it is concluded that the way in which the extinction coefficient (or hypochromism) varies with the degree of base pairing depends on the distribution of base pairs among sequences of various lengths. To illustrate this for a particular hypothetical case, a calculation is given for the hypochromism G as a function of the fraction f of bases paired, letting the pairing occur at random among complementary bases in two parallel strands.

The hypochromism is defined as $G = (\epsilon_0 - \epsilon)/\epsilon_0$, where ϵ_0 is the average extinction coefficient of the isolated bases and ϵ is that of the nucleic acid. For base pairs in sequences of n pairs we define $G_n = (\epsilon_0 - \epsilon_n)/\epsilon_0$. Then

$$G = \sum_{n=1}^{\infty} G_n W_n \quad (1)$$

where W_n is the weight fraction of base pairs in sequences of length n . Equation (1) implies no particular distribution of sequence lengths, but does contain the assumption that there is no interaction between neighboring sequences. For a random distribution of sequence lengths, $W_n = nf^n(1-f)^2$. An approximation to the theoretical curves of Rich and Tinoco⁴ for G_n/G_∞ is obtained in the exponential form (2)

$$G_n/G_\infty = 1 - 0.18e^{-0.0345(n-1)} - 0.82e^{-0.332(n-1)} \quad (2)$$

The dashed curve in Fig. 1 is a plot of equation (2), showing this to be an acceptable approximation. From equations (1) and (2) one then obtains expression (3) useful for numerical calculations

(3) I. Tinoco, Jr., *J. Am. Chem. Soc.*, **82**, 4785 (1960).
(4) A. Rich and I. Tinoco, Jr., *ibid.*, **82**, 6409 (1960).