Photo-Chemically Induced Dynamic Nuclear Polarization Study of Reversible Hydrogen Transfer between Dyes and Phenolic Oxidation Inhibitors

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Summary A CIDNP study indicates that the primary step in the dye-sensitized photo-oxidation of phenols involves a largely reversible hydrogen transfer from the phenol hydroxy-group to the keto-oxygen of the triplet dye molecule.

WE report on the results of a photo-CIDNP study of the primary steps of the photo-oxidation of phenols (ArOH) in the presence of dyes (D). This photo-oxidation has been recently studied by several groups,[1,2] its mechanism being probed by flash photolysis[3] and e.s.r.[4] techniques.

Irradiation of CD_3OD solutions of phenols, including methyl phenols such as 2,6-di-t-butyl-4-methylphenol (Ia), *p*-cresol (Ib), and α-tocopherol (Ic), in the presence of rose bengal (II), results in strong polarization of the ring and methyl protons of the phenol molecule. Strong enhancement (A) of the proton signals was shown by the 4-methyl protons in (Ia) and (Ib), by the *ortho*-methyl protons in (Ic), and by the *meta*-protons in (Ia). Emission (E) was observed in the *ortho*-protons of (Ib). Similar results were obtained in CD_3OD–D_2O, CD_3OD–CS_2, or CD_3CN solutions. Other xanthene dyes produce the same effects. The largest nuclear polarizations are observed in the methyl protons of 4-methyl-phenols [apparent maximal enhancement of *ca.* 400 in (Ia)], though weaker CIDNP effects are seen in the ring protons of other phenols. The present systems [*e.g.*, (II) + (Ia), (Ib), or (Ic)] were found to be quite stable at the light levels required for observing CIDNP, in agreement with the continuous irradiation results of Zwicker and Grossweiner.[3] Oxygen has no noticeable effects, similar results being obtained in thoroughly outgassed and in oxygen-saturated solutions. This last finding indicates that in case of sensitization by xanthene dyes the process responsible for CIDNP in ArOH is the hydrogen transfer reaction from the hydroxy-group of the phenol to the keto oxygen of the triplet dye molecule ^3D, to give the phenoxyl radical $ArO^{\cdot}$ and the semi-reduced dye radical $HD^{\cdot}$. $ArO^{\cdot}$ and $HD^{\cdot}$ may then undergo the reverse hydrogen transfer [reactions (1)—(3)]. This reversible hydrogen transfer scheme has been previously suggested on the basis of the flash-photolysis results.[3] Any stable oxidation products of the phenols appear to originate from irreversible reactions of $ArO^{\cdot}$ (*e.g.* dimerization or reactions with oxygen[1–3]).

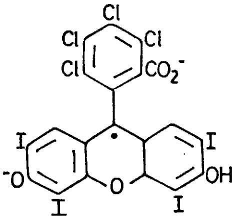
$$D \xrightarrow{h\nu} {}^3D \qquad (1)$$

$$ArOH + {}^3D \rightleftharpoons \overline{{}^3Ar\text{–}O^{\cdot} + H\text{–}D^{\cdot}} \qquad (2)$$

$$\overline{{}^3Ar\text{–}O^{\cdot} + H\text{–}D^{\cdot}} \rightarrow Ar^{*}OH + D \qquad (3)$$

CIDNP arises in this system in the triplet geminate pair GP1, $^3\overline{ArO^{\cdot} + HD^{\cdot}}$, the asterisk * indicating nuclear polarization. The *g* factor of the phenoxyl radical is 2·0052.[5]

That of HD·[6] is estimated as *ca.* 2·003, on the basis of the reported *g* factors for several triphenyl methyl radicals.[7] Thus for GPl Δg is positive. The proton hyperfine values A_i in ArO· are positive for 4-methyl protons and the *meta*-ring protons, and negative for the *ortho*- and *para*-protons.[8]



HD• [anion radical of (II)]

Thus the sign of the net effect Γ_{NE} in ArOH, obtained by Kaptein's method[9] is positive (A) for 2-, 4-, or 6-methyl protons and for *meta*-ring protons, and negative (E) for *ortho*- and *para*-ring protons, both μ and ϵ being positive.

These results are entirely consistent with the experimental observations. Zwicker and Grossweiner[3] report similar rate constants (within a factor of 2) for the reaction of triplet xanthene dyes with either phenol or the phenoxide anion, the phenoxyl radical ArO· being formed in both cases. The same polarization pattern, as in neutral solutions, was obtained in the system (Ia) + (II) in the presence of strong bases, *e.g.* OD^- or CD_3O^-. The polarization pattern observed here is probably due to reversible electron transfer rather than hydrogen transfer. In any case both hydrogen and electron transfer steps result in similar nuclear polarizations. In this system the CIDNP effect is also unaltered by the addition of CF_3CO_2H.

As shown already,[3] steps (2) and (3) account for most of the dissipated energy of the singlet-excited dye molecules. Since these steps account also for the observed polarization we conclude that the CIDNP in the present system is related to the major chemical process and not to a minor side reaction.

From the present point of view our results seem to indicate that sensitized photo-oxidation of phenols by oxygen in the presence of dyes[1] is initiated by steps (2) and (3) rather than by direct hydrogen abstraction by singlet oxygen, $ArOH + {}^1O_2 \rightarrow ArO^{\cdot} + HO_2^{\cdot}$. Quenching of the triplet state of acetophenone by phenols has been reported to lead to CIDNP,[10] the process being equivalent to steps (1)—(3) of the present work.

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