E.s.r.-Spin Trapping Investigation of the Photoreduction of Quinones by Alcohols in Solution. Mediation of Alkoxyl Radicals and Relevance to CIDEP Phenomena

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Summary E.s.r.-spin trapping experiments reveal that alkoxyl radicals are produced in the reactions between triplet quinones and alcohols; interpretation of CIDEP phenomena in these systems must take account of secondary radical reactions.

The photochemistry of quinones has recently aroused great interest, particularly in view of their role in establishing the triplet mechanism of electron spin polarization.[1] However, many aspects of their photochemistry are still not well understood; we report here experiments that throw new light on the photoreduction of quinones by alcohols, and emphasize that polarization ratios determined in these systems must be interpreted with caution.

Table. Radicals trapped during the photolysis of quinones (*ca.* 10^{-2} M) in alcohols in the presence of 10^{-2} M $PhCH{=}N^+(O^-)Bu^t$.

Quinone	Alcohol	Trapped radical, $RO\cdot$[a]
Chloranil	MeOH	$MeO\cdot$
Benzoquinone	MeOH	$MeO\cdot$
Benzoquinone	EtOH	$EtO\cdot$
Benzoquinone	Pr^iOH	$Pr^iO\cdot$
Naphthoquinone	MeOH	$MeO\cdot$
Duroquinone	MeOH	$MeO\cdot$
Anthraquinone	MeOH	$MeO\cdot$

[a] Hyperfine splittings for the adducts $PhCH(OR)N(O\cdot)Bu^t$ were in good agreement with those reported in ref. 5.

It is generally supposed[2] that triplet quinone (Q^T) reacts with primary or secondary alcohol (R_2CHOH) in fluid solution to give an hydroxyalkyl radical ($R_2\dot{C}OH$); abstraction of the hydroxylic hydrogen to give an alkoxyl radical ($R_2CHO\cdot$) seems only to have been considered in the solid state.[3] Alkoxyl radicals cannot be detected directly in solution,[4] but their mediation can be inferred by the detection of their adducts (nitroxide radicals) with benzylidine nitrone [$PhCH{=}N^+(O^-)Bu^t$]. In this way, some abstraction of the hydroxylic hydrogen from alcohols has been demonstrated for the radical $SO_4^{\cdot-}$[5] and for photoexcited inorganic ions (Pb^{4+}, UO_2^{2+},[5] and Ce^{4+}[6]), all of which are good oxidants. It therefore seemed possible that photoexcited organic oxidants such as quinones would also yield a mixture of alkoxyl and hydroxyalkyl radicals, possibly *via* direct abstraction and/or initial electron transfer [reaction (1)] and subsequent reaction with solvent [reactions (2) and (3)].

$$Q^T + R_2CHOH \longrightarrow Q^{\cdot-} + R_2CH\dot{O}H^+ \qquad (1)$$

$$R_2CH\dot{O}H^+ + R_2CHOH \longrightarrow R_2CHO\cdot + R_2CHOH_2^+ \qquad (2)$$

$$R_2CH\dot{O}H^+ + R_2CHOH \longrightarrow R_2\dot{C}OH + R_2CHOH_2^+ \qquad (3)$$

Nitroxide radicals detected in several quinone–alcohol systems are listed in the Table. Adducts of alkoxyl radicals were detected in each system. We consider production of these radicals *via* abstraction by triplet quinone from parent hydroxylamine [$PhCH(OR)N(OH)Bu^t$], which could feasibly be produced thermally,[7] unlikely since triplet benzophenone, which itself reacts rapidly with hydroxylamine,† gave only adducts of hydroxyalkyl radicals, and in both cases spectra were unaffected by the addition of 10^{-2} M CF_3CO_2H.

The semiquinone radicals produced ($Q^{\cdot-}$ and/or $QH\cdot$) were detected in time-resolved experiments[8] and shown not to react significantly with the trap, although they are scavenged to some extent by product nitroxide radicals.

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† Photolysis of benzophenone with 10^{-2} M *NN*-diethylhydroxylamine in either benzene or methanol solution gave strong signals from $Et_2NO\cdot$. Signals were not observed in the absence of benzophenone.

The absence of adducts of hydroxyalkyl radicals must not be taken to indicate that hydroxyalkyl radicals are not produced. They may be formed in a primary step and also the concentration of $PhCH{=}N^+(O^-)Bu^t$ used (10^{-2} M) is unlikely completely to suppress their formation through reaction (4).[9] Presumably their oxidation by ground state quinone[10] [reaction (5)] is faster than their addition to $PhCH{=}N^+(O^-)Bu^t$. Rapid oxidation also explains the

$$R_2CHO\cdot + R_2CHOH \longrightarrow R_2\dot{C}OH + R_2CHOH \qquad (4)$$

$$R_2\dot{C}OH + Q \longrightarrow QH\cdot + R_2CO \qquad (5)$$

absence of these adducts in other systems containing strong oxidants.[5] [In the absence of an alkoxyl radical scavenger, product yields are likely to be independent of alkoxyl radical production owing to the efficiency of reaction (4)].

Although we are unable at present to obtain a precise estimate of the quantum yield for alkoxyl radical production in these systems, the yield of alkoxyl radical adduct [calculated from the ratio of the estimated concentrations of adduct and primary alcohol radical (*ca.* 5×10^{-7} M) produced in each pulse of light[8]] is a few percent in the benzoquinone–methanol system even at the relatively low concentrations (10^{-2} M) of nitrone employed. This suggests that indirect production of the adduct, *e.g.*, from reaction of triplet quinone with nitrone, is unlikely in view of the short lifetime of triplet benzoquinone in alcohols.[11] The interpretation of electron polarizations in quinone–alcohol systems consequently demands a consideration of the mediation of these radicals (in which spin-lattice relaxation should be extremely rapid) as well as the effects of radical oxidation. Thus reaction (5) provides a second source of semiquinone radical, the polarization in which is dependent on the rate of reaction (5) and the relaxation time of $R_2\dot{C}OH$, both of which will be related to the nature of the alcohol.

Radical oxidation is also likely in quinone–amine systems [*e.g.* reaction (6)] and would rationalise both the lack of a direct correlation between the magnitudes of polarization factors and triplet lifetimes found in these systems and the apparent dependence of the initial polarization on the specific amine used.[12]

$$R^1\dot{C}HNR^2_2 + Q \longrightarrow R^1C{=}NR^2_2 + QH\cdot \qquad (6)$$

(*Received*, 1*st October* 1975; *Com.* 1123.)

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