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The Role of an *o*-Quinone Methide in the Photochemistry of Duroquinone

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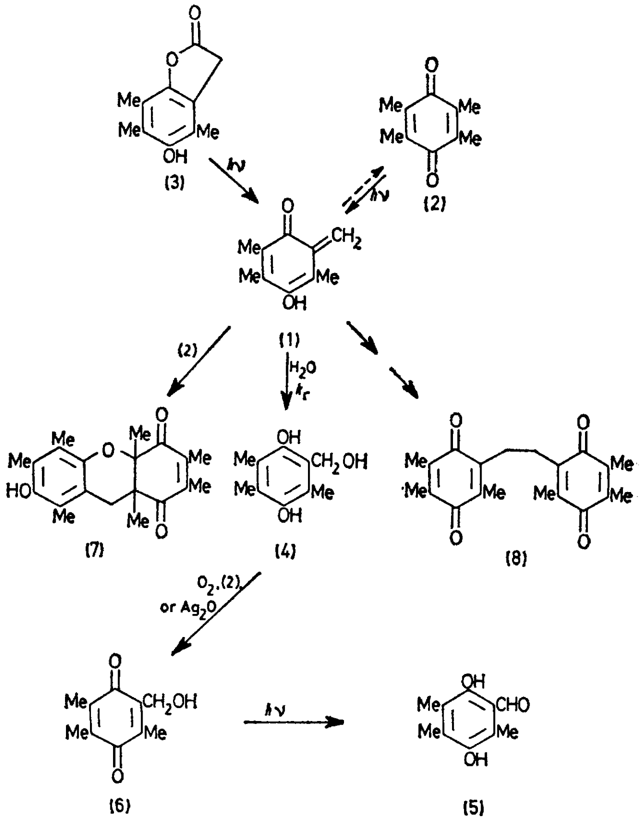
Summary 2-Hydroxy-1,3,4-trimethyl-*o*-benzoquinone methide (**1**) is an intermediate in the photochemistry of both duroquinone (**2**) and 2,4,5-trimethylhomogentisic lactone (**3**), but its formation is not a major pathway for decay of the duroquinone triplet state.

The triplet state (DQ^T) of duroquinone (**2**) is quenched by water. Both physical quenching,[1] by an unspecified mechanism, and chemical quenching,[2] by proton loss leading to the anion of the *o*-quinone methide (**1**) have been proposed. We now report that although (**1**) is an intermediate in the photochemistry of both duroquinone (**2**) and the lactone (**3**) in aqueous solution, and can be observed directly by flash photolysis of (**3**), its formation is not a major pathway for decay of DQ^T in water.



Irradiation ($\lambda > 320$ nm) of duroquinone ($< 5 \times 10^{-4}$ M) under N_2 in 5% acetonitrile in water affords the benzaldehyde (**5**) as the major photoproduct and the hydroxymethylbenzoquinone (**6**)‡ as one of several minor photoproducts. Traces of diduroquinone,[8] (**7**) and the dimer (**8**) were also isolated. Irradiation of the hydroxymethylquinone (**6**) afforded (**5**) quantitatively,[3] suggesting that the hydroquinone (**4**) [which is readily oxidised to (**6**) by duroquinone or in the air] is the major primary product of irradiation of low concentrations of duroquinone in aqueous solution. Nucleophilic addition of water to the *o*-quinone methide (**1**) is a likely mechanism[4,5] for the formation of (**4**).

Attempts to observe (**1**) by flash photolysis of duroquinone proved inconclusive and we therefore sought an alternative method of generation. Irradiation (Hg arc through quartz) of the lactone (**3**)[4] in aqueous acetonitrile,

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‡ Satisfactory elemental analysis and n.m.r., u.v., i.r., and mass spectra were obtained for this new compound.

followed by silver oxide oxidation of the total product mixture, afforded two major photoproducts, the hydroxymethylquinone (**6**) and the dimer (**8**) together with a trace of duroquinone (**2**). Dimerisation of the *o*-quinone methide (**1**) to a readily oxidised hydroquinone precursor of (**8**) has precedent[6] and (**1**) is the vinylogous enol of (**2**).

Conventional (microsecond) flash photolysis of (**3**) (2×10^{-4} M) in ethanol gave rise to a transient with the broad visible absorption specrtum [λ_{max} (EtOH) 445 nm] and long lifetime characteristic[5] of *o*-quinone methides. This transient is long-lived in ethanol ($\tau_{\frac{1}{2}}$ 12 s) and acetonitrile ($\tau_{\frac{1}{2}}$ 30 s) but its mixed order decay precludes the accurate determination of rate parameters in these solvents. Increasing proportions of water in ethanol or acetonitrile accelerate the rate of decay markedly until in 5% ethanol in water the decay is essentially first order (τ 8×10^{-2} s), leading to $k_r = 2 \times 10^{-1}$ l mol^{-1} s^{-1}. Our failure to observe (**1**) upon flash photolysis of (**2**) in aqueous solution most probably reflects both the low probability of photochemical reaction of duroquinone in water ($\phi_{disappearance}$ $0{\cdot}03 \pm 0{\cdot}01$) and overlap of the absorption spectrum of (**1**) and other transients formed[1,7,8] upon flash photolysis of (**2**).

Since $\phi_{disappearance}$ of duroquinone (**2**) in water (0·03) is very small compared with ϕ_{isc} ($0{\cdot}8 \pm 0{\cdot}01$),[1,10] quinone methide formation cannot be a major pathway for the decay of DQ^T unless reformation of (**2**) from (**1**) is appreciable. This is not so, since enolisation of (**1**) back to (**2**) can be neglected under our experimental conditions,[9] only traces of (**2**) are formed upon irradiation of (**3**), and the quantum yield for deuterium incorporation into (**2**) irradiated in D_2O is $<0{\cdot}01$. $\phi_{disappearance}$ of (**2**) in water is thus an upper limit for the quantum yield of quinone methide formation. The lifetime of DQ^T determined[10] by laser flash photolysis is the same within experimental error in both H_2O and D_2O. Thus protonation of DQ^T can also be ruled out as the rate-determining quenching step. The shorter lifetime of DQ^T in water[1,2] compared to ethanol may be a consequence of altered ordering of the ground and triplet state energy levels in the stronger hydrogen-bonding solvent. Alternatively electron-transfer quenching may occur more readily in aqueous solution. We note the highly efficient quenching[1,2,8,10] of DQ^T by durohydroquinone ($k = 2{\cdot}0 \times 10^9$ l mol^{-1} s^{-1}), which must surely involve triplet exciplex formation, and recent e.s.r. evidence[11] for photochemically induced one-electron transfer between benzoquinone and both ethanol and water.

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