

Photochemistry of Cation Radicals in Solution: Photoinduced Electron-transfer Reactions between Alcohols and the *N,N,N',N'*-Tetraphenyl-*p*-phenylenediamine Cation Radical

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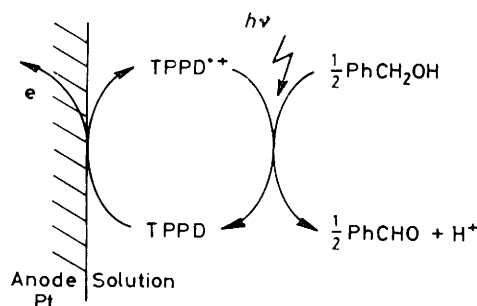
Irradiation of the *N,N,N',N'*-tetraphenyl-*p*-phenylenediamine cation radical (TPPD^{•+}) with benzyl alcohol causes its reduction to TPPD and oxidation of the alcohol into benzaldehyde; with benzhydrol and 1-phenylethanol the corresponding symmetrical ethers are formed in a photocatalytic process in which TPPD^{•+} is recycled *via* two successive electron transfers.

Previously we reported the first example of the photoinduced oxidizing properties of stable cation radicals with 1,1-diphenylethylene and some *para*-disubstituted derivatives.¹ We now report the photoinduced properties of the *N,N,N',N'*-tetraphenyl-*p*-phenylenediamine cation radical (TPPD^{•+}) in the presence of alcohols.

Controlled potential oxidation of TPPD (2 mM) in deoxygenated acetonitrile with LiClO₄ (0.1 M) or in methylene dichloride with Bu₄NClO₄ (0.1 M) at 0.5 V (*vs.* Ag/Ag⁺, 10 mM) afforded the stable cation radical TPPD^{•+}.² *i*-E curves on a rotating platinum disk electrode showed a one-electron reversible reduction wave ($E_{1/2}$ 0.24 V) and an oxidation wave ($E_{1/2}$ 0.675 V).² Upon addition of benzyl alcohol, benzhydrol, or 1-phenylethanol there was no evidence of reactivity in the dark.

Irradiation of TPPD^{•+} (λ_{max} 342, 405, and 815 nm) in the presence of benzyl alcohol (0.3 M) with a 500 W high-pressure mercury lamp at $\lambda > 360$ nm (effective at $\lambda = 366$ nm, not absorbed by the alcohol) caused the reduction wave of TPPD^{•+} to disappear. At the same time, the oxidation wave of TPPD ($E_{1/2}$ 0.24 V), followed by a complex wave and a new reduction wave ($E_{1/2} -0.2$ V) typical of the release of protons appeared. A separate experiment showed that the complex oxidation wave is characteristic of the photochemical transformation of TPPD which absorbs the 366 nm line. To avoid this, the irradiation was carried out under conditions of controlled-potential oxidation of TPPD (0.5 V). After three turnovers the values of the limiting current of the *i*-E curve indicated no change in the TPPD^{•+} concentration and the release of one proton for one electron exchanged. Quantitative h.p.l.c. of the irradiated solution showed that for two electrons exchanged, one molecule of benzaldehyde is formed. The overall process is represented in Scheme 1 and is an example of a photoinduced redox catalysis. In classical redox catalysis, an electron-transfer reagent (mediator), which may be electrochemically regenerated, initiates a redox reaction of the substrate at lower electrode potential than necessary for the direct process. In the dark, TPPD^{•+} is an inefficient mediator towards benzyl alcohol but upon irradiation a two-electron oxidation is accomplished.

In the presence of benzhydrol (90 mM) or 1-phenylethanol (135 mM), the expected photoproducts are TPPD and benzophenone or acetophenone. Surprisingly during photolysis ($\lambda > 360$ nm, no anodic oxidation of TPPD), TPPD^{•+} remained constant in concentration and quantitative h.p.l.c. showed the appearance of the corresponding unexpected symmetrical ethers (equation 1). Traces of styrene were detected in the case of 1-phenylethanol. Benzophenone and acetophenone were not formed and no release of protons occurred.



Scheme 1

The system is photocatalytic. In the case of benzhydrol, the irradiation was stopped when 16% of the alcohol remained and 82% of bis(diphenylmethyl) ether was formed corresponding to 18 turnovers calculated on the basis of the participation of one TPPD^{•+} cation radical per molecule of ether produced. In the case of 1-phenylethanol after 16 turnovers 42% of the alcohol remained and 49% of bis(1-phenylethyl) ether was formed [22.5% *meso* form, 26.5% racemic mixture]. Preparative h.p.l.c. allowed the isolation of the photoproducts for their characterisation. The photochemical two-electron oxidation of



i TPPD^{•+}; *hν*, $\lambda > 360$ nm; MeCN with LiClO₄ (0.1 M) or CH₂Cl₂ with Bu₄NClO₄ (0.1 M); R = Ph or Me

benzyl alcohol into benzaldehyde by TPPD^{•+} is reminiscent of the light-induced oxidation of primary and secondary alcohols into their corresponding carbonyl compounds by inorganic or organic salts.³⁻⁶ In particular benzyl alcohol, benzhydrol, and 1-phenylethanol in water-dimethyl sulphoxide mixtures are oxidised into benzaldehyde, benzophenone, and acetophenone respectively, by photoexcited Fe(CN)₆³⁻, Ag⁺, and Cu²⁺ ions.⁴ The mechanism has been studied for primary and secondary aliphatic alcohols.^{5,6} The rate-determining step is the formation of an alkoxy radical *via* an electron transfer from the alcohol to the excited state of the oxidant followed by a deprotonation. The alkoxy radical abstracts an α -hydrogen atom from a second alcohol molecule and yields the more stable hydroxyalkyl radical which is oxidised into the corresponding carbonyl compound. However, it has been shown during pulse radiolysis studies^{7,8} that in the presence of an oxidisable solute reduction of the alkoxy radical may compete with the hydrogen abstraction. For example *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) ($E_{1/2}^{\text{ox}}$ 0.14 V)⁹ is oxidised into TMPD^{•+} by the methoxyl,⁷ ethoxyl,⁸ and isopropoxyl¹⁰ radicals.

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When benzhydrol ($E_{1/2}^{ox}$ 1.78 V) \ddagger and 1-phenylethanol ($E_{1/2}^{ox} = 1.89$ V) \ddagger are exposed to excited TPPD $^{*+}$ a photo-induced electron-transfer process may occur leading to H $^+$, the phenylated alkoxy radical PhCH(R)O \cdot , and TPPD which react further *via* a redox reaction to give the alkoxide ion and regenerated TPPD $^{*+}$. The liberated protons participate in ether formation. Nevertheless the observation in the 525—620 nm region of a transient absorption similar to the dication TPPD $^{2+}$ absorption (λ_{max} 592 nm) upon conventional flash photolysis (μ s) of a CH $_2$ Cl $_2$ solution containing Bu $_3$ NClO $_4$ (0.5 mM) TPPD $^{*+}$ (5 μ M) and 1-phenylethanol (0.15 M) leads us to consider equally initial photochemical reduction of the alcohol 10 into its anion radical PhCH(Me)OH $^{\cdot-}$ by TPPD $^{*+}$. After the cleavage of the anion radical into PhC \dot{H} Me and OH $^-$, the oxidation of the neutral radical into its cation by TPPD $^{2+}$ regenerates TPPD $^{*+}$. Subsequent reactions of PhCH(Me) $^{\cdot+}$ yield ethers or styrene.

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\ddagger Measured by cyclic voltammetry on a platinum electrode in MeCN containing LiClO $_4$ (0.1 M) *vs.* Ag/Ag $^+$ (10 mM). Irreversible process; thus the values have no thermodynamic significance.

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