The Photoreduction of Aromatic Nitro-compounds in Solution

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EVIDENCE has come from electron spin resonance (e.s.r.) studies of photolysed aromatic nitro-compounds in solution that hydrogen abstraction from the solvent can occur to give species of the type $Ar\dot{N}O_2H$.[1–4] Proof of this for nitrobenzene photolysed in tetrahydrofuran (T.H.F.) at room temperature has come from e.s.r. work by Ward,[2] which indicates that an α-hydrogen of the solvent is transferred to the nitro-group oxygen. In this instance, at least, photolysis at wavelengths longer than the strong $\pi \rightarrow \pi^*$ absorption at 2600 Å but within the region of the much weaker overlapping band at approximately 3350 Å is effective. This weak absorption is most probably associated with an $n \rightarrow \pi^*$ transition, although the assignment has been open to considerable debate.[5] These features, together with the observation that nitrobenzene radical anions are formed in the photolysis of basic ethanolic solutions of nitrobenzene,[6] have suggested to us that aromatic nitro-compounds and ketones may behave similarly, in that the excited state involved in the hydrogen abstraction is a triplet. If so, quenching is expected by a suitable acceptor and there is the possibility of detecting acceptor triplets by energy transfer from the excited donor. Perfluoronaphthalene has been selected as acceptor as it has a first excited singlet level at a higher energy that of the $n \rightarrow \pi^*$ transition of nitrobenzene and a triplet level lower than that of the nitro-compound (nitrobenzene 60 kcal./mole; perfluoronaphthalene 56·6 kcal./mole). Radiation from a medium pressure mercury lamp was cut off at wavelengths shorter than 3300 Å by a thick block of glass so that excitation was confined to the $n \rightarrow \pi^*$ band. The thoroughly de-gassed T.H.F. solutions examined were: (A), 10^{-2} M-nitrobenzene; (B), 10^{-2}

M-nitrobenzene and 10^{-1} M-perfluoronaphthalene; and (C), 10^{-1} M-perfluoronaphthalene. *In situ* irradiation at room temperature of solution A gave a well-resolved e.s.r. spectrum of the species $Ph\dot{N}O_2H$. No e.s.r. spectrum could be detected from solution B, which meant that at least a fifty-fold reduction in concentration of the radical had occurred in the presence of perfluoronaphthalene. Photolysis at -160°C of the frozen T.H.F. solution A gave an e.s.r. absorption with a g-value close to 2 and a total spread of approximately 70 gauss. This was ascribed to the species $Ph\dot{N}O_2H$. No $\Delta m_S = 2$ transition could be detected. Photolysis of solution B at this temperature did not show the above feature but gave a much broader resonance (total spread approximately 300 gauss) and, in addition, showed a clear $\Delta m_S = 2$ absorption. This behaviour was consistent with the population of triplet perfluoronaphthalene by triplet–triplet energy transfer from the excited nitrobenzene. Solution C gave no resonance on photolysis, and this behaved as expected for a situation where the singlet–singlet transition of perfluoronaphthalene was not excited. These observations parallel closely the e.s.r. studies of photolysed benzophenone in ethanol with naphthalene used as a quencher,[7] and suggest that a mechanism of the type established by the detailed work of Porter and Wilkinson[8] for the primary stages of the photochemical decomposition of this ketone is probable also for nitrobenzene.

Radicals of the type $Ar\dot{N}O_2H$ have been obtained from the photolysis of a number of fluoroaromatic nitro-compounds in T.H.F.,[3,4] but in other instances clear evidence of the formation of nitroxides through interaction with the solvent has been obtained.

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