Electron-radiolysis of Diphenylpicrylhydrazyl in Tetranitromethane. Evidence for a Free Radical Nitration Process

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Products and yields for the electron radiolytical decomposition of DPPH in tetranitro methane have been determined. Reaction occurs *via* attack of NO_2 radicals, the dinitro adduct being the main product at the lowest doses investigated.

Radical[1–4] as well as ionic mechanisms have been proposed for photolytically induced reactions between tetranitromethane (TNM) and aromatics[5]. A possible role of "charge-transfer complexes" as intermediates in the photochemical nitration of carbazole in TNM has also been assumed[6]. TNM, introduced into radiation chemistry by HENGLEIN[7] and provides a sensitive monitor for the presence of active one-electron reducing intermediates (H, HO_2, e^-_{aq}) forming the stable nitroform anion $C(NO_2)_3^-$ in their presence.

As part of a program investigating the validity of the DPPH method[11] in kinetic studies we report here further evidence supporting a free radical mechanism for the nitration of DPPH in TNM solvent. With a view to obtaining further information on reaction (1)[1]

$$e^- + C(NO_2)_4 \rightarrow C(NO_2)_4^- \rightarrow C(NO_2)_3^- + NO_2 \quad (1)$$

studies of the radiolysis of TNM in the presence of DPPH as radical scavenger were performed. In order to preserve the correspondance between this work and conventional scavenging kinetics studies all experiments were performed a concentrations characteristic of the latter method ($\cong 0.5 - 1 \cdot 0 \times 10^{-6}$ M/lt).

The product distribution obtained an irradiating deaerated DPPH solutions in TNM ($5 \cdot 1 \times 10^{-5}$ m/lt) with 10 MeV electrons to doses of $0 \cdot 6 - 12 \cdot 5 \times 10^{20}$ eV/g is shown in Table I. Such a product distribution would most probably arise via the simplified reaction scheme I.

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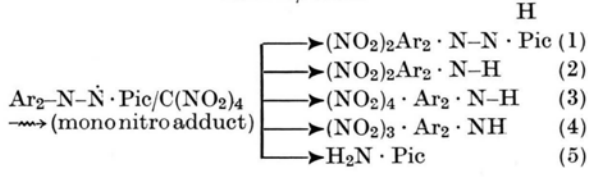
Table I. Product yields from the electron-radiolysis of deaerated TNM–DPPH solutions (DPPH = 5.1×10^{-5} M/l).

Starting Material	absorbed dose 10^{20} eV/g^{-1}	Products [% yield] (1)	(2)	(3)	(4)	(5)
TNM–DPPH	0.6	39.2	2.3	0.5	trace	–
	3.1	35.1	4.0	0.7	0.2	trace
	6.2	18.0	5.1	1.4	0.6	0.2
	9.4	10.1	6.2	3.0	1.3	0.5
	12.5	trace	7.0	4.4	2.3	0.8

Scheme I. Simplified reaction sequence for the formation of nitration products in the radiolysis of DPPH/TNM.



The formation of the dinitro adduct resulting from attack of NO_2 at the para positions of both phenyl rings is very striking. These positions are known from ESR studies[12] to be positions of high electron spin density. Thus attack by the presumably electrophilic NO_2 at these positions is not unexpected.

It has already been established that the major course of the radiolysis in the case of nitro-aromatics and nitroalkanes involves attack of NO_2 at the para positions of the DPPH phenyl rings with displacement of a hydrogen atom. Subsequent competitive scavenging of the latter and trapping of NO_2 radicals by the resulting adduct ($DPPH_2$) leads to the observed hydrazine products. The present results can be interpreted on a similar basis. The fact that no nitroform was detected indicates that $H^\cdot$ scavenging by DPPH is much more effective than by TNM (or TNM^-). The product distribution displays a marked dependance on dose in which only the dinitrated hydrazine (1) predominates at the lowest dose investigated (0.6×10^{20} eV/g). At higher doses lower molecular weight products (presumably secondary) arise *via* cleavage of the hydrazine N–N bond. In contrast to previous investigations[8–9] it is interesting to note that no hydrazine ($DPPH_2$) and no mono-nitrated hydrazine ($DPPH_2$–NO_2) were detected on conducting the present experiments to similar doses. The formation of the diphenylamines (3) and (4) can probably be accounted for by secondary radiolysis of 2.

It is interesting to point out that in the only other product study[13] of radical reactions with DPPH of which the authors are aware, several compounds were postulated (though not isolated) for which the nitro analogues were not found in this work; (2,4,6-trinitrophenol, 1,2,4,6-tetranitrobenzene, *p*-hydroxydiphenylamine).

In view of these results it is essential to emphasise that care must be exercised in designing and interpreting kinetic experiments based on the assumption of the formation of a 1:1 adduct between radical intermediate and DPPH. Particular attention must be given to conducting experiments to minimal turnovers such that competition for reactive intermediate between the mono adduct and DPPH itself is effectively inoperative. Failure to observe this condition will obviously result in incorrect stoichimetry and apparently low rates of disappearance of DPPH. While these remarks are, for the moment, valid only for the particular case of the NO_2/DPPH system it would seem advisable, as already pointed out elsewhere[7], to test any system investigated for this contingency.

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