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Substituent effects on rates of one-electron oxidation of phenols by the radicals ClO2, NO2, and SO3

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for the adduct $+ O_2$ reaction include the following:

$$CH_3SCH_3OH + O_2 \rightarrow CH_3S(O)CH_3 + HO_2$$
 (17a)
(Me₂SO)

$$\rightarrow$$
 CH₃O₂ + CH₃SOH (17b)

CH₃SOH is probably converted to CH₃SO₃H (methanesulfonic acid) by reaction with O2 while the atmospheric fate of Me2SO is unclear. Me₂SO has a very low vapor pressure and may be rapidly removed via heterogeneous processes.

At 298 K our results demonstrate that reaction 1 in 1 atm of air proceeds 70% via abstraction and 30% via (irreversible) addition. Photooxidation studies have been reported by Niki et al.23 and Hatakeyama and Akimoto,²⁴ where SO₂ yields from OHinitiated oxidation of CH₃SCH₃ were reported to be 22% and 21%, respectively. Large yields of methanesulfonic acid were observed

in both studies. At present, there is insufficient information to allow SO₂ production to be associated with either the abstraction route or the addition route. However, it should be noted that our results suggest that abstraction is the dominant reaction pathway for T > 300 K while addition is the dominant pathway for T < 100270 K. Hence, temperature-dependent product analysis studies should shed some light on the detailed pathways for SO2 and CH₃SO₃H production.

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Substituent Effects on Rates of One-Electron Oxidation of Phenois by the Radicals CIO₂, NO_2 , and SO_3^-

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Rate constants for the reactions of ClO₂, NO₂, and SO₃ radicals with several substituted phenoxide ions have been measured by pulse radiolysis. They vary from the immeasurably slow (<10⁴) to almost diffusion-controlled rates (>10⁹ M⁻¹ s⁻¹) and depend on the redox potentials of the phenoxide ions and the inorganic radicals. With the weak oxidant SO₃⁻ reverse reactions were observed in certain cases; i.e., the phenoxyl radical oxidizes sulfite ions. An attempt is made to correlate the rate constants with Hammett's substituent constants and the results are compared with those obtained previously for the reactions of various inorganic radicals with phenols and phenoxide ions.

Introduction

One-electron oxidation of phenoxide ions to phenoxyl by the azide radical takes place very rapidly

$$XC_6H_4O^- + N_3 \rightarrow XC_6H_4O^{\bullet} + N_3^-$$
 (1)

with $k_1 = 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for a variety of substituted phenols, with little selectivity. On the other hand, reaction of N₃ with the neutral phenols is much more selective

$$XC_6H_4OH + N_3 \rightarrow XC_6H_4O^{\bullet} + H^{+} + N_3^{-}$$
 (2)

and its rate constant varies from $4 \times 10^7 \,\mathrm{M}^{-1} \,\mathrm{s}^{-1}$ for p-cyanophenol to $4 \times 10^9 \,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ for hydroquinone at pH 5.8.1 This difference in selectivity is obviously owing to changes in the one-electron redox potential of the phenols associated with their acid-base equilibria (eq 3). At high pH the phenoxide ions examined have

$$XC_6H_4OH \Rightarrow XC_6H_4O^- + H^+ \tag{3}$$

redox potentials in the range of 0-1 V,^{2,3} while in neutral solutions the redox potentials are higher by $\sim 0.5 \text{ V}$. The potential for the azide radical was estimated to be $E(N_3/N_3^-) = 1.9 \text{ V.}^4$ This is high enough to make its reaction with any of the phenoxide ions practically diffusion controlled; only in neutral solutions does selectivity become apparent. To achieve high selectivity in the oxidation of phenoxide ions it is necessary to use radicals which are much weaker oxidants than N_3 . One such radical is \dot{SO}_3^- , which was found to oxidize hydroquinone very rapidly at high pH but not phenol.^{3,5} In fact, with phenol it enters into the equilibrium

$$\dot{S}O_3^- + C_6H_4O^- \rightleftharpoons SO_3^{2-} + C_6H_4O^{\bullet}$$
 (4)

with $k_4 = 6 \times 10^5$ and $k_{-4} = 1 \times 10^7 \,\mathrm{M}^{-1} \,\mathrm{s}^{-1.3}$ This indicates that SO_3^- is a weak oxidant $(E(SO_3^-/SO_3^{2-}) = 0.63 \text{ V vs. NHE})^3$ which will not attack many phenols. The radicals ClO2 and NO2 are known to be slightly stronger oxidants $(E(ClO_2/ClO_2) = 0.94$ V and $E(NO_2/NO_2^-) = 1.03$ V vs. NHE)^{6,7} that can oxidize phenoxide ions relatively slowly and p-methoxyphenoxide more rapidly.8 Therefore, it appears that radicals having a redox potential in the range of 1 V are good candidates for exploring the effect of substituents on rates of oxidation of phenoxide ions. We have examined the reactivity of ClO₂ and NO₂ with a variety of substituted phenols, attempted to measure the rate constants for SO₃ with several additional phenols, and compared the results with those obtained previously with N_3 and with other radicals.

Experimental Section⁹

Sodium chlorite was obtained from Eastman, sodium nitrite was a Fisher Certified ACS reagent, and sodium sulfite was a Mallinckrodt Analytical reagent. The phenols were obtained from Aldrich. Water was purified by a Millipore Milli-Q system. Fresh solutions were prepared before each experiment. They were

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⁽⁹⁾ Certain commercial equipment, instruments, or materials are identified in this paper in order to specify adequately the experimental procedure. Such identification does not imply recognition or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified are necessarily the best available for the purpose.

TABLE I: Rate Constants for Oxidation of Phenoxide Ions by Various Radicals

	k , a M^{-1} s^{-1}			
compd	ClO ₂	NO ₂	SO ₃ -	
hydroquinone	1.5 × 10 ^{9 b}	1.1×10^{9}	$3 \times 10^{8} c$	
resorcinol	1.4×10^{9}	3.8×10^{8}	1.5×10^{8}	
p-methoxyphenol	$7.4 \times 10^{8 b}$	1.4×10^{8} b	1.2×10^{84}	
m-methoxyphenol	4.9×10^{7}	1.8×10^{7}	1.1×10^{6}	
p-cresol	2.6×10^{8}	3.4×10^{7}	e	
m-cresol	4.7×10^{7}	1.3×10^{7}	≤10 ⁴ f	
phenol	2.9×10^{7} g	8.6×10^{68}	$6 \times 10^{5 h}$	
p-bromophenol	2.7×10^{7}			
p-cyanophenol	$\leq 4 \times 10^3$			
p-nitrophenol	$\leq 4 \times 10^5$			

^a Determined in the present study at pH 12.2-12.4 unless otherwise indicated. b From ref 8, pH 12.0. From ref 5, estimated from Figure 1 for pH 12.5. From ref 3. No oxidation of p-cresol by SO₃ was observed: the reverse reaction is expected to occur. Reaction is very slow in either direction. From ref 8, pH 12.1. From ref 3, pH 11.1. The reverse reaction is faster $(1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1})$.

bubbled with N₂O and then the pH was adjusted with KOH. Other details of the experiments and the pulse radiolysis apparatus are as described before.3,5,8

The radicals ClO₂, NO₂, and SO₃ were produced by reaction of OH radicals with the corresponding anion. The rate constants for their reactions with the phenols were monitored by following the buildup of the phenoxyl radical absorption at 400-430 nm. Second-order rate constants were derived from linear plots of the first-order rate constants vs. phenol concentration and are accurate to $\pm 15\%$. All measurements were done at room temperature, 21 ± 1 °C.

Results and Discussion

The rate constants for oxidation of phenoxide ions by ClO₂, NO₂, and SO₃⁻ radicals are summarized in Table I. They cover a very wide range, from the immeasurably slow for the cyano and nitro derivatives to the almost diffusion controlled for hydroquinone. The pattern of reactivities of ClO₂ and NO₂ is very similar, with a ratio of $k(ClO_2)/k(NO_2) = 4 \pm 2$. The higher rate constants for ClO2, despite the slightly lower redox potential, are in line with the faster self-exchange rate of ClO₂/ClO₂, as discussed before.8

The rate constants for SO₃ are generally lower and in the case of phenol and the two cresols the reaction occurs predominantly in the reverse direction, i.e. the phenoxyl radicals oxidize sulfite ions owing to the lower redox potential of the sulfite radical.

It is noted that m-methoxyphenol is oxidized by SO_3^- while p-cresol is not. In contrast, p-cresol is oxidized by ClO₂ and NO₂ more rapidly than is m-methoxyphenol. To understand this apparent discrepancy we examined reaction 5 between the two

$$4-CH_3C_6H_4O^* + 3-CH_3OC_6H_4O^- \rightleftharpoons 4-CH_3C_6H_4O^- + 3-CH_3OC_6H_4O^*$$
 (5)

phenols and found it to proceed to the right, with $k_5 = 1 \times 10^6$ M⁻¹ s⁻¹. This indicates that p-cresol has a higher redox potential than m-methoxyphenol, in agreement with the observation on their reactions with SO_3^- . The reverse behavior with ClO_2 and NO_2 must be due to factors other than redox potentials, such as the rates of self-exchange of XPhO^{*}/XPhO⁻.

There is insufficient information on the redox potentials of the phenols in Table I to permit detailed correlation with rate constants. An attempt has been made, therefore, to correlate the reactivities with Hammett's substituent constants σ . The dependence of the relative rate constants (log k/k_0 , where k_0 is for the unsubstituted phenol) on the substituent constant (Figure 1) shows the general trend expected for an electrophilic reactant but the detailed correlation is limited and the data points are somewhat scattered. The limitation of the plot results from two factors. At the upper rate constant range the reactions approach the diffusion-controlled limit and thus the line curves toward a plateau. At the lower rate constant range the redox potential of the phenol

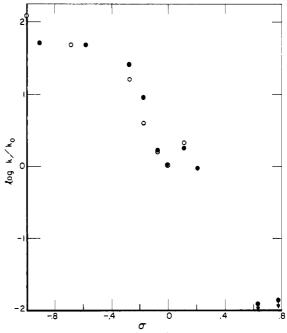


Figure 1. Dependence of the relative rate constants for oxidation of phenoxide ions by ClO₂ (•) and NO₂ (O) on Hammett's substituent constants σ (taken from Wiberg, K. B. Physical Organic Chemistry; Wiley: New York, 1964; p 410, and corrected to account for a mixture of OH and O substituents in the case of hydroquinone and resorcinol). The following σ values were used: p-O⁻, -1.0; m-O⁻, -0.71; p-OH, -0.36; m-OH, -0.002; p-CH₃, -0.17; m-CH₃, -0.07; p-OCH₃, -0.27; m-OCH₃, 0.115; p-Br, 0.23; p-CN, 0.63; p-NO₂, 0.78.

TABLE II: Reactivities of Phenol and Phenoxide Ion with Various

radical	k, M ⁻¹ s ⁻¹	E, V vs. NHE	ρ
		1O-	
N_3	$4.3 \times 10^{9} a$	1.90 ^b	-0.05^{c}
0 <u>-</u>	$6.5 \times 10^{8} d$	1. 7 6e	-0.1 ^f
PO ₄ 2-	5.9×10^{8}		
CO ₃ -	$2.4 \times 10^{8 h}$		-1.0^{h}
Br ₂	2.9×10^{8i}	1.63°	-1.1^{i}
$(SCN)_2^-$	$3.4 \times 10^{8}i$	1.50^{b}	-1.2^{i}
BrO ₂	2.6×10^{9j}	1.33^{k}	
I_2^-	5.7×10^{7i}	1.13^{b}	
Õ,	1.4×10^{9} l	1.01 ^m	
ClO ₂	2.9×10^{7}	0.94^{n}	-3
NO_2	8.6×10^{6}	1.03^{o}	-3
NH_2	$3 \times 10^{6 p}$		-3.3^{p}
SO ₃ ⁻	$6 \times 10^{5} q$	0.63^{q}	
	Ph	ОН	
SO₄⁻	3×10^{9}	2.5-3.15	
Cl ₂	2.5×10^{8} t	2.09e	-1.5^{t}
N_3	5×10^{7} a	1.90^{b}	-2.5^{c}
Br ₂ -	6×10^{6i}	1.63°	
$(SCN)_2^-$	1×10^{7i}	1.50^{h}	
O ₃	1.3×10^{3} l	1.01"	-5"
ClO ₂	$2.4 \times 10^{-1} ^{v}$	0.94"	-10 ^w

^a From ref 1. ^b From ref 4. ^c Estimated from the data of ref 1. ^d From ref 12. ^e From ref 13. ^f Estimated from the data of ref 12. Maruthamuthu, P.; Neta, P., unpublished result. hFrom ref 14. From ref 16. kEstimated in ref 17. From ref 18. "From ref 19. "From ref 6. "From ref 7. "From ref 10. "From ref 3. 'Estimated by comparison with the rate constant for tyrosine, ref 20. 'Estimated in ref 21. 'From ref 22. "Estimated from the data in ref 18. "From ref 23. "Estimated from the data of ref 23.

approaches that of the oxidizing radical or surpasses it, which results in a large decrease in rate constant beyond the range accessible by the present technique. As a result of these limitations and the scatter of data points it is not possible to obtain an exact ρ value for these reactions. A rough estimate of the slope suggest a value of $\rho = \sim -3$ for both ClO₂ and NO₂. This value is similar to that derived for the reaction of NH2 radicals with substituted

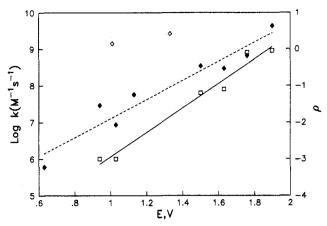


Figure 2. Dependence of the rate constant k (\spadesuit) and reaction constant ρ (\square) (derived from substituent effects) on the redox potential of the oxidizing radical. (The open diamonds are for O₃ and BrO₂, see text).

phenoxide ions (-3.3), ¹⁰ although the absolute rate constants for NH₂ are generally about an order of magnitude lower than those for NO2.

It is interesting to compare the reactivities of phenols and phenoxide ions with various inorganic radicals. Table II presents the rate constants and redox potentials for various radicals. It is clear from the table and from the plot in Figure 2 that a reasonable correlation exists between the rate constants and the driving force for the reaction, as expected from the Marcus theory. 11 Some scatter of the data is expected, e.g. due to differences in the self-exchange rates of the various radicals as discussed before for ClO₂ and NO₂.8 In the case of BrO₂ and O₃, however, the deviations are quite large and probably indicate uncertainties in the reported values of k or E. The ordering of radicals in Table II permits us to estimate the redox potentials for PO₄²⁻ and CO₃⁻ radicals as 1.5-1.8 V and for the NH₂ radical as 0.7-0.8 V.

The lower part of Table II indicates that the rate constants for oxidation of phenols are considerably lower than those for phenoxide ions. Part of this effect is due to the lower driving force of the reaction resulting from the higher redox potential of PhOH as compared with that of PhO-. The redox potential of PhO- was determined at high pH to be 0.70 V.^3 From the p K_a of phenol (10.0) the redox potential of PhOH at pH 7, where most of the rate constants under consideration have been determined, is calculated to be 0.88 V. After correcting for the decreased driving force it still appears that oxidation of PhOH is about an order of magnitude slower than that of PhO-. This difference may result from the fact that oxidation of phenol to phenoxyl radical involves elimination of a proton as well (see, e.g., reaction 2) which apparently slows down the overall observed rate of reaction.

The selectivity of the oxidizing radical is represented by the value of p derived from substituent effects. Table II shows that ρ is very low when the driving force is high and the rate constants approach the diffusion-controlled limit. The selectivity clearly increases for the slower reactions (with lower driving force). The data available are insufficient for a detailed correlation but the trend is clearly demonstrated in Figure 2. This trend is predictable also from the shape of the theoretical curve of $\log k$ vs. ΔE based on the Marcus theory.

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Registry No. p-MeOC₆H₄OH, 150-76-5; m-MeOC₆H₄OH, 150-19-6; PhOH, 108-95-2; p-BrC₆H₄OH, 106-41-2; p-CNC₆H₄OH, 767-00-0; p-NO₂C₆H₄OH, 100-02-7; ClO₂, 10049-04-4; NO₂, 10102-44-0; SO₃-, 14265-45-3; hydroquinone, 123-31-9; resorcinol, 108-46-3; p-cresol, 106-44-5; m-cresol, 108-39-4.

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