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POLAR EFFECTS IN FREE RADICAL REACTIONS. THE MECHANISM OF PHOTOCHEMICAL ADDITION OF ETHERS AND SUBSTITUTED TOLUENES TO 9,10-PHENANTHRENEQUINONE

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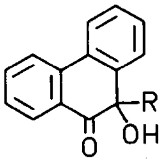
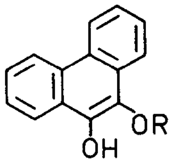
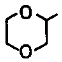
We have reported[1] that photochemical addition of toluene and substituted toluenes to 9,10-phenanthrenequinone (PQ) proceeds in a 1,2-manner to give derivatives (I) of 9,10-dihydro-9-hydroxy-10-ketophenanthrene in contrast to the 1,4-addition to aldehydes[2] and ethers[3] which produce derivatives (II) of 9,10-dihydroxy-

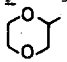
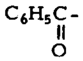


I



II

I a, R = $p\text{-}CH_3C_6H_4CH_2\text{-}$
b, R = 
c, R = $C_6H_5OCH_2\text{-}$

II a, R = $p\text{-}CH_3C_6H_4CH_2\text{-}$
b, R = 
c, R = $C_6H_5OCH_2\text{-}$
d, R =  $C_6H_5\overset{\displaystyle\text{C}}{}\!\underset{\|}{\underset{O}{}}\text{-}$ ($C_6H_5C(=O)\text{-}$)

phenanthrene. It has now been established, both by interruption of irradiations at 3650 Å at very low conversions and by irradiations at 4300-4360 Å, where the reactions are irreversible, that photoadditions of toluenes to PQ produce mixtures of adducts of types I and II. As illustrated in Table I, the relative proportions of I and II depended on the polar character of substituents in a series of p-substituted toluenes, the proportion of 1, 2-adduct increasing with increasing electron donating ability of the substituent. Only adducts of type II could be detected in irradiations of ethers under similar irreversible conditions.

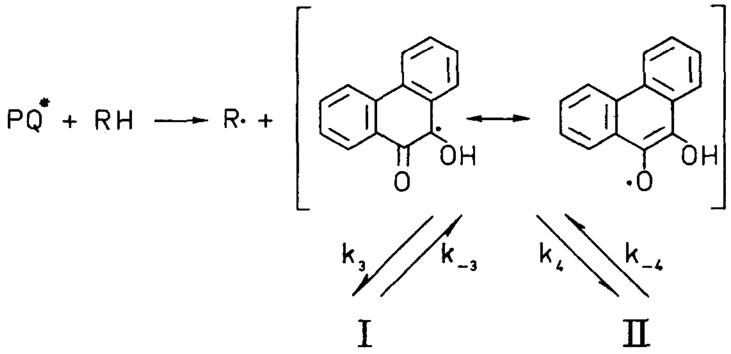
TABLE I

Additions to PQ at 4300-4360 Å

	Ratio I:II[a, b]
p-$CH_3OC_6H_4CH_3$	> 20[c]
p-$(CH_3)_3CC_6H_4CH_3$	4
p-$CH_3C_6H_4CH_3$	1
$C_6H_4CH_3$	0.67
p-$NO_2C_6H_4CH_3$	0.43
Dioxane	< 0.05[d]
Anisole	< 0.05[d]

(a) Adduct mixtures were analyzed by ultraviolet spectrophotometry as described in ref. 1. (b) Composition of product mixtures remained constant over the range 10-89% reaction. (c) The 1, 4-adduct resulting from reaction at the methoxy group constituted a minor product of this reaction. (d) No isomeric adduct was detected.

Both chain[4] and non-chain[5] radical mechanisms have been suggested for PQ photoadditions. However, the relative rates (*cf.* ref. 1) of benzaldehyde, dioxane, and *p*-xylene additions were not affected by the presence of added thiophenol, hydroquinone, or trace amounts of oxygen[6] as determined in a series of competition reactions. With 10 mole percent of added thiophenol, which retards or inhibits non-chain radical processes,[7] a modest (*ca.* 25%)retardation was observed. In addition, it has been established that quantum yields in these reactions are not greater than unity at 4360 Å. These results suggest that additions to PQ proceed *via* a non-chain, radical combination process in which abstraction of hydrogen from aldehyde, ether or toluene by photoexcited PQ leads to formation of the resonance-stabilized semiquinone radical and a radical derived from the second reactant. Combination of the two radicals could then occur in either of two ways leading to the two types of products observed. The relative forward and reverse rates of the two



combination processes (k_3, k_4, k_{-3}, and k_{-4}) would then determine the results observed in a specific instance.

It seems reasonable to assume that the semiquinone radical is polarized[8] to an appreciable extent with partial positive charge dispersed through the carbon skeleton and a corresponding negative charge localized on the oxygen atom sharing the unpaired electron. The rates of addition to carbon *vs.* oxygen *might* then depend on the polarity of the second radical species; the rate of reaction at oxygen being greater for more electrophilic radicals and *vice versa*. Such an interpretation is in accord with the substituent effects observed with substituted toluenes and, if correct, leads to the conclusion that ether radicals are appreciably more electrophilic than benzyl radicals.

Further experiments to test the validity of these proposals are in progress.[9]

This interpretation is consistent with the observation that photochemical interconversions of Ia to IIa and *vice versa* can be achieved at 3650 Å and proceed intramolecularly. It is also noteworthy that prolonged irradiation of IIc at 3650 Å resulted in complete conversion to Ic. In preparative experiments, using a broad spectrum of light above 3000 Å, the observation of 1,2-addition with toluenes and 1,4-addition with ethers simply reflects the relative rates of the forward and reverse reactions.

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(6) The presence of stoichiometric amounts of oxygen results in oxidative cleavage of adducts, cf. A. Benrath and A. von Meyer, *Ber.*, **45**, 2707 (1912)

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(8) For recent discussions of radical polarity see J. F. Harris, Jr. and F. W. Stacey, *J. Am. Chem. Soc.*, **83**, 840 (1961); T. J. Dougherty, *ibid.*, **86**, 460 (1964); G. A. Russell and R. C Williamson, *ibid.*, **86**, 2357 (1964); R. L. Huang and H. H. Lee, *J. Chem. Soc.*, 2500 (1964).

(9) Satisfactory analytical data and spectroscopic properties were observed for all new compounds described.