A Re-interpretation of the Photo-induced Free Radicals produced from Nitrobenzenes in Tetrahydrofuran

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THE original postulate of Ward,[1] that the e.s.r. signal observed on ultraviolet photolysis of nitrobenzene in tetrahydrofuran is due to the monohydronitrobenzene radical $PhNO_2H\cdot$, has been assumed by all subsequent workers.[2–5] We suggest a new structure for the observed radical species (hereafter referred to as X•) in the light of further evidence.

Asmus[6] has reported that the decay of the monohydronitrobenzene radical in aqueous acid obeys second-order kinetics and is rapid ($k_2 = 6 \times 10^8\ \text{M}^{-1}\ \text{sec.}^{-1}$). This may be contrasted with the stability of X•. Our detailed kinetic studies on substituted nitrobenzenes have shown that X• decays slowly in the dark, the decay obeying first-order kinetics ($k_1 = 0{\cdot}1$—$0{\cdot}3\ \text{sec.}^{-1}$) in both aqueous and nonaqueous media.

Ultraviolet photolysis of nitrobenzene in di-isopropyl ether yields a species X• which does not show in its e.s.r. spectrum the small doublet hyperfine splitting (h.f.s.) obtained when tetrahydrofuran is the solvent. Analogous results have been obtained with chlorine-substituted nitrobenzenes (see Table).

The magnitude of the additional doublet h.f.s. (0·4 G) seen in tetrahydrofuran is very small for a proton attached to an atom adjacent to a major site of unpaired spin density. An h.f.s. of *ca.* 2 G is expected by analogy with reported h.f.s. in alcohol and hydroxybenzene radicals.[7]

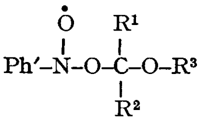
TABLE

Radicals X· in tetrahydrofuran: e.s.r. hyperfine splittings (in gauss)

Parent compound	a_N	a_2	a_3	a_4	a_5	a_6	Others	ΔH
Nitrobenzene	15·06	3·12	1·06	3·12	1·06	3·12	0·39[a]	0·15
2-Chloro-1-nitrobenzene[b]	17·5	—	0·9	2·0	0·9	2·0	—	—
3-Chloro-1-nitrobenzene	14·15	3·04	—	3·04	1·06	3·04	—	0·55
4-Chloro-1-nitrobenzene	14·51	3·14	1·12	0·28[c]	1·12	3·14	0·35[a]	0·20
2,4-Dichloro-1-nitrobenzene	17·6	—	1·10	—	1·10	2·45	—	0·6
2,3,4-Trichloro-1-nitrobenzene	18·27	—	—	—	1·12	2·0	—	0·6
2,4,6-Trichloro-1-nitrobenzene	24·3	—	0·45	—	0·45	—	0·06[a]	0·5
2,3,5,6-Tetrachloro-1-nitrobenzene	25·0	—	—	—	—	—	—	1·0

[a] Doublet h.f.s. [b] Recorded at −20°, all others recorded at room temperature. [c] Chlorine quartet h.f.s. ΔH = peak to peak linewidth of first derivative curve.

The above evidence may be rationalised if X· has the structure



$$Ph'\!-\!\overset{\overset{\bullet}{O}}{\overset{|}{N}}\!-\!O\!-\!\underset{\underset{R^2}{|}}{\overset{\overset{R^1}{|}}{C}}\!-\!O\!-\!R^3$$

(where Ph′ = substituted phenyl, R = alkyl or H) in a solvent $R^1R^2HCOR^3$. The radical is the adduct of nitrobenzene and a solvent radical. The latter is formed in a hydrogen abstraction reaction of electronically excited nitrobenzene with the solvent.[1,2] The following scheme is formulated:

$$Ph'NO_2 \xrightarrow{h\nu} Ph'NO_2^{*} \qquad (1)$$

$$Ph'NO_2^{*} + R^1R^2HCOR^3 \rightarrow Ph'NO_2H\cdot + R^1R^2\underset{\bullet}{C}OR^3 \qquad (2)$$

$$2\,Ph'NO_2H\cdot \xrightarrow{\text{rapid}} \text{products} \qquad (3)$$

$$R^1R^2\underset{\bullet}{C}OR^3 + Ph'NO_2 \rightarrow X\cdot \qquad (4)$$

It can be shown, from reported data on analogous reactions,[6] that reaction (4) is the major reaction path of the ether radical under the conditions prevailing during the photolysis. The stationary concentrations of radical X· under ultraviolet illumination have been measured in different solvents and the correlations accord with solvent radical structure–reactivity concepts advanced by Norman.[8]

An ion-pair structure $PhNO_2^{\cdot-}\ {}^{+}CR^1R^2OR^3$ is possible and has been postulated[9] to account for observations on nitrobenzenes in aqueous flow systems. The structure is dubious for X· in view of (a) the large differences between the nitrogen h.f.s. of X· and the corresponding nitro-anion radicals (b) the decay of X· is known to be insensitive to solvent polarity and acidity.

Values of the hyperfine splittings of the photo-induced radicals X· which we have obtained are given in the Table.

The nitroxide structure suggested for X· is consistent with all the structural and kinetic data. We have also recorded an e.s.r. spectrum which may be tentatively assigned to the monohydronitrobenzene radical.

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