On the Reaction of Methyl and Phenyl Radicals with *p*-Benzoquinone in Aqueous Solution

By **Dieter Veltwisch** and **Klaus-Dieter Asmus**,* Hahn-Meitner-Institut für Kernforschung Berlin GmbH, Bereich Strahlenchemie, Postfach 39 01 28, D-1000 Berlin 39, Federal Republic of Germany

$^\bullet\mathrm{CH_3}$ and $^\bullet\mathrm{C_6H_5}$ radicals (from the reaction of $^\bullet$OH with dimethyl and diphenyl sulphoxide) react with *p*-benzoquinone with k $(4.5 \pm 1.0) \times 10^7$ and $(1.2 \pm 0.2) \times 10^9$ dm^3 mol^{-1} s^{-1}, respectively. In both cases an immediate formation of a transient is observed which could be identified as the unsubstituted semiquinone radical. The reaction mechanism is considered to proceed *via* addition of the $^\bullet\mathrm{CH_3}$ or $^\bullet\mathrm{C_6H_5}$ radicals to one *p*-benzoquinone molecule and immediate subsequent reaction of these radical adducts with a second *p*-benzoquinone molecule. The latter process is likely to be an electron transfer. The pulse radiolysis results are supported by steady-state irradiation product analysis.

p-BENZOQUINONE has been reported to be a good trap for alkyl and aryl radicals.[1-3] Thus pulse radiolysis studies have revealed a fast reaction of the $^\bullet\mathrm{C_6H_5}$ radical occurring with k 1×10^9 dm^3 mol^{-1} s^{-1} and leading to a transient optically absorbing species.[3] A more mechanistic study is given on the $^\bullet\mathrm{CH_3}$ radical reaction with *p*-benzoquinone by Torssell and his co-workers.[1,2] In their studies the methyl radicals are produced *via* the reaction of dimethyl sulphoxide with $^\bullet$OH radicals which are themselves generated by a Fenton-type mechanism. They observed mono-, di-, and tri-methylquinones (16%), sulphones (3%), and small amounts of hydroquinones as stable reaction products.[1] The mechanism was proposed to proceed *via* a methyl radical addition to *p*-benzoquinone to yield a methylsemiquinone, and subsequent oxidation of the latter by Fe^{3+} ions.[2] Analogous secondary reactions were considered to be responsible for the di- and tri-methylated compounds. No direct evidence could, however, be produced for any of the possible intermediates.

The present pulse- and γ-radiolysis studies were undertaken to obtain more detailed information on the mechanism of the alkyl and aryl radical reaction with *p*-benzoquinone and to characterize observable intermediates. Both the $^\bullet\mathrm{CH_3}$ and $^\bullet\mathrm{C_6H_5}$ radicals were produced by the $^\bullet$OH radical-induced oxidation of the respective sulphoxides.[4,5]

$$\mathrm{R_2SO} + {}^\bullet\mathrm{OH} \longrightarrow \mathrm{R_2SO(OH)}^\bullet \longrightarrow \mathrm{R}^\bullet + \mathrm{RSO_2}^-/\mathrm{H}^+ \quad (1)$$

The lifetime of the intermediate $^\bullet$OH adduct, R$_2$SO(OH)$^\bullet$, is only very short (*ca.* 50 ns for $\mathrm{R} = \mathrm{CH_3}$ and <10 ns for $\mathrm{R} = \mathrm{C_6H_5}$).[5] The respective R$^\bullet$ radicals are therefore available for chemical reactions more or less instantaneously after the generation of the $^\bullet$OH radicals. The yield of reaction (1) is almost quantitative for $\mathrm{R} = \mathrm{CH_3}$ while for $\mathrm{R} = \mathrm{C_6H_5}$ it accounts only for *ca.* 34% of the hydroxyl radicals. The remainder of the $^\bullet$OH radical yield in this case undergoes addition to the aromatic system to form hydroxycyclohexadienyl radicals.[5]

EXPERIMENTAL

Most of the experimental details have been presented in the preceding paper,[6] and only additional aspects will be dealt with here.

p-Benzoquinone and methyl-*p*-benzoquinone in particular were vacuum sublimed prior to use. The purity of the compounds was generally checked by gas or liquid chromatographic methods.

The γ-radiolysis experiments were carried out by exposing appropriate solutions to the field of a 15 000 Curie ^{60}Co source. The absorbed dose rate was 6.15×10^2 J kg^{-1} h^{-1} (6.15×10^2 Gy h^{-1} or 6.15×10^4 rad h^{-1}). The total dose applied to the solutions was usually 1.76×10^2 J kg^{-1}. Dosimetry was done with the Fricke dosimeter.[7]

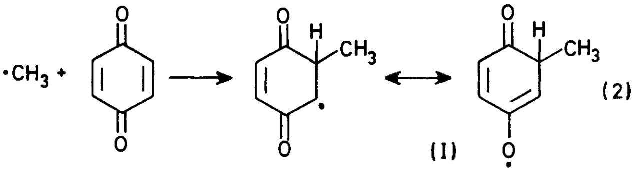
The consumption of *p*-benzoquinone and the yields of methylated *p*-benzoquinone were measured with a newly developed h.p.l.c. method [8] using a Varian 8500 with a Variscan u.v. spectrophotometer (245 nm) and a silica gel Nucleosil 50/5 (25 cm × 0.3 mm) column. The eluant was a solution of 2% v/v tetrahydrofuran and 0.17% v/v H$_2$O in n-heptane. Prior to h.p.l.c. analysis the quinones were concentrated by extraction from the aqueous solution with small amounts of benzene. The partition coefficients between benzene and water were determined as 8.9 ± 0.8 for *p*-benzoquinone and 22.7 ± 2 for methyl-*p*-benzoquinone. Phenyl-*p*-benzoquinone was measured with a reverse-phase column (Waters RCC5 μ C18) with eluants of 65 and 70% CH$_3$OH and 35 and 30% H$_2$O, respectively.

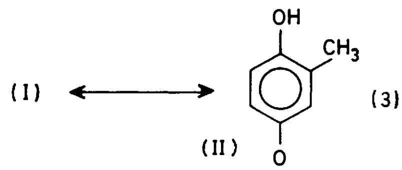
The experimental limits of error for rate constants and yields are estimated to be $\pm 10\%$ unless otherwise stated. All experiments were carried out at room temperature.

RESULTS AND DISCUSSION

(1) *Reaction of* $^\bullet\mathrm{CH_3}$ *Radicals*.—(a) *γ-Radiolysis*. A steady-state γ-irradiation of a neutral, N$_2$O-saturated solution of 2×10^{-1} mol dm^{-3}-dimethyl sulphoxide and 10^{-3} mol dm^{-3}-*p*-benzoquinone (Q) led to the formation of methyl-*p*-benzoquinone (MQ) with a yield of G(MQ) 5.3 (0.55 μmol J^{-1} absorbed energy). Higher methylated quinones were formed only in negligible amounts ($G \leqslant 0.1$ or $\leqslant 0.01$ μmol J^{-1}).

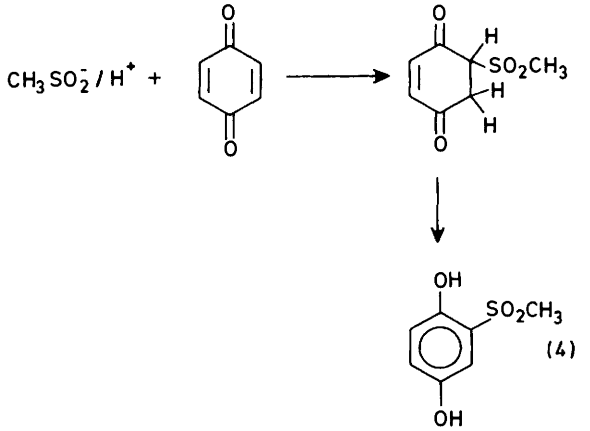
The yield of MQ is practically identical with the yield of $^\bullet\mathrm{CH_3}$ radicals formed in reaction (1). Mechanistically it can be assumed that the initial step is a methyl radical addition to the *p*-benzoquinone to yield a radical which may further tautomerize to the methylsemiquinone (II). If now MQ was formed simply by disproportionation of (I) or (II), its yield should amount to only half the $^{\bullet}CH_3$ yield, *i.e.* $G \approx 2.65$ or ≈ 0.275 μmol J^{-1}, which is clearly not the case. Also the other disproportionation product, namely methylhydroquinone, was not detected. (The analytical procedures are described in ref. 8.)





Similarly the *p*-benzoquinone destruction cannot be explained by such a simple mechanism. In the same solutions as above a total of G 14.1 or 1.46 μmol J^{-1} of *p*-benzoquinone is destroyed. The formation of one molecule of methyl-*p*-benzoquinone is therefore accompanied by the destruction of (mathematically) *ca.* 2.7 molecules of *p*-benzoquinone.

One equivalent of *p*-benzoquinone destruction can be accounted for by the addition of methylsulphinic acid



[formed in reaction (1) with equal yield as $^{\bullet}CH_3$ radicals] to *p*-benzoquinone.

Such reactions are known and have in particular been characterized for arylsulphinic acids.[9] In the present investigation the yield of free sulphinic acid was monitored *via* the radiation-induced change in proton concentration in neutral, N_2O-saturated solutions of 2×10^{-1} mol dm^{-3}-$(CH_3)_2SO$ in the absence or presence of 10^{-3} mol dm^{-3}-*p*-benzoquinone. In the absence of *p*-benzoquinone the yield of protons was G 5.6 (0.58 μmol J^{-1}), *i.e.* corresponding to the yield of $^{\bullet}CH_3$ radicals. In the presence of *p*-benzoquinone, however, the change in proton concentration was drastically decreased to about one-tenth (G 0.5 ± 0.3 or 0.05 ± 0.03 μmol J^{-1}). This result is taken as strong support for reaction (4) to occur practically quantitatively.

(b) *Pulse radiolysis experiments.* Further insight into the overall reaction mechanism is provided by pulse radiolysis experiments. Thus time-dependent changes in conductivity and optical density could be observed in pulse-irradiated, N_2O-saturated solutions of, for example, 2×10^{-1} mol dm^{-3}-$(CH_3)_2SO$ and 5×10^{-4} mol dm^{-3}-*p*-benzoquinone at pH 5.4.

The conductivity–time curve is shown in Figure 1a. It exhibits a two-step process. The initial fast increase in conductivity is due to the formation of methylsulphinic acid *via* reaction (1), *i.e.* is based on the $CH_3SO_2^-$ anion and H_{aq}^+ production. With the yield of G 5.3 (0.55 μmol J^{-1}) (for quantitative evaluation see later) and the specific conductivities of $l(CH_3SO_2^-) = 42$ and $l(H_{aq}^+) = 315$ Ω^{-1} cm^2 (at 18 °C),[5] the contribution of this initial process amounts to $G\,\Sigma l_i$ *ca.* 1 900. This value is marked on Figure 1a by the small horizontal line and is, in fact, obtained by extrapolation of the slow second step to the time at the end of the pulse. (The actual con-

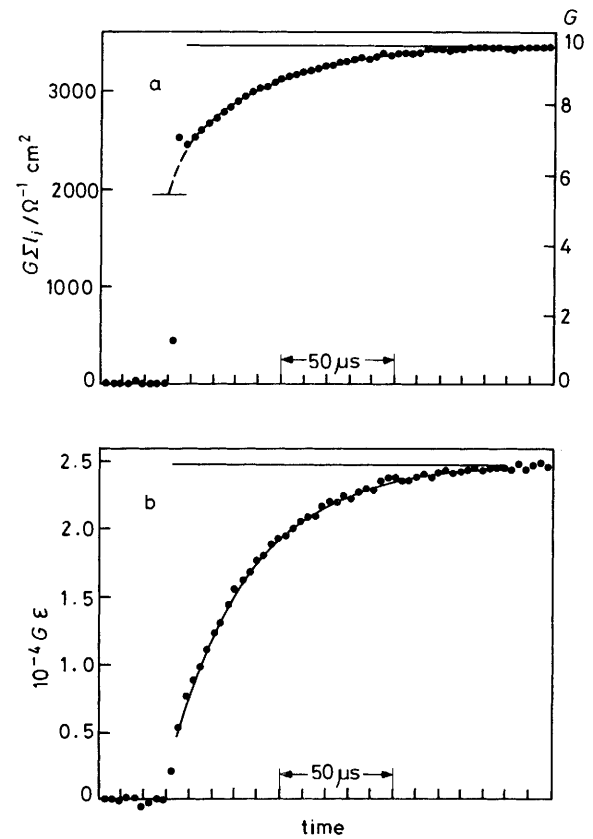


FIGURE 1 Conductivity–time curve a and optical absorption at 430 nm–time curve b in pulse-irradiated, N_2O-saturated solutions of 2×10^{-1} mol dm^{-3}-$(CH_3)_2SO$ and 5×10^{-4} mol dm^{-3}-*p*-benzoquinone at pH 5.4. Pulse width 1 μs

ductivity signal is ' distorted ' at very early times due to the $H_{aq}^+ + OH^-$ neutralization which at this pH occurs with $t_{\frac{1}{2}}$ *ca.* 1 μs.)

The second and considerably slower step of the change in conductivity occurs exponentially with a half-life of 30 μs. The half-lives decrease linearly with *p*-benzoquinone concentration and allow us to derive a second-order rate constant of $k = (4.5 \pm 1.0) \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$.

The final plateau yield of the conductivity signal corresponds to a total of $G\ \Sigma l_i$ 3 450, from which a contribution of $G\ \Sigma l_i = 3\ 450 - 1\ 900 = 1\ 550$ is derived for the slow step. This magnitude suggests that it also refers to an anion–H_{aq}^+ pair formation. Assuming an average l(anion) *ca.* 40 (±20) $\Omega^{-1}\ cm^2$ the yield of the second slow step is calculated as G 4.35 (or 0.45 μmol J^{-1}).

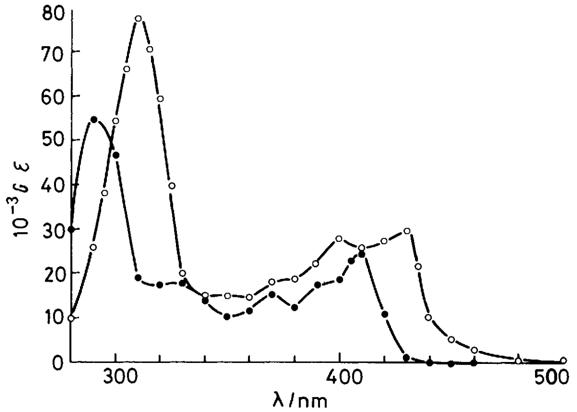
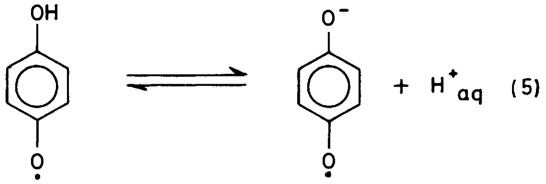


FIGURE 2 Optical absorption spectra from pulse-irradiated, N_2O-saturated solutions of 10^{-1} mol dm^{-3}-$(CH_3)_2SO$ and 10^{-3} mol dm^{-3}-*p*-benzoquinone at pH 5.6 (○) and pH 2.35 (●)

The simultaneously taken trace of the optical density (at 430 nm) as a function of time is shown in Figure 1b and exhibits the same kinetic characteristics as the second step in the conductivity curve. For further identification of this slowly formed, optically absorbing, and conducting species the whole spectra were recorded from pulse-irradiated, N_2O-saturated solutions of 10^{-1} mol dm^{-3}-$(CH_3)_2SO$ and 10^{-3} mol dm^{-3}-*p*-benzoquinone at different pH values. The spectra obtained at pH 5.6 and 2.35 are shown in Figure 2. They resemble the known spectra of the acid and neutral forms of the semiquinone radical [10] which exist in the acid–base equilibrium (5) with reported pK_a values of 4.0—4.1.[10,11]



(5)

The assignment is supported by appropriate pK_a measurements. The relevant experimental data are given in Figure 3. Curves a and b show the optical densities (expressed in terms of G ε) at 430 and 310 nm, and curve c the yield of the slowly formed conductivity (see Figure 1a) as a function of pH in N_2O-saturated solutions of 10^{-1} mol dm^{-3}-$(CH_3)_2SO$ and 10^{-3} mol dm^{-3}-*p*-benzoquinone. All three curves exhibit breaking points at pH 3.9—4.0 within an accuracy of probably less than ±0.2 pH units which clearly differ from, for example, pK_a 4.45 of the methylated semiquinone. Unambiguous proof was finally provided by a steady-state radiolysis e.s.r. experiment with N_2O-saturated solutions of 10^{-1} mol dm^{-3}-$(CH_3)_2SO$ and 5×10^{-4}-*p*-benzoquinone (pH 7.5 and 9.3) through the characteristic five-line spectrum of the unsubstituted semiquinone radical anion [a (4 H) 2.53 G].

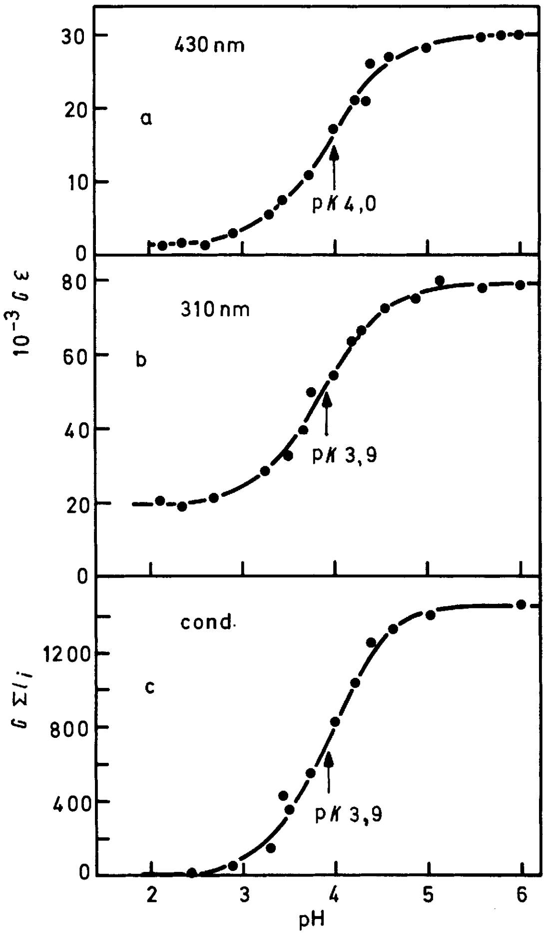


FIGURE 3 pH-Dependence of the optical density (expressed in terms of G ε) at 430 nm a, 310 nm b, and of the conductivity signal (expressed in terms of $G\Sigma l_i$), c, in pulse-irradiated, N_2O saturated solutions of 10^{-1} mol dm^{-3}-$(CH_3)_2SO$ and 10^{-3} mol dm^{-3}-*p*-benzoquinone

Extinction coefficients for both the neutral and the anionic form of the semiquinone radical are listed in the Table. They are based on the assumption that the slow change in conductivity (Figure 1a) at pH > 5 is a quantitative measure for the semiquinone radical production. Our result agrees well with (radical anion) or is slightly higher (neutral species) than literature values which so far have been published only for the low-energy bands.[11,12]

In the absence of suitable scavengers the semiquinone disappears by a second-order disproportionation process (6) to yield *p*-benzoquinone and hydroquinone (QH_2).

$$2Q^{-\bullet}(+2H_{aq}^{+}) \longrightarrow Q + QH_2 \qquad (6)$$

Conductivity measurements at longer times reveal that reaction (4), *i.e.* the addition of sulphinic acid to *p*-benzoquinone, does not take place on the $\leqslant 10$ ms time scale of our pulse radiolysis experiments. The bimolecular rate constant for this process is therefore $k_4 < 10^5$ dm^3 mol^{-1} s^{-1}.

	λ/nm	ϵ/dm^3 mol^{-1} cm^{-1} Exp.	Lit.	
$Q^{-\bullet}$	430	7 200	7 200 [12]	7 300 [11]
	310	19 000		
$^{\bullet}QH$	410	5 850	4 500 [12]	5 500 [11]
	290	13 400		

Extinction coefficients of the semiquinone radical and semiquinone radical anion. Estimated experimental limits of error ±20%.

Upon addition of tetranitromethane an electron transfer reaction (7) is observed at pH values where the

$$Q^{-\bullet} + C(NO_2)_4 \longrightarrow Q + C(NO_2)_3^{-} + NO_2 \qquad (7)$$

anionic form of the semiquinone prevails. This reaction can be identified through the exponential $C(NO_2)_4$ concentration-dependent decay of the $Q^{-\bullet}$ absorption (*e.g.* at 430 nm) or the simultaneous build-up of the stable $C(NO_2)_3^{-}$ absorption (at 350 nm). From the kinetic analysis of the respective absorption–time curves a bimolecular rate constant of k_7 7.1×10^7 dm^3 mol^{-1} s^{-1} can be evaluated for reaction (7). This rate constant was substantiated in a separate experiment in pulse-irradiated, deoxygenated solutions of 2×10^{-3} mol dm^{-3}-*p*-benzoquinone, 2×10^{-1} mol dm^{-3}-t-butyl alcohol, and various small concentrations of $C(NO_2)_4$, where the semiquinone radical is directly formed by reduction of *p*-benzoquinone with hydrated electrons and hydrogen atoms.

An experiment similar to the latter was also conducted with methyl-*p*-benzoquinone. From this a bimolecular rate constant of k_8 1.3×10^8 dm^3 mol^{-1} s^{-1} was derived for the reduction of tetranitromethane by methylsemiquinone radical anions. The disagreement of this rate constant with the experimental value of 7.1×10^7 dm^3 mol^{-1} s^{-1} in $(CH_3)_2SO$–*p*-benzoquinone solutions may also be taken as supporting evidence for the simple semiquinone radical to be the absorbing species in the latter system. This argument should, however, not be regarded as conclusive since the respective rate constants differ only by a factor of two.

$$MeQ^{-\bullet} + C(NO_2)_4 \longrightarrow MeQ + C(NO_2)_3^{-} + NO_2 \qquad (8)$$

The occurrence of the electron transfer reactions (7) and (8), and the fact that $k_8 > k_7$, are in accord with the known one-electron redox potentials of tetranitromethane, $E°[C(NO_2)_4/C(NO_2)_3^{-} + NO_2] = +0.31$ V,[13] and the respective values for *p*-benzoquinone, $E°(Q/Q^{-\bullet})$ +0.099 V, and methyl-*p*-benzoquinone, $E°(MQ/MQ^{-\bullet})$ +0.023 V.[14]

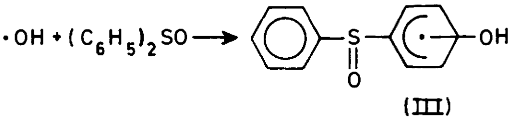
Protonation of the semiquinoid radical anions, on the other hand, would shift the respective redox potentials to the more positive side and thus slow down any electron transfer to tetranitromethane (any quantitative correlations are not warranted, however, since the reduction of tetranitromethane is a dissociative electron capture, *i.e.* is not reversible, and also kinetic effects may come into play.)

(2) *Reaction of* $^{\bullet}C_6H_5$ *Radicals*.—Qualitatively very similar observations were made for the reaction of $^{\bullet}C_6H_5$ radicals with *p*-benzoquinone. Differences are only apparent in yield and rate constants.

The phenyl radicals were produced through the reaction of $^{\bullet}OH$ radicals with diphenyl sulphoxide which, however, occurs only with *ca.* 34% efficiency [5] *via* reaction (9).

$$^{\bullet}OH + (C_6H_5)_2SO \longrightarrow {^{\bullet}C_6H_5} + C_6H_5SO_2^{-}/H^{+} \qquad (9)$$

In N_2O-saturated solutions containing 5×10^{-3} mol dm^{-3}-$(C_6H_5)_2SO$ and 8×10^{-4} mol dm^{-3}-*p*-benzoquinone (pH 5.2) the yield of $^{\bullet}C_6H_5$ radicals and phenylsulphinic acid amounts to $G = 1.8$ (*ca.* 0.19 μmol J^{-1}). This value takes into consideration that under experimental conditions a small yield of e_{aq}^{-} (G 0.3) reacts directly with *p*-benzoquinone and is not converted into $^{\bullet}OH$ *via* reaction with N_2O. The majority of $^{\bullet}OH$ radicals (G *ca.* 3.5 or 0.36 μmol J^{-1}) add to the aromatic system to yield a hydroxycyclohexadienyl radical [reaction (10)].[5]



(10)

(III)

The transient optical absorption spectrum obtained in such solutions upon pulse irradiation is given by the open circle curve in Figure 4a. It is composed of two contributions which at high time resolution can easily be separated from each other. As can be seen from the absorption–time curve in Figure 4b (taken at 320 nm) an initial fast growth in absorption is followed by a second slower step. The whole spectrum of the fast growing component is shown in the triangle curve. It is assigned to the hydroxycyclohexadienyl radical (III) since its shape and maximum wavelength at 330 nm are characteristic for such radicals.

The spectrum of the slowly formed transient species is given by the full circle curve. It again resembles that of the semiquinone radical anion (see also Figure 2). The pH dependence of this slowly formed optical absorption, *e.g.* at 310 nm, exhibits the same shape as shown in Figure 3 for the methyl radical-induced process, and reveals a pK_a of 3.9 ± 0.2. A possible assignment of the optical absorption to the phenyl radical adduct or to any of its equivalent forms is ruled out, since the pK_a at least of (VI) should probably be considerably lower than 3.9 owing to the electron-withdrawing phenyl substituent.

The experimental data therefore suggest also in this case the formation of a simple $Q^{-\bullet}$ semiquinone radical anion. The formation of an optically absorbing species with ε 2×10^3 dm^3 mol^{-1} cm^{-1} at 320 nm in the reaction of $^\bullet C_6H_5$ radicals with *p*-benzoquinone has also been reported in the literature, but no identification was given.[3]

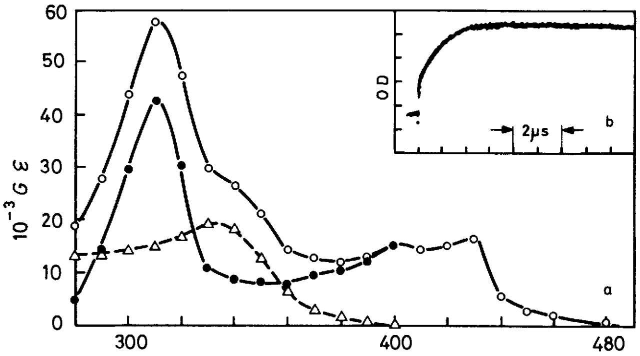
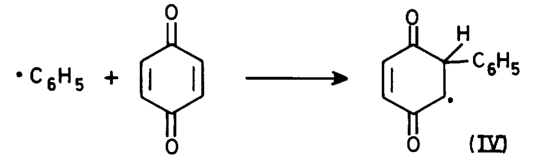


FIGURE 4 a, Transient optical absorption spectra in pulse-irradiated N_2O-saturated solutions of 5×10^{-3} mol dm^{-3}-$(C_6H_5)_2SO$ and 8×10^{-4} mol dm^{-3}-*p*-benzoquinone at pH 5.4. Pulse width 5 ns. ○, Total absorption at 5 μs after pulse; △, absorption after 50 ns (hydroxycyclohexadienyl radical); ●, slowly formed absorption (semiquinone radical anion). b, Inset, trace of optical absorption at 320 nm *versus* time.

The total yield of the semiquinone radicals is found to be *G* 2.2 (0.23 μmol J^{-1}). After correction for direct e_{aq}^- and $H^\bullet$ contributions a yield of *G* 1.9 ± 0.2 remains for the $^\bullet C_6H_5$-induced formation. This establishes a 1 : 1 correlation between $^\bullet C_6H_5$ radicals and semiquinone and indicates the same situation as in the methyl radical-induced mechanism. Accordingly the first step is



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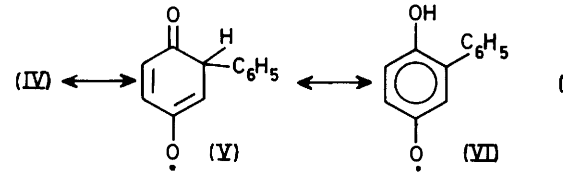

(12)

assumed to be the phenyl radical addition [reaction (11)] followed by a reaction of the adduct (IV)—(VI) with a second molecule of *p*-benzoquinone to yield the semiquinone. Alternative possibilities are ruled out on the following grounds: (1) a one-step electron transfer from $^\bullet C_6H_5$ to *p*-benzoquinone since $^\bullet C_6H_5$ is not a reductant and furthermore no phenol was detected; (2) hydrogen atom abstraction by $^\bullet C_6H_5$ since it would not yield semiquinone; and (3) reduction of *p*-benzoquinone by the hydroxycyclohexadienyl radical (III) since the yield of the latter does not correlate with the yield of semiquinone and the overall spectrum (Figure 4) indicates the simultaneous presence of both (III) and semiquinone.

The kinetics of the semiquinone formation are of first order with the half-lives being inversely proportional to the *p*-benzoquinone concentration. From these data a bimolecular rate constant of $k_{11} = (1.2 \pm 0.2) \times 10^9$ dm^3 mol^{-1} s^{-1} was calculated for the phenyl radical addition in reaction (11). This rate constant is almost two orders of magnitude higher than for the corresponding $^\bullet CH_3$ radical reaction. It is explained by the generally higher reactivity of a σ-radical ($^\bullet C_6H_5$) as compared with a π-radical ($^\bullet CH_3$).

In product analysis it was possible to identify phenyl-*p*-benzoquinone as one of the stable reaction products. Due to some irreproducible effects in the analytical h.p.l.c. procedure, however, only an estimate of *G ca.* 2—3 can be given for its yield. Such a value would indicate a 1 : 1 correlation between the $^\bullet C_6H_5$ radical and phenyl-*p*-benzoquinone yields. Owing to the large uncertainty of the latter, this correlation should, however, not be considered to be as conclusively established as the $^\bullet CH_3$–methyl-*p*-benzoquinone ratio in the corresponding methyl radical-induced system.

Among the other products showing up in the h.p.l.c. chromatogramme, the formation of a very polar compound is indicated which may be the phenylsulphinic acid adduct to *p*-benzoquinone [see reaction (4)].

(3) *Reaction Mechanism.*—The experimental results suggest the following reaction mechanism. The initial step is an addition of $^\bullet CH_3$ or $^\bullet C_6H_5$ to *p*-benzoquinone to yield $MeQ^{-\bullet}$–$MeQH^\bullet$ or $PhQ^{-\bullet}$–$PhQH^\bullet$ radicals in any of their mesomeric, tautomeric, and acid–base forms [equations (2)/(3), (11)/(12), and (5)]. This initial process is followed by reaction of the radical adducts with a second molecule of *p*-benzoquinone, *e.g.* reactions (13) and (14). Such a scheme explains quantitatively the production of unsubstituted semiquinone with a yield equivalent to the $^\bullet CH_3$ or $^\bullet C_6H_5$ radical yield.

$$MeQ^{-\bullet} + Q \longrightarrow MeQ + Q^{-\bullet} \qquad (13)$$

$$PhQ^{-\bullet} + Q \longrightarrow PhQ + Q^{-\bullet} \qquad (14)$$

On this basis it is also possible to account quantitatively for the yield of methyl-*p*-benzoquinone, and *p*-benzoquinone destruction in the methyl radical-induced mechanism. Under the experimental conditions, the yield of $^\bullet OH$ radicals available for reaction (1) is *G ca.* 5.3 (0.55 mol J^{-1}). The methyl radicals can be assumed to add quantitatively to *p*-benzoquinone [reaction (2)] since combination of two $^\bullet CH_3$ radicals [2*k* (2.5—3.2) × 10^9 dm^3 mol^{-1} s^{-1} [15]] cannot compete with this process at the low steady-state concentration of the $^\bullet CH_3$ radicals ($<10^{-8}$ mol dm^{-3}) under γ-radiolysis conditions. In consequence, the yield of methyl-*p*-benzoquinone is expected to be *G* 5.3 which is exactly the experimentally found value.

p-Benzoquinone is consumed by reactions (2) and (13), and also by sulphinic acid addition in reaction (4). Assuming that all these reactions occur quantitatively the reaction of each $^{\bullet}OH$ radical results in the destruction of three *p*-benzoquinone molecules, *i.e.* $G(-Q) = 3 \times 5.3 = 15.9$ (1.65 μmol J^{-1}). In addition, some more *p*-benzoquinone is consumed by direct reduction through hydrogen atoms and a small fraction of hydrated electrons [reactions (15) and (16)] ($QH^{\bullet}$ and $Q^{-\bullet}$

$$Q + H^{\bullet} \longrightarrow QH^{\bullet} \tag{15}$$

$$Q + e_{aq}^{-} \longrightarrow Q^{-\bullet} \tag{16}$$

equilibrate depending on pH). These processes occur with G 0.6 and *ca.* 0.3, respectively, which leads to a total $G(-Q)$ $15.9 + 0.9 = 16.8$ (1.74 μmol J^{-1}). All semiquinone radicals which are formed with a total yield of $5.2 + 0.6 + 0.3 \approx 6.2$ (0.64 μmol J^{-1}) in reactions (13), (15), and (16), will undergo disproportionation *via* reaction (7) and thereby regenerate *p*-benzoquinone with half this yield. Thus the overall yield of *p*-benzoquinone destruction would amount to $G(-Q) = 16.8 - 3.1 = 13.7$ (1.42 μmol J^{-1}). This value can certainly be considered to be in good agreement with the experimentally found of G 14.1 (1.46 μmol J^{-1}).

The rate constant for reaction (13) can be estimated to be *ca.* 4×10^{8} dm^{3} mol^{-1} s^{-1} on the basis of ΔG° -7.3 kJ mol^{-1} (ΔE° 0.076 V) for this reaction[14] and a rate constant–free energy correlation which has been established for the electron transfer between various semiquinones and quinones.[16] The initial methyl radical addition to *p*-benzoquinone would therefore be slower than the subsequent electron transfer reaction and thus become the rate-determining step for the semiquinone radical formation. A similar electron transfer mechanism has also been suggested by Torssell[2] who in his system explains methyl-*p*-benzoquinone formation by an oxidation of the intermediate methyl radical adduct, $MQ^{-\bullet}$, through Fe^{3+} ions. In the light of our results the latter may, in fact, not be needed since $MeQ^{-\bullet}$ can effectively be oxidized by *p*-benzoquinone itself.

A problem arises, however, if the same electron transfer concept is applied to the phenyl radical-induced reaction. The rate-determining step of the semiquinone formation is in this case characterized by a rate constant of 1.2×10^{9} dm^{3} mol^{-1} s^{-1}. It appears less reasonable to assign this rate constant to a simple electron transfer from the phenyl radical adduct (IV)—(VI) to *p*-benzoquinone. The above quoted rate constant is therefore associated, as in the $^{\bullet}CH_3$ system, with the initial $^{\bullet}C_6H_5$ radical addition to the *p*-benzoquinone, *i.e.* reaction (11). This would mean, however, that a relatively long-lived radical adduct (IV)—(VI) or at least a delayed semiquinone formation [slow reaction (14)] should be detectable. But this is clearly not the case. Another interesting observation is that the initial radical adducts (I), (II), or (IV)—(VI) are apparently able to reduce *p*-benzoquinone but not tetranitromethane although the latter is a slightly better oxidant on the redox scale. In conclusion, it therefore seems that the formation mechanism of semiquinone radicals at least in the phenyl radical-induced system is possibly more complex than just a simple electron transfer between a randomly diffusing substituted semiquinone and a *p*-benzoquinone molecule.

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