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Formation and Reactivity of Phenylperoxyl Radicals in Aqueous Solutions

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The reaction of phenyl radicals with oxygen, to produce phenylperoxyl radicals, and the reactions of several phenylperoxyl radicals with a number of organic compounds in aqueous solutions have been studied by pulse radiolysis. Phenyl radicals were produced by reduction of aryl halides with hydrated electrons. The rate constant for the reaction of 4-carboxyphenyl with O_2 was determined from the rate of buildup of the peroxyl radical absorption at 520 nm as a function of $[O_2]$ and found to be 1.6×10^9 L mol^{-1} s^{-1}. Phenyl radicals react with 2-PrOH by H abstraction; a rate constants of 4×10^6 L mol^{-1} s^{-1} was determined for 4-carboxyphenyl by competition with the reaction of this radical with O_2. Phenylperoxyl radicals react with 4-methoxyphenolate ions, trolox C (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid), ascorbate ions, chlorpromazine, and ABTS [2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonate ion)] by one-electron oxidation. The rate constants for such reactions, determined from the rate of formation of the one-electron oxidation product as a function of substrate concentration, were found to be near 10^8–10^9 L mol^{-1} s^{-1}. The reaction with neutral phenols, however, was much slower and could not be observed under the pulse radiolysis conditions. Phenylperoxyl radicals are found to be much more reactive than methylperoxyl and more reactive than most substituted methylperoxyls, except for the halogen-substituted radicals. Electron-withdrawing substituents at the 4-position of phenylperoxyl increase the rate constant and electron-donating groups decrease the rate constant for oxidation by this radical, in accordance with the Hammett substituent constants.

Introduction

Rate constants have been measured for a large number of reactions of peroxyl radicals with organic substrates.[1] Most of the radicals studied were substituted alkylperoxyls. A strong effect of the substituent on the reactivity has been observed in reactions with several substrates, such as ascorbate,[2,3] TMPD (tetramethyl-*p*-phenylenediamine),[2] and chlorpromazine [2-chloro-10-(3-(dimethylamino)propyl)phenothiazine hydrochloride] (ClPz).[4] In general, electron-withdrawing groups on the methylperoxyl radical increase its reactivity in electron-transfer, addition, and H-abstraction reactions. The most reactive radicals are the polyhalogenated ones, such as $CX_3O_2^{\bullet}$. On this basis, phenylperoxyl radicals are expected to be more reactive than methylperoxyl, but they have not been characterized or studied. Since a recent report[5] indicated that phenyl radicals react rapidly with O_2 (reaction 1),we decided to study the reactivity of

$$C_6H_5^{\bullet} + O_2 \rightarrow C_6H_5O_2^{\bullet} \qquad (1)$$

phenylperoxyl radicals with several organic compounds. We find that these radicals are indeed much more reactive than methylperoxyl.

In the course of these studies, we encountered some difficulty with the recent results[5] on reaction 1, which we wish to outline before discussing our results. Reaction 1 has been examined for 4-carboxyphenyl, $^{-}O_2CC_6H_4^{\bullet}$, which was produced by laser flash photolysis of 4-iodobenzoate ions in aqueous solutions.[5]

$$^{-}O_2CC_6H_4I \xrightarrow{h\nu} {}^{-}O_2CC_6H_4^{\bullet} + I^{\bullet} \qquad (2)$$

To measure the rate constant for the reaction of the phenyl radical with O_2, the authors used phenol as a probe, suggesting reaction 3,and monitoring the buildup of absorption at 380 nm as a function

$$^{-}O_2CC_6H_4^{\bullet} + HOC_6H_5 \rightarrow {}^{-}O_2CC_6H_5 + {}^{\bullet}OC_6H_5 \qquad (3)$$

of O_2 concentration (using varying N_2/O_2 ratios in a mixture bubbled under atmospheric pressure). As expected, they found that increasing $[O_2]$ led to a decrease in the observed optical absorbance and an increase in the observed rate constant, according to $k_{obs} = k_0 + k_1[O_2]$. From the linear plot of k_{obs} vs $[O_2]$, they calculated $k_1 = 3.8 \times 10^9$ L mol^{-1} s^{-1}. Although this value is reasonable in view of the rate constants measured for similar reactions with aliphatic radicals,[1] the authors used incorrect O_2 concentrations; they quote a value of 2.65×10^{-4} mol L^{-1} for the solubility of O_2 in water at 760 Torr of O_2 at 25 °C and cite Battino's review.[6] That review, however, as well as many other sources, give values of $(1.2$–$1.3) \times 10^{-3}$ mol L^{-1} for the solubility of oxygen under these conditions. It appears that they used the solubility of oxygen under air, i.e., 4.8 times too low, and thus, their rate constant is 4.8 times too high.

With respect to reaction 3, it should be noted that although phenyl radicals have been shown to add to the aromatic ring of several compounds,[7-9]

$$^{-}O_2CC_6H_4^{\bullet} + C_6H_5OH \rightarrow {}^{-}O_2CC_6H_4\dot{C}_6H_5OH \qquad (4)$$

and although the 380-nm absorption used in the previous study[5] may be due to reaction 3 or to adduct formation,[10] the reported measurements are valid and a value of $k_1 = 7.9 \times 10^8$ L mol^{-1} s^{-1} (corrected for the O_2 concentration) can be accepted. On the other hand, if the iodine atom produced by photolysis (reaction 2) reacts with phenol to give phenoxyl radical on the same time scale as reaction 3 (our preliminary laser flash photolysis experiments show that this reaction takes place ca. 5 times more slowly), this may introduce some error in the measurement of k_1.

To study the reaction of phenyl radicals with oxygen and the reactions of phenylperoxyl radicals with organic compounds, we utilize the pulse radiolysis technique. By this technique, phenyl radicals are produced by reductive dehalogenation, and thus, no iodine(or halogen) atoms are formed. Further, we utilize 4-methoxyphenol rather than phenol, becuase it is more reactive and the 4-methoxyphenoxyl radical exhibits a red-shifted peak (420 nm) 3 times more intense than that of phenoxyl.

[⊗] Abstract published in *Advance ACS Abstracts*, July 15, 1994.

Experimental Section[11]

The materials used were of the highest grade commercially available and were used as received. 2-Propanol was obtained from Mallinckrodt and *tert*-butyl alcohol from Fisher. Chlorpromazine (ClPz) hydrochloride and 4-methoxyphenol were obtained from Sigma; trolox C (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid, a vitamin E analogue), ABTS [2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonic acid), diammonium salt], and other aryl halides and phenols were from Aldrich. Water was purified by a Millipore Super-Q system. Fresh solutions were prepared before each experiment and were saturated with air, O_2, N_2, or various O_2/N_2 mixtures. Samples were transferred to the irradiation cell and were irradiated with 50-nm pulses of 2 MeV of electrons from a Febetron 705 pulser. Other details of the pulse radiolysis apparatus and data processing were as described before.[2,4]

Rate constants for reactions of phenylperoxyl radicals with organic substrates were measured by following the buildup of absorption of the organic radical produced (ClPz at 520 nm, ascorbate at 360 nm, trolox at 430 nm, ABTS at 415 nm, 4-methoxyphenol at 420 nm, phenol at 400 nm). Each experiment was carried out with at least three different concentrations of the substrate, varying by at least a factor of 4. Second-order rate constants were derived from plots of the first-order rate vs concentration (under conditions where the rate-limiting step is not the reaction of phenyl radicals with O_2). All measurement were carried out at 20 ± 2 °C.

Results and Discussion

Formation of Phenyl Radicals. As in the previous studies,[2,4] we utilize the hydrated electron, formed upon radiolysis of water, to effect reductive dehalogenation of aryl halides to aryl radicals.

$$H_2O \rightsquigarrow e_{aq}^- + H^\bullet + {}^\bullet OH + H^+ + H_2 + H_2O_2 \tag{5}$$

$$ArX + e_{aq}^- \rightarrow Ar^\bullet + X^- \tag{6}$$

The aryl halides used in this study react with e_{aq}^- with $k = 5 \times 10^9$ to 2×10^{10} L mol^{-1} s^{-1},[12] so at millimolar concentrations, reaction 6 is complete within <1 μs.[13] The other radicals formed upon radiolysis, $H^\bullet$ and ${}^\bullet OH$, also can react with the aryl halides rapidly ($k = (1\text{–}5) \times 10^9$ L mol^{-1} s^{-1}) by addition to the ring. To prevent these reactions, we added 2-PrOH at sufficiently high concentrations to react with most of these radicals ($k_{7H} = 7.4 \times 10^7$, $k_{7OH} = 1.9 \times 10^9$ L mol^{-1} s^{-1}).

$$(CH_3)_2CHOH + H^\bullet/{}^\bullet OH \rightarrow (CH_3)_2\dot{C}OH + H_2/H_2O \tag{7}$$

Although the radical produced by reaction 7 has reducing properties[14] and can reduce CCl_4,[15] for example, its reactions with the aryl halides used in this study are too slow to be observed under pulse radiolysis conditions and the radical will preferentially react with O_2,[16] to form a weakly oxidizing peroxyl radical, $(CH_3)_2C(OH)O_2^\bullet$.[2]

The spectrum monitored 1 μs after pulse irradiation of 3×10^{-3} mol L^{-1} 4-bromobenzoate solution containing 0.5% or 5% 2-PrOH at pH 11.5 and deoxygenated by bubbling with N_2 (Figure 1) shows absorption at 300 nm with a tail extending to 450 nm, identical to that obtained in the absence of the aromatic compound. This spectrum is ascribed[17] to the $(CH_3)_2\dot{C}OH$ radical produced by reaction 7.[18] The absorption of the 4-carboxyphenyl radical formed by reaction 8 is expected to be below 300 nm,[9] but the

$$BrC_6H_4CO_2^- + e_{aq}^- \rightarrow Br^- + {}^\bullet C_6H_4CO_2^- \tag{8}$$

peak could not be established due to strong absorbance by the starting material.

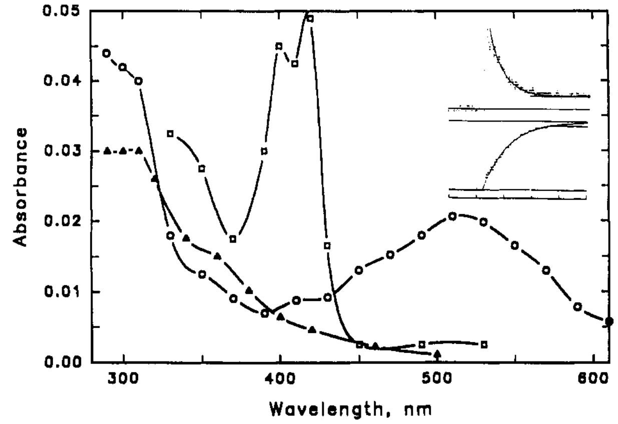

Figure 1. Transient optical absorption spectra monitored by pulse radiolysis of aqueous solutions containing 3×10^{-3} mol L^{-1} 4-bromobenzoate ions and 0.07 mol L^{-1} 2-PrOH at pH 11.5. (▲) Deoxygenated by bubbling with N_2, monitored 1 μs after the pulse; a similar spectrum was found in the absence of the aromatic compound. (○) Air saturated, monitored ~5 μs after the pulse; a similar spectrum but with different intensity was found with higher concentrations of 2-PrOH and with *t*-BuOH but was not observed in the absence of the aromtic compound. (□) Air saturated, in the presence of 2×10^{-3} mol L^{-1} 4-methoxyphenol, monitored ~5 μs after the pulse; inserted traces show decay of absorption at 520 nm (top) and formation at 420 nm (bottom) on a time scale of 2 μs per division (different absorbance scales).

Reactions of Phenyl Radicals. The phenyl radicals produced by reaction 8 under the above conditions may react with 2-PrOH ($k_9 = 3 \times 10^7$ L mol^{-1} s^{-1} has been reported for the reaction of 4-hydroxyphenyl radicals).[8]

$${}^\bullet C_6H_4CO_2^- + (CH_3)_2CHOH \rightarrow C_6H_5CO_2^- + (CH_3)_2\dot{C}OH \tag{9}$$

In O_2-saturated solutions, however, the radicals may react with O_2.

$${}^\bullet C_6H_4CO_2^- + O_2 \rightarrow {}^\bullet O_2C_6H_4CO_2^- \tag{10}$$

The transient spectrum in these solutions (Figure 1) exhibits a broad peak near 520 nm and an intense absorption below 320 nm. This spectrum may be ascribed to the (4-carboxyphenyl)peroxyl radical.[19] The $(CH_3)_2\dot{C}OH$ radicals produced from 2-PrOH also react rapidly with O_2 to form the peroxyl radicals, $(CH_3)_2C(OH)O_2^\bullet$. These radicals, however, absorbs only below 350 nm and rapidly decompose at high pH to form $O_2^{\bullet -}$ radicals,[16a] which absorb at 250 nm.[20]

At the concentrations of O_2 and 4-bromobenzoate used, a substantial fraction of the hydrated electrons react with O_2 to produce $O_2^{\bullet -}$ radicals directly (k for reaction of e_{aq}^- with O_2 is 1.9×10^{10} and with 4-bromobenzoate 7.7×10^9 L mol^{-1} s^{-1}).[12] If we raise the concentration of 4-bromobenzoate to increase the contribution of its reaction with e_{aq}^-, we also raise the fraction of H and OH radicals that react with 4-bromobenzoate instead of with 2-PrOH, and if we raise the concentration of 2-PrOH, this solute will compete with O_2 for the phenyl radicals and decrease the contribution of reaction 10 as compared with reaction 9. These changes in the yield of the phenylperoxyl radicals have been observed experimentally, and because of the complexity of the various competing reactions, we cannot obtain a quantitative yield of these radicals and we do not attempt to calculate their molar absorptivity from these experiments. The absorbance found in our experiments, however, is sufficiently intense to be utilized for kinetic purposes.

The rate of formation of the 520-nm absorption was found to be dependent on O_2 concentration. For best results, we used a 3.3×10^{-3} mol L^{-1} 4-bromobenzoate solution at pH 6.5, not containing alcohol, and measured the rate of formation at 520

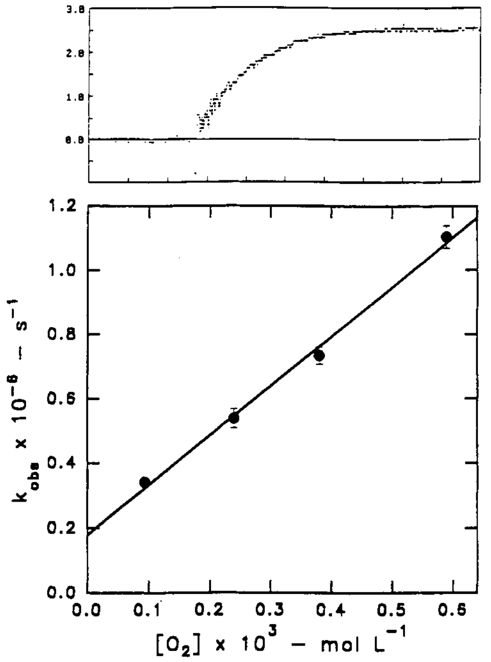

Figure 2. Rate of formation of (4-carboxyphenyl)peroxyl radicals monitored at 520 nm as a function of O_2 concentration. The solutions contained 3.3×10^{-3} mol L^{-1} 4-bromobenzoate at pH 6.5 and were equilibrated with various mixtures of N_2/O_2. The concentration of O_2 in water under 1 atm of pure O_2 was taken as 1.2×10^{-3} mol L^{-1}.

nm at various O_2 concentrations.[21] Figure 2 shows a typical trace at one concentration and a plot of the rate vs $[O_2]$, from which we calculate a rate constant of $(1.6 \pm 0.3) \times 10^9$ L mol^{-1} s^{-1} for reaction 10.

Experiments in aqueous solutions saturated with air and with bromobenzene, either in the absence of or presence of 1% *t*-BuOH, showed a buildup at 520 nm with a rate of $(8 \pm 2) \times 10^5$ s^{-1}, about 30% higher than the value measured with 4-carboxyphenyl. If we assume that this system would exhibit an intercept similar to that of Figure 2, we can estimate the rate constant for reaction 1 as $k_1 = \sim 2.5 \times 10^9$ L mol^{-1} s^{-1}. We did not attempt to determine this value more accurately because if we bubble the solution with various N_2/O_2 mixtures to vary the oxygen concentration, we lose much of the bromobenzene.

In conclusion, it appears that phenyl and substituted phenyl radicals react with O_2 with rate constants near 2×10^9 L mol^{-1} s^{-1}, similar to the rate constants reported for many alkyl and substituted alkyl radicals.[1]

On the basis of the above results for reaction 10, we can utilize this system as a probe to measure rate constants for phenyl radicals with other reactants that produce no readily observable optical absorptions. We carried out such experiments for 2-PrOH. We used air-saturated solutions of 3.3×10^{-3} mol L^{-1} 4-bromobenzoate at pH 6.5 and varied [2-PrOH] from 0 to 0.13 mol L^{-1}. Increasing alcohol concentrations caused an increase in the rate of formation of the 520-nm absorption (Figure 3), and from the concentration dependence, we calculate $k_9 = (4 \pm 1) \times 10^6$ L mol^{-1} s^{-1}. The same value was also derived from the ratio k_9/k_{10} evaluated from the decrease in absorbance at 520 nm (Figure 3), combined with k_{10} derived above. The rate constant we find for reaction 9 is 8 times lower than the literature value for the reaction of 4-hydroxyphenyl with 2-PrOH,[8] which was derived from competition between 2-PrOH and 4-bromophenol monitored through the final yield of phenol and using the earlier value[9] of $k = 7 \times 10^7$ L mol^{-1} s^{-1} for reaction of 4-hydroxyphenyl with 4-bromophenol. The difference between the two results may suggest a lower reactivity of 4-carboxyphenyl as compared with 4-hydroxyphenyl or may be due to inaccuracies in both methods.

Reactions of Phenylperoxyl Radicals. Upon addition of 2×10^{-3} mol L^{-1} 4-methoxyphenol to an air-saturated 4-bromobenzoate solution at pH 11.5, the spectrum of the peroxyl radical at 520 nm is replaced with the characteristic absorption of the 4-methoxyphenoxyl radical (Figure 1), indicating the occurrence of reaction 11. The traces inserted in Figure 1 show that the rate

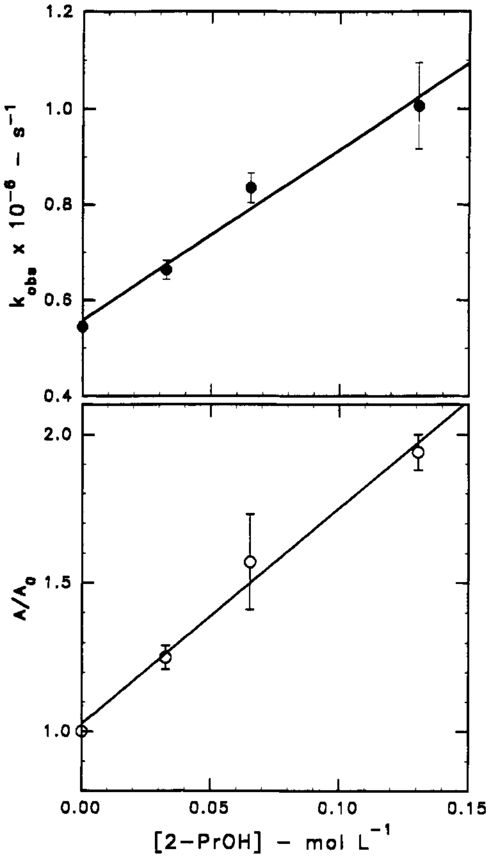

Figure 3. Competition kinetics between the reactions of phenyl radicals with O_2 and with 2-PrOH. (Top) Rate of formation of the 520-nm absorption as a function of 2-PrOH concentration in air-saturated solutions containing 3.3×10^{-3} mol L^{-1} 4-bromobenzoate at pH 6.5. (Bottom) Absorbance ratio as a function of [2-PrOH].

$$^{\bullet}O_2C_6H_4CO_2^- + CH_3OC_6H_4O^- \rightarrow {}^-O_2C_6H_4CO_2^- + CH_3OC_6H_4O^{\bullet} \quad (11)$$

of formation at 420 nm corresponds to the rate of decay at 520 nm. If we assume quantitative reaction of the phenylperoxyl radical to yield 4-methoxyphenoxyl, we find that the molar absorptivity of the former is 0.3 times that of the latter radical. By taking a molar absorptivity of 5500 L mol^{-1} cm^{-1} for 4-methoxyphenoxyl at 420 nm,[22] we calculate a value of 1600 L mol^{-1} cm^{-1} for the molar absorptivity of (4-carboxyphenyl)peroxyl radical at 520 nm.

The 420-nm absorption of the 4-methoxyphenoxyl radical was not observed at pH 7, indicating that reaction of phenylperoxyl radicals with neutral 4-methoxyphenol is too slow to observe under pulse radiolysis conditions. The parallel reaction with unsubstituted phenol is expected to be even slower.

$$^{\bullet}O_2C_6H_4CO_2^- + CH_3OC_6H_4OH \rightarrow HO_2C_6H_4CO_2^- + CH_3OC_6H_4O^{\bullet} \quad (12)$$

Reaction 11 is clearly an electron-transfer reaction, whereas reaction 12 may involve hydrogen abstraction. Solvent effects on the rate constants for reactions of halogenated peroxyl radicals with phenols,[23] however, support the electron-transfer mechanism for reactions with neutral phenols as well (at least in polar solvents), despite the much lower reactivity of phenols compared with phenolate ions.

TABLE 1: Rate Constants for Reactions of Phenylperoxyl Radicals with Organic Compounds

radical	compound	pH	k,[a] L mol^{-1} s^{-1}
4-$^{-}O_2CC_6H_4O_2\cdot$	4-methoxyphenolate	11.5	$(2.7 \pm 0.4) \times 10^8$
	4-methoxyphenol	7.1	$\leq 1 \times 10^7$
	phenolate	11.2	$\leq 2 \times 10^7$
	ascorbate	7.0	$(8.7 \pm 1.3) \times 10^7$
	trolox	11.5	$(2.6 \pm 0.5) \times 10^8$
	trolox	7.1	$(1.0 \pm 0.2) \times 10^8$
	ABTS	11.2	$(7.0 \pm 1.0) \times 10^8$
	ABTS	7.1	$(9.3 \pm 1.2) \times 10^8$
$C_6H_5O_2\cdot$	ABTS	~6	$(6.6 \pm 1.0) \times 10^8$
	ClPz	~6	$(1.5 \pm 0.3) \times 10^8$
	4-methoxyphenolate	11.5	$(2.0 \pm 0.3) \times 10^8$
4-$CH_3C_6H_4O_2\cdot$	ABTS	~6	$(4.9 \pm 0.8) \times 10^8$
4-$HOC_6H_4O_2\cdot$	ABTS	~6	$(3.4 \pm 0.6) \times 10^8$
4-$ClC_6H_4O_2\cdot$	ABTS	~6	$(1.0 \bullet 0.3) \times 10^9$
4-$CNC_6H_4O_2\cdot$	ABTS	~6	$(2.5 \pm 0.4) \times 10^9$
	4-methoxyphenolate	11.4	$(7.1 \pm 1.1) \times 10^8$

[a] There are two major sources of uncertainty in the derived rate constants: the statistical uncertainty in the first- and second-order fits, which were generally between 2% and 10%, though in a few cases they were higher, and errors in the measurements of volumes and weights, which we estimate as 10%.

The rate constant for reaction 11, determined from the rate of formation of the 420-nm peak as a function of 4-methoxyphenolate concentration (between 5×10^{-5} and 3×10^{-4} mol L^{-1}), was found to be $(2.7 \pm 0.4) \times 10^8$ L mol^{-1} s^{-1} (Table 1). When the solution was bubbled with N_2, reaction 11 was not observed, supporting the conclusion that the monitored reaction is of the peroxyl radical. In neutral solution, the rate of reaction of the peroxyl radical was too slow to measure, and we estimate $k \leq 1 \times 10^7$ L mol^{-1} s^{-1}.

Rate constants were measured in a similar way for reactions of other compounds: ascorbate ions, trolox, chlopromazine, and ABTS, monitored at 360, 420, 520, and 415 nm, respectively (Table 1). No reaction was detected for the unsubstituted phenolate ion, and we estimate its reactivity to be at least 10 times lower than that of 4-methoxyphenolate. Trolox, which is a more complex 4-alkoxyphenol, exhibits a reactivity in basic solution similar to that of 4-methoxyphenolate, but its reactivity in neutral solution is considerably higher than that of 4-methoxyphenol, in line with previous findings.[24] The rate constant found for ascorbate indicates that phenylperoxyl radicals are more reactive than most alkylperoxyl and substituted alkylperoxyl radicals,[2] except for those containing halogens at the α-position. The rate constants for chlorpromazine and ABTS are even higher than those reported for monochloromethylperoxyl but lower than those for the polyhalogenated peroxyl radicals.[1] This high reactivity of phenylperoxyl is clearly due to the electron-withdrawing property of the phenyl group which enhances electron acceptance by the oxyl site.

The reactivity of 4-substituted phenylperoxyl radicals is also affected by the substituent. The rate constant for reaction with ABTS increases by a factor of 7 between the least reactive (4-hydroxyphenyl)peroxyl to the most reactive (4-cyanophenyl)-peroxyl, with other radicals having intermediate rate constants. Again the reactivity is increased by electron-withdrawing substituents. A Hammett's plot of log k vs the substituent constant σ_p (Figure 4) gives a straight line with a slope of $\rho = 0.88$. A similar slope is found for the results of 4-methoxyphenolate, though all the rate constants are about 3.4 times lower than those for ABTS.

In summary, phenylperoxyl radicals are fairly reactive one-electron oxidants. They react with a number of organic reductants, including vitamin C and trolox, a water-soluble analogue of vitamin E, in neutral solution, but with most phenols only in alkaline solutions. The reactivity of phenylperoxyl is increased by electron-withdrawing substituents on the phenyl group.

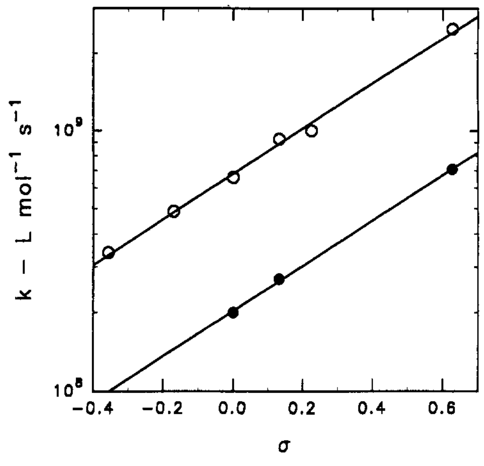

Figure 4. Logarithmic plot of the rate constant for reaction of 4-substituted phenylperoxyl radicals with ABTS (○) in neutral solutions and with 4-methoxyphenolate (●) in alkaline solutions vs the Hammett's substituent constant σ_p (using H, 0.00; CO_2^-, 0.132; CH_3, −0.17; OH, −0.357; Cl, 0.226; CN, 0.628, from: Wiberg, K. B. *Physical Organic Chemistry*, Wiley: New York, 1964; p 410).

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(10) It is possible to distinguish between the phenoxyl radical, which exhibits two main peaks at 385 and 402 nm, the latter being very narrow (Schuler, R. H.; Buzzard, G. K. *Int. J. Radiat. Phys. Chem.* **1976**, *8*, 563) and does not react with O_2, and the adducts, which are expected to have broader absorptions centered around 320–360 nm (see, e.g.: Habersbergerova, A.; Janovsky, I.; Kourim, P. *Radiat. Res. Rev.* **1972**, *4*, 123) and to react rapidly with O_2.

(11) The mention of commercial equipment or material does not imply recognition or endorsement by the National Institute of Standards and Technology nor does it imply that the equipment or material identified are necessarily the best available for the purpose.

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(13) In principle, reaction 6 leads to the formation of the aromatic radical anion, which subsequently undergoes dehalogenation. The rates of dehalogenation for all compounds used in this study, however, are $>10^6$ s^{-1}. See, e.g.: Neta, P.; Behar, D. *J. Am. Chem. Soc.* **1981**, *103*, 103 and references therein.

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(18) In an attempt to eliminate this absorption, we used *t*-BuOH, since the spectrum of its radical is much weaker than that of the radical derived from 2-PrOH.[17] However, *t*-BuOH does not scavenge the H atoms effectively, and these were found to add to the aromatic compound to give a transient absorption in the 320–380-nm range.

(19) Sommeling et al. (ref 5) observed an absorption at ca. 500 nm, which they attributed to this arylperoxyl radical. They also mention (in a note added in proof) that a visible spectrum for phenylperoxyl has been observed by C. von Sonntag.

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(21) The H and OH radicals are allowed to react with the 4-bromobenzoate to produce adducts, known to absorb at 300–400 nm, with negligible absorbance at 500 nm. These adducts also react with O_2 to form peroxyl radicals, which absorb below 300 nm, and our results indicate that these do not absorb at 500 nm.

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