Charge Transfer Spectra and Reaction Intermediates: Photochemical Nitration of Carbazoles with Tetranitromethane

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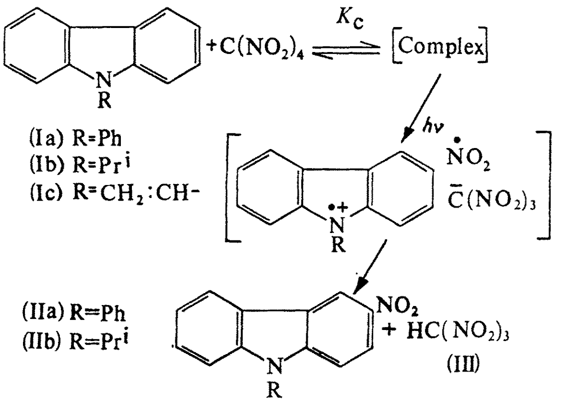
TETRANITROMETHANE (TNM) is an initiator for the cationic polymerisation of *N*-vinylcarbazole[1,2] (Ic) although the mechanism of initiation is not clear. Electron transfer to TNM results in dissociative capture[3] [yielding $\dot{N}O_2$ and $\bar{C}(NO_2)_3$], and Bruice and his co-workers[4] have confirmed this process for the oxidation of phenoxide ions by TNM.

Reactions between TNM and olefins,[5,6] however, yield products apparently arising from NO_2^+ as intermediate. Nitration of anilines,[7] phenols,[7] and azulenes[8,9] with TNM appears to involve electrophilic substitution, although Szwarc and his co-workers have shown[6] that cationic intermediates are involved in the reaction between TNM and 1,1-diphenylethylene but not, apparently, in similar reactions involving anthracene, biphenyl, or benzophenone.



For all cases in which reaction products have been isolated,[1,2,4–9] TNM gives rise to charge-transfer spectra when mixed with the other reactant, so the intermediacy of an intermolecular complex in the reaction mechanism has been assumed. We have studied the reaction of TNM with *N*-alkylcarbazoles.

Thermal interaction between 0·25M-TNM and 0·25M-*N*-ethylcarbazole (Ia) was very slow both in AcOH and CH_2Cl_2; 3-nitro-*N*-ethylcarbazole (m.p. 126—127° lit.[10] 126°) (IIa) was obtained (90%, 4 weeks, room temp.). No reaction was apparent over the same period in MeOH.

Irradiation of the reaction mixtures[11] [TNM (0·25M) and (Ia) (0·25M) (C_6H_6), 250 w, medium pressure in glass vessels, mercury lamp] gave (IIa) (>90%, *ca.* 90 min.). Slightly lower yields were obtained in MeOH or C_6H_{12}, under identical conditions. *N*-Isopropylcarbazole (Ib) gave *N*-isopropyl-3-nitrocarbazole (IIb) (m.p. 148—150°, lit.[10] 149—152°) in similar yields.

Nitroform (III) is the other main product and is readily removed by extraction into water, after which the nitrocarbazole derivatives were most conveniently extracted and purified by column chromatography on neutral alumina. Cation-radicals from *N*-alkylcarbazoles[12] readily couple in the 3-position but that from *N*-vinylcarbazole[2,13] reacts at the vinyl group. Consequently the suggested reaction sequence (Scheme) could explain most of the reported reactions of TNM (*cf.* however ref. 6).

The possible role of 'charge-transfer complexes' as reaction intermediates has been fully reviewed:[14] for most cases it is at least possible that the charge-transfer spectrum observed *does not* represent a reaction intermediate. However for photochemical reactions occurring *via* the charge-transfer excited state,[15] collisional interaction between the donor and acceptor components is a minimum requirement even though binding energies from charge-transfer forces may be very small.[16]

High yields of nitrocarbazoles were obtained only when the concentrations of carbazole and tetranitromethane were sufficient to give a concentration of 'charge-transfer complex' in excess of *ca.* 2×10^{-2} M, otherwise TNM was destroyed by photochemical side-reactions. [For the complex between TNM and (Ia) in cyclohexane, $\lambda_{max} = 410$ nm (ϵ_{max} 10^2 M^{-1} cm.$^{-1}$, and $K_c = 7$ M^{-1})]. A marked effect of concentration on the (thermal) nitration of guaiazulene by TNM has been observed.[9]

The reaction may have synthetic value for other reactive aromatic systems, and for polymers containing aromatic side groups [*e.g.* poly(*N*-vinylcarbazole)].

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