Electrophilic Reaction of the OH Radical with Phenol. Determination of the Distribution of Isomeric Dihydroxycyclohexadienyl Radicals[1]

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Abstract: Using pulse radiolysis with optical detection and high-pressure liquid chromatography techniques it is shown that the isomeric dihydroxycyclohexadienyl radicals formed in aqueous solution by reaction of OH with phenol react with quinones by electron transfer to yield semiquinones and dihydroxybenzenes. The rate constants for these electron-transfer reactions depend on the redox potential of the quinone and on the isomer structure of the dihydroxycyclohexadienyl radical; i.e., the rate constants are large (10^7–10^9 M^{-1} s^{-1}) in the case of the ortho and para isomers and small ($\leq 10^7$ M^{-1} s^{-1}) in the case of the meta and ipso isomers. The isomeric dihydroxycyclohexadienyl radicals differ also with respect to their rates of H^+-catalyzed dehydration to yield phenoxyl radical. It is thus possible to distinguish kinetically between the different dihydroxycyclohexadienyl radicals. On this basis and from the product analysis data the fractions of OH attack at the ipso, ortho, meta, and para position of phenol are 0.08, 0.48, 0.08, and 0.36, respectively. These data show the strong preference of the electrophilic OH radical for attack at the ring positions activated by the phenolic OH group.

Introduction

The OH radical reacts with substituted benzenes predominantly by addition to the ring and not by interaction with the substituent.[3-8] The pattern of OH attachment to the ring positions is expected, on the basis of the polar character[9] of OH, to depend on the electron-donating/-withdrawing properties of the substituent. In most cases the distribution of isomeric radicals is difficult to determine since the isomers differ only slightly with respect to their chemical and physical properties and since their lifetime is short owing to rapid bimolecular and, sometimes, unimolecular reactions. Particularly as a result of the latter, the information regarding the pattern of OH attack may become lost. It is therefore necessary to convert the radicals into stable products on a time scale that is fast compared to the competing decay reactions. For this purpose reagents are necessary that are sufficiently reactive to ensure quantitative conversion yet selective enough to prevent rearrangement or decomposition reactions involving the radical intermediates or the final products from occurring. In the present paper it is shown that quinones react as one-electron oxidants with dihydroxycyclohexadienyl radicals and that this reaction, which leads to dihydroxybenzenes, can be performed in a quantitative yet selective way such that information regarding the pattern of OH attack at the aromatic ring can be obtained. Phenols have previously been produced from hydroxycyclohexadienyl radicals by oxidation by inorganic oxidants.[5-7]

Experimental Section

The compounds were obtained from Eastman, Aldrich, and Fluka and were of the highest purity available. They were used as received. For the pulse radiolysis experiments, solutions were prepared using reagent-grade water from a Millipore Milli-Q system. In order to convert e^-_{aq} into OH, the solutions were saturated with N_2O. They were irradiated with 5-ns electron pulses from an Arco LP-7 linear accelerator using dose rates of $\sim 2 \times 10^{16}$ eV/g per pulse which correspond to initial radical concentrations of ~ 2 μM. The computer-controlled pulse radiolysis apparatus[10] was used for data acquisition. The concentrations of phenol were ~ 10 mM and the pH was 6–7.5. At least three different concentrations of oxidant ranging from 0.05 to 0.5 mM were used to obtain the second-order rate constants presented in the tables. The yields of reduced oxidants were measured with reference to a N_2O-saturated 0.1 M formate solution containing 0.5 mM oxidant. In this system, $G(\text{oxidant}^{-}\cdot) = G(\text{OH}) + G(\text{H})$.

For product-analysis studies, 15–20 mM solutions of phenol in triply distilled water and containing ~ 0.5 mM oxidant were saturated with N_2O and ^{60}Co-γ irradiated using dose rates of $\sim 5 \times 10^{17}$ eV g^{-1} min^{-1} as determined by Fricke dosimetry ($G(\text{Fe}^{\text{III}}) = 15.6$). Based on phenol and oxidants, substrate conversion was kept below 1 and 20%, respectively. Samples (150 μL) of the irradiated solutions were analyzed using the high-pressure liquid chromatography apparatus previously described.[7,11]

Results and Discussion

Radiolysis of water is a convenient way of producing defined amounts of radicals:

$$H_2O \rightarrow e^-_{aq}, \text{OH}, \text{H} \qquad (1)$$

In N_2O-saturated solution, e^-_{aq} is quantitatively converted into OH radicals:

$$e^-_{aq} + N_2O + H_2O \rightarrow OH^- + N_2 + OH \qquad (2)$$

such that the yield of OH per 100 eV of absorbed radiation, $G(\text{OH})$, is equal to 6.0.[12] Since $G(\text{H}) = 0.56$, in irradiated N_2O-saturated aqueous solutions the OH radical constitutes >90% of all the radicals produced.

1. Product Analysis Studies. The reaction of OH and H with phenol proceeds by addition to yield (isomeric) dihydroxy- and (isomeric) hydroxycyclohexadienyl radicals, respectively.[13] Table I contains the yields of catechol, resorcinol, and hydroquinone obtained on reaction of OH with phenol at pH ~ 6 in the presence of a series of oxidants for the dihydroxycyclohexadienyl radicals. With ferricyanide present, only resorcinol can be determined quantitatively since catechol and hydroquinone are destroyed rapidly in thermal reactions. The yield of resorcinol corresponds to 8% of the OH radicals produced.

In the presence of quinones as oxidants for the dihydroxycyclohexadienyl radicals the yields of resorcinol are smaller than that measured in the presence of ferricyanide. The yields of resorcinol decrease with decreasing redox potential of the oxidant, i.e., in going from ferricyanide to anthraquinone 2-sulfonate. From Table I it can also be seen that the absolute yields of the isomeric dihydroxybenzenes decrease and that the ratio of the yields changes as the pH is changed from ~ 6 to lower pH values.

The experimental results are explained in terms of production, by reaction of OH with phenol, of four isomeric dihydroxycyclohexadienyl radicals (reaction 3). These radicals are oxidized with the rate constants $k(\text{ox})_i$, $k(\text{ox})_o$, $k(\text{ox})_m$, and $k(\text{ox})_p$. These oxidation reactions are in competition with H^+- and OH^--catalyzed dehydration reactions[13] to yield the

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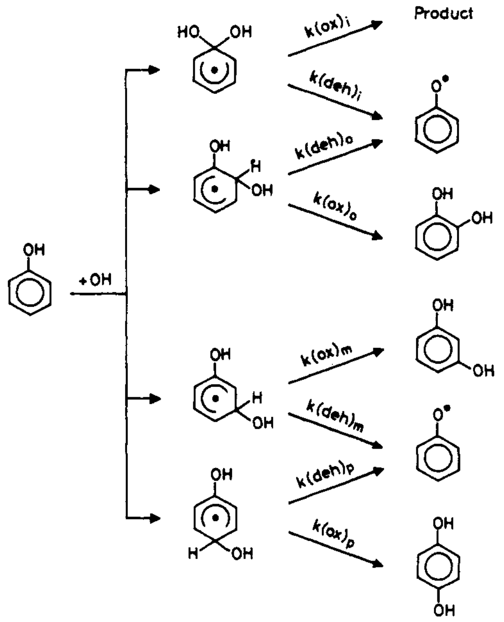
Table I. Yields[a] of Dihydroxybenzenes Produced by Reaction of OH with Phenol in the Presence of Oxidants[b]

oxidant	pH	catechol	resorcinol	hydroquinone
$K_3Fe(CN)_6$ (0.4-1.1 mM)	6.1-6.2	*c*	0.47 ± 0.05 (8%)	*c*
p-benzoquinone (0.42 mM)	5.9	2.86 ± 0.12 (48%)	0.23 ± 0.03 (4%)	
2-methylbenzoquinone (0.43 mM)	6.0	2.95 ± 0.15 (49%)	*d*	2.16 ± 0.06 (36%)
(0.40 mM)	2.95	2.51 ± 0.20 (42%)	*d*	1.23 ± 0.10 (21%)
2,5-dimethylbenzoquinone (0.55 mM)	6.0	2.88 ± 0.12 (48%)	0.16 ± 0.02 (3%)	2.17 ± 0.06 (36%)
(0.40 mM)	3.0	2.60 ± 0.20 (43%)	<0.02	1.20 ± 0.10 (20%)
2,6-dimethylbenzoquinone (0.56 mM)	6.1	2.82 ± 0.12 (47%)	0.15 ± 0.02 (3%)	2.19 ± 0.06 (37%)
anthraquinone 2-sulfonate (0.36 mM)	6.0	2.71 ± 0.15 (45%)	<0.02	2.10 ± 0.08 (35%)
(0.37 mM)	3.0	<0.02	<0.02	1.19 ± 0.10 (20%)

[a] The yields are given in terms of *G* values. The numbers in parentheses are yields per OH produced, based on *G*(OH) = 6.0. [b] The concentration of phenol was 15-19 mM. [c] Not quantitatively determinable owing to thermal oxidation by ferricyanide. [d] Resorcinol and 2-methylhydroquinone eluted together.

phenoxyl radical. As shown in section 3, the rate constants *k*(deh) for dehydration from different isomeric dihydroxycyclohexadienyl radicals are different.

The yields of catechol and hydroquinone, as obtained at pH 6 in the presence of *p*-benzoquinone, 2-methyl-, 2,5-, or 2,6-dimethylbenzoquinone, amount to 48 and 36% of *G*(OH), respectively (Table I). Since the yield of resorcinol represents 8% of OH, a complete material balance is obtained if it is assumed that 8% of the OH radicals add at the ipso position of phenol to yield 1,1-dihydroxycyclohexadienyl radical (see reaction 3) followed by elimination of water to yield phenoxyl



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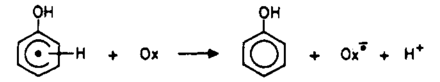
radical and subsequent reduction of phenoxyl, probably by reaction with the reduced oxidant, $Ox^{-}\cdot$, to produce phenol and oxidant:

$$\text{phO}\cdot + \text{Ox}^{-}\cdot \rightarrow \text{phO}^{-} + \text{Ox} \qquad (4)$$

A yield of 8% for addition of OH at C_1 is reasonable in view of the observation[8,14] of essentially the same fraction in the reaction of OH with anisole. The value of 8% may contain a contribution due to H abstraction by OH from the phenolic OH group. This type of reaction has been proposed to contribute in OH reactions with aliphatic alcohols.[15]

By analogy with the 1,1-*methoxy*hydroxycyclohexadienyl radical, where oxidation could not compete with elimination,[14] it is suggested that all the 1,1-dihydroxycyclohexadienyl radicals decay by water elimination and not by oxidation. From the fact that no products were detected other than the isomeric dihydroxybenzenes, it is concluded that the (isomeric) hydroxycyclohexadienyl radicals formed[13] by addition of the H atom to phenol react with the oxidants to regenerate phenol (eq 5).



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2. Pulse Radiolysis Studies. Dihydroxycyclohexadienyl radicals were produced by pulse irradiating N_2O-saturated aqueous solutions containing 10 mM phenol at pH 6-7.5. On addition of 0.05-0.4 mM of the quinones listed in Table II, formation of the semiquinone anions was observed. With *p*-benzoquinone, 2-methylbenzoquinone, duroquinone, and anthraquinone 2-sulfonate the buildup, after the pulse, of semiquinone anion consisted of only one exponential component. In the case of 2,5- and 2,6-dimethylbenzoquinone as oxidants slight deviations in the buildup kinetics of semiquinone anion from the single-exponential type were observed. These deviations are interpreted in terms of formation of semiquinone anion via two parallel processes with rate constants differing by a factor of ~2. However, the signal-to-noise ratio in the experimental traces was not sufficient to permit an exact analysis of the relative contributions and the rate constants of the two processes. The rate constants for reduction of 2,5- and 2,6-dimethylbenzoquinone presented in Table II are therefore characterized by an error limit of ±50% as compared to ±10% for the other rate constants.

Although the rate constants for reduction of the quinones listed in Table II are all $>1 \times 10^9$ M^{-1} s^{-1}, the yields of semiquinone formed within 100 μs after the pulse are <100% of *G*(OH), which means that a fraction of the dihydroxycyclohexadienyl radicals react with rate constants $\leq 2 \times 10^7$ M^{-1} s^{-1}. In the case of *p*-benzoquinone, 2-methyl-, and 2,5- and 2,6-dimethylbenzoquinone this "unreactive" fraction amounts to ~20% while with 2,3,5,6-tetramethylbenzoquinone and anthraquinone 2-sulfonate as oxidants the fraction of OH adducts not scavengeable within 100 μs after the pulse corresponds to ~60%.[16] The 20% fraction is suggested to consist of 1,3- and 1,1-dihydroxycyclohexadienyl radicals (or phenoxyl radicals produced from them by rapid water elimination), while the 60% group is proposed to contain in addition 1,2-dihydroxycyclohexadienyl radicals formed by OH attachment to the ortho position of phenol. On the basis of this interpretation all quinones investigated (Table II) are unreactive ($k \leq 2 \times 10^7$ M^{-1} s^{-1}) with respect to 1,1- and 1,3-dihydroxycyclohexadienyl radicals; *p*-benzoquinone, 2-methyl-, and 2,5- and 2,6-dimethylbenzoquinone react with 1,2- and 1,4-dihydroxycyclohexadienyl radicals with equal rate constants (k = (2-4) $\times 10^9$ M^{-1} s^{-1}) and therefore do not discriminate between these radicals, whereas both 2,3,5,6-tetramethylbenzoquinone (duroquinone) and anthraquinone 2-sulfonate oxidize one isomer (the 1,4 isomer; $k \sim 2 \times 10^9$ M^{-1} s^{-1}) much more rapidly than the other (the 1,2 isomer; $k \leq 2 \times 10^7$ M^{-1} s^{-1}; see section 3).

As seen from Table II, the rate constant for reduction of

Table II. Rate Constants for Electron Transfer from Isomeric Dihydroxycyclohexadienyl Radicals to Oxidants and Yields of *o*- and *p*-Dihydroxycyclohexadienyl Radical from the Reaction of OH with Phenol[a]

oxidant	$k(\mathrm{ox})_p/\mathrm{M}^{-1}\,\mathrm{s}^{-1}$	$k(\mathrm{ox})_o/\mathrm{M}^{-1}\,\mathrm{s}^{-1}$	$k(\mathrm{ox})_m/\mathrm{M}^{-1}\,\mathrm{s}^{-1}$	$[G(o \text{ isomer}) + G(p \text{ isomer})]/G(\mathrm{OH})$
$K_3Fe(CN)_6$	$3.6 \times 10^{9\,b}$	$3.6 \times 10^{9\,b}$	$(1-2)10^{7\,c}$	0.83
	$4.0 \times 10^{9\,d}$			
p-benzoquinone	3.7×10^9	3.7×10^9	$\sim 2 \times 10^{6\,c}$	0.81
2-methylbenzoquinone	2.2×10^9	2.2×10^9		0.79
2,5-dimethylbenzoquinone	$\sim 2 \times 10^9$	$\sim 1 \times 10^9$	$\sim 1 \times 10^{6\,c}$	0.78
2,6-dimethylbenzoquinone	$\sim 2 \times 10^9$	$\sim 1 \times 10^9$	$\sim 1 \times 10^{6\,c}$	0.78
duroquinone	1.8×10^9	$\leq 2 \times 10^7$		0.39^e
anthraquinone 2-sulfonate	2.1×10^9	$\leq 2 \times 10^7$	$\leq 2 \times 10^{5\,c}$	0.37^e
p-nitrobenzoate	$\leq 3 \times 10^7$	$\leq 3 \times 10^7$	$\leq 3 \times 10^7$	

[a] Determined at pH 6-7.5 and 20 °C. [b] Determined by monitoring the decay of $Fe(CN)_6^{3-}$ at 420 nm. [c] Estimated from the product analysis data of Table I and assuming that the rate constant for dehydration of the OH adduct is $10^3\ \mathrm{s}^{-1}$ at pH 6-7. [d] Determined from competition experiments involving the effect of ferricyanide on the yield of phenoxyl radical at pH 8.2. At the same pH the rate constant for formation of phenoxyl was measured directly and is used as the reference value. [e] Value represents $G(p \text{ isomer})/G(\mathrm{OH})$ (see text).

ferricyanide is $\sim 4 \times 10^9\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$.[17] A single exponential type decay of the absorption at 420 nm of ferricyanide was observed. At 100 μs after the pulse this decrease corresponded to 83% of the OH radicals. This value is similar to that observed in the case of *p*-benzoquinone and its mono- and dimethyl derivatives. The value is interpreted in terms of reaction within 100 μs of the *o*- and *p*- but not the *i*- and *m*-dihydroxycyclohexadienyl radicals.

3. Identification of the Isomeric Dihydroxycyclohexadienyl Radicals. From the pH dependence of the yields of the isomeric dihydroxybenzenes obtained in the presence of 2-methyl- and 2,5-dimethylbenzoquinone as oxidants of the dihydroxycyclohexadienyl radicals (Table I) the following relation can be written:

$$k(\mathrm{ox})_m/k(\mathrm{deh})_m < k(\mathrm{ox})_p/k(\mathrm{deh})_p < k(\mathrm{ox})_o/k(\mathrm{deh})_o \quad (6)$$

A similar relation was found to hold for isomeric methoxyhydroxycyclohexadienyl radicals.[14] Neglecting the k_m values and since for 2-methyl- and 2,5-dimethylbenzoquinone $k(\mathrm{ox})_o \sim k(\mathrm{ox})_p$ (Table II), in order for relation 6 to be fulfilled, $k(\mathrm{deh})_p > k(\mathrm{deh})_o$. To test this prediction, pulse radiolysis experiments were performed using optical detection and monitoring the buildup, at pH 3-4, of the absorption of phenoxyl at 400 nm. The growth kinetics of phenoxyl radical (Figure 1) was found to be analyzable in terms of formation of phenoxyl by two parallel processes with approximately equal contributions to the total formation of phenoxyl which corresponded, at pH 3, to ~80% of $G(\mathrm{OH})$. The rate constants for production of phenoxyl by reaction of H^+ with the two kinetically distinquishable OH adduct isomers are $k(\mathrm{deh})_o \sim 1 \times 10^8\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ and $k(\mathrm{deh})_p \sim 1 \times 10^9\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$, in good agreement with data reported by Land and Ebert.[13] On the basis of relation 6, these rate constants have to be assigned to the *o*- and *p*-dihydroxycyclohexadienyl radical, respectively. The rate constants are larger and the ratio $k(\mathrm{deh})_p/k(\mathrm{deh})_o$ is smaller than those[14] for reaction with H^+ of the corresponding methoxyhydroxycyclohexadienyl radicals, a reaction which yields the anisole radical cation.[14,18]

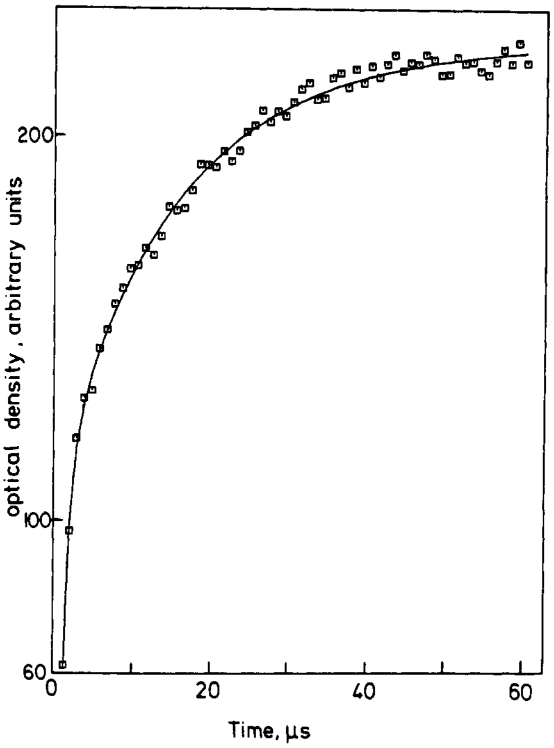


Figure 1. Buildup of the absorption of the phenoxyl radical at 400 nm after pulse irradiation of a N_2O-saturated 3 mM phenol solution at pH 3.35. The solid line is from a computer fit[14] assuming two parallel processes leading to the production of the phenoxyl radical. Note that the origin of the *y* axis is below the *x* axis.

On the basis of the identification of the *o*- and *p*-dihydroxycyclohexadienyl radical with respect to their rates of H^+-catalyzed dehydration, the isomer responsible for reducing duroquinone or anthraquinone 2-sulfonate with $k = 2 \times 10^9\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ can be identified from the pH dependence of the yields of *o*- and *p*-dihydroxybenzene as contained in Table I. From the pulse radiolysis experiments involving, e.g., anthraquinone 2-sulfonate $k(\mathrm{ox})_p/k(\mathrm{ox})_o$ is either $\sim 10^2$ or $\sim 10^{-2}$. If the former is the correct number, introducing competition between anthraquinone 2-sulfonate and H^+ for the dihydroxycyclohexadienyl radicals by increasing $[H^+]$ should result in only a small decrease in the yield of hydroquinone but in a pronounced reduction in that of catechol. As seen from Table I, the yield of hydroquinone decreases by a factor of only 2 in going from pH 6 to 3, whereas that of catechol decreases to <3% of its original value. For anthraquinone 2-sulfonate $k(\mathrm{ox})_p/k(\mathrm{ox})_o$ is therefore $\sim 10^2$ and it is suggested that the same is true for duroquinone (see Table II).

Competition between oxidation and dehydration takes place also with the *m*-dihydroxycyclohexadienyl radical. The dependence of the yield of resorcinol on the oxidizing power of the oxidant (Table I) reflects differences in the rate constants $k(\mathrm{ox})_m$ between the oxidants. At pH 6 oxidation is quantitative only if ferricyanide is the oxidant, whereas in the presence of, e.g., anthraquinone 2-sulfonate only <3% of the *m*-dihydroxycyclohexadienyl radicals are oxidized.

4. Mechanism of the Reaction between Oxidants and Dihydroxycyclohexadienyl Radicals. As in the case of methoxyhydroxycyclohexadienyl radicals,[14] the pronounced depen-

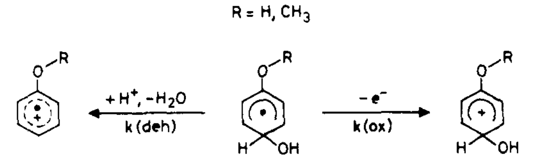
Table III. Relative Reactivities of Isomeric Dihydroxycyclohexadienyl (R = H)[a,b] and Methoxyhydroxycyclohexadienyl (R = CH_3)[c] Radicals with One-Electron Oxidants

oxidant	redox pot.[d]/mV	$k(ox)_p(R = H)/k(ox)_o(R = H)$	$k(ox)_p(R = CH_3)/k(ox)_o(R = CH_3)$	$k(ox)_p(R = H)/k(ox)_p(R = CH_3)$	$k(ox)_o(R = H)/k(ox)_o(R = CH_3)$
$K_3Fe(CN)_6$	+360	1.0	1.0	1.5	1.5
p-benzoquinone	+99	1.0	3.8	0.9	3.2
2-methylbenzoquinone	+23	1.0	6.6	1.0	6.3
2,5-dimethylbenzoquinone	−67	~2	18.5	~1	~9
2,6-dimethylbenzoquinone	−80	~2	21.5	~1	~12
duroquinone	−235	≥90	≤100	~40	
anthraquinone 2-sulfonate	−380	≥100		≥200	

[a] For the definition of R see eq 7. [b] This work. [c] From ref 14. [d] See ref 19.

dence of the rate constant $k(ox)$ on the isomeric structure of the dihydroxycyclohexadienyl radical (Table II) is evidence for a highly polar transition state as expected[5,14] only on the basis of an electron-transfer mechanism. With all oxidants investigated, the ratios $k(ox)_o/k(ox)_m$ and $k(ox)_p/k(ox)_m$ are >100; however, the stronger oxidants ferricyanide, *p*-benzoquinone, and 2-methylbenzoquinone do not distinguish between the *o*- and the *p*-dihydroxycyclohexadienyl radicals. Discrimination between these isomers becomes possible with the weaker oxidants duroquinone and anthraquinone 2-sulfonate. As in the case of isomeric methoxyhydroxycyclohexadienyl radicals,[14] this is due to $k(ox)_o$ being more sensitive than $k(ox)_p$ to the redox potential[19] of the oxidant.

A comparison of the relative reactivities of isomeric dihydroxy- and methoxyhydroxycyclohexadienyl radicals with one-electron oxidants is shown in Table III. Equation 7 describes the processes involved, using the para isomer as an example, and it defines R. The dependence on the oxidant's redox potential of the ratio $k(ox)_p/k(ox)_o$ is seen to depend on the nature of the substituent R of the hydroxycyclohexadienyl radical. Discrimination between the ortho and para isomers sets in at a higher redox potential level with *methoxy*hydroxycyclohexadienyl than with *di*hydroxycyclohexadienyl radicals. For example, for 2-methylbenzoquinone $k(ox)_p/k(ox)_o$ is 6.6 if R = CH_3; however, the ratio is 1.0 if R = H. (An analogous phenomenon is observed for $k(deh)_p/k(deh)_o$; this ratio is 10 if R = H as compared[14] to 15 for R = CH_3.) The stronger oxidant ferricyanide does not discriminate between the ortho and para isomers even if R = CH_3.



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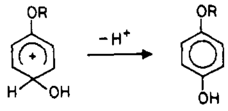

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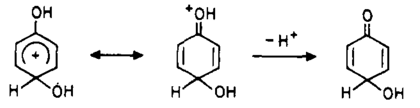
There is also a pronounced effect of R on the $k(ox)$ values for corresponding isomers, provided that the redox potential of the quinone is sufficiently low. For example, for duroquinone and anthraquinone 2-sulfonate the ratio $k(ox)_p(R = H)/k(ox)_p(R = CH_3)$ is equal to ~40 and >200, respectively, whereas with the stronger oxidants *p*-benzoquinone or the mono- and dimethylbenzoquinones the ratio is ~1. The ortho isomers are again more sensitive than the para isomers to the redox potential of the oxidant. For example, $k(ox)_o(R = H)/k(ox)_o(R = CH_3)$ is equal to 3.2 and 12, respectively, for *p*-benzoquinone and 2,6-dimethylbenzoquinone. These oxidants do not show any ability to discriminate between the para isomers.

The increase in reactivity and the concomitant decrease in selectivity observed in going from R = CH_3 to R = H is suggested to be due to the fact that OH is a somewhat stronger electron donor than OCH_3. As a result, the activation energy for formation of the positive species (eq 7) will be lower for R = H than for R = CH_3. There is also the possibility that in the case of R = H the transition state is stabilized by contributions from a reaction involving deprotonation from OH, as symbolized by eq 9 for the case of the one-electron-transfer reaction. The final step leading to the observed products is suggested to proceed according to eq 8 or 10. The oxidation mechanism eq 7 and 8 is similar to that previously proposed[5] for other benzene derivatives and inorganic oxidants.



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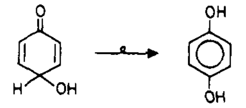

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Pronounced effects of minor changes in substitution have recently also been found for electron-transfer reactions between α-alkoxyalkyl radicals and tetranitromethane.[20]

5. Selectivity of OH Attack. Comparing the product analysis results with the observations made by pulse radiolysis, it is evident that (a) the yield of hydroquinone (36% of the OH radicals) is in agreement with the ~38% value derived for 1,4-dihydroxycyclohexadienyl radical from the pulse radiolysis experiments involving duroquinone and anthraquinone 2-sulfonate as oxidants, and (b) the sum of the yields of catechol and hydroquinone (84%) corresponds to that (80%) of 1,2- and 1,4-dihydroxycyclohexadienyl radicals scavenged by *p*-benzoquinone, 2-methyl-, or 2,5- or 2,6-dimethylbenzoquinone. The distribution of *o*- and *p*-dihydroxycyclohexadienyl radicals and the sum of their yields are thus seen to be equal to those of catechol and hydroquinone formed from the radicals by oxidation. The *m*-dihydroxycyclohexadienyl radical could not be directly identified because its rate of oxidation by even the strongest oxidant (ferricyanide) is still too slow and the yield of the isomer is too low for its detection by pulse radiolysis. However, because of the agreement in the mass balances relating to the ortho and para isomers of the radicals and the products it is reasonable to assume that the yield of resorcinol reflects the fraction of OH attack at the meta position of phenol. If this is the case, the ratio of the probabilities *p* for attachment of OH to *one* ring position, *p*(para):*p*(ortho):*p*(meta), is 9:6:1, which is equal to that observed[6,14] in the reaction of OH with anisole. The OH radical is thus seen to exhibit a strong preference for addition at the positions activated by the OH group. This preference results from the electrophilic character[9] of OH and is in agreement with previous data obtained in similar systems.[5,6,14,21-25] The degree of preference is, however, remarkable in view of the fact that the rate constant for reaction of OH with phenol (k = 1.4 ×

10^{10} M^{-1} s^{-1})[13] is at the upper end of the diffusion-controlled limit.

References and Notes

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(2) Institut für Strahlenchemie im Max-Planck-Institut für Kohlenforschung, D-4330 Mülheim, West Germany. The work described was performed when S. Steenken was a Visiting Scientist at the Notre Dame Radiation Laboratory.

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Proton-Transfer and Electron-Transfer Processes in Reaction of *p*-Nitrotoluene with Bases. A Spectrophotometric Study[1]

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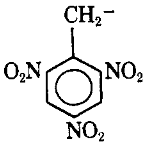
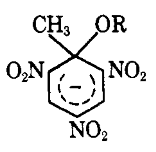
Abstract: The interaction of *p*-nitrotoluene (PNT) with a variety of basic systems has been studied spectrophotometrically. The bases employed, in decreasing order of base strength, were potassium hydride, dimsyl potassium, triphenylmethylpotassium, fluorenylpotassium, and potassium *p*-nitroanilide, while the solvents used were dimethyl sulfoxide, tetrahydrofuran, and dimethoxyethane, with 18-crown-6 ether present in the latter two cases. The major species produced in the reactions were *p*-nitrobenzyl anion (PNT^-), *p*-nitrotoluene radical anion ($PNT^-\cdot$), and *p,p′*-dinitrostilbene radical anion ($DNS^-\cdot$). The principal processes in the PNT-base systems are believed to be (i) $PNT + B^- \rightleftarrows PNT^- + BH$; (ii) $PNT + B^- \rightleftarrows PNT^-\cdot + B\cdot$; (iii) $PNT^- + PNT \rightleftarrows PNT\cdot + PNT^-\cdot$. $DNS^-\cdot$ is formed through secondary processes via *p,p′*-dinitrobibenzyl. Discussion of process (i) is given in terms of the relative pK_as of PNT and the respective BH species, while (ii) is analyzed on the basis of the reduction potential of PNT and the oxidation potential of B^-. For the case of the PNT/Ph_3C^- system, the electron-transfer process (ii) is kinetically preferred but this equilibrium is rapidly established. On the other hand the proton-transfer process (i) is greatly favored thermodynamically and is effectively irreversible; as a result the proton transfer predominates. This is in accord with observation of PNT^- as the initially formed species in this system. The processes occurring in the other base systems are similarly analyzed. The assignment of the absorption due to the *p*-nitrobenzyl anion is at variance with an earlier literature report deduced from examination of the PNT/*t*-BuOK/*t*-BuOH system. Electron-transfer and proton-transfer processes in the PNT/*t*-BuO^- system are also discussed.

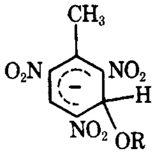
The interaction of aromatic nitro compounds with bases can give rise to processes involving charge transfer, electron transfer, proton transfer and σ-complex formation, as well as to nucleophilic substitution when a displaceable group is present.[2-9] In the case of 2,4,6-trinitrotoluene interacting with alkoxide bases, we have identified and studied in detail the processes involving proton transfer yielding the 2,4,6-trinitrobenzyl anion (**1**) and σ-complex formation resulting in adducts **2a** or **2b**.[10-12] Under other conditions, the dianion **3** has also been identified.[13]



1



2a



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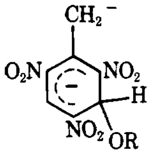
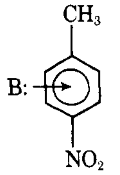


3

The *p*-nitrotoluene (PNT)-base system has been especially challenging in that, whereas stable σ complexes have apparently not been observed, the processes involving charge transfer (**4**), electron transfer (**5**), and proton transfer (**6**), as well as free-radical species (**7**), have all been reported.[14-16] However, the system is complicated by the instability of these species as generated under typical reaction conditions; the product which is isolated in the reaction of PNT with alkoxide ion is actually *p,p′*-dinitrobibenzyl (DNBB, **8**) or *p,p′*-dinitrostilbene (DNS,



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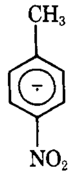
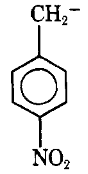
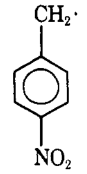


5 ($PNT^-\cdot$)



6 (PNT^-)



7 ($PNT\cdot$)

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