Arylperoxyl Radicals. Formation, Absorption Spectra, and Reactivity in Aqueous Alcohol Solutions

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Aryl radicals (phenyl, 4-biphenylyl, 2-naphthyl, 1-naphthyl, and 9-phenanthryl) were produced by the reaction of the corresponding aryl bromide with solvated electrons and reacted rapidly with oxygen to produce the arylperoxyl radicals. These radicals exhibit optical absorptions in the visible range, with λ_{max} at 470, 550, 575, 650, and 700 nm, respectively. Arylperoxyl radicals react with 2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonate ion) (ABTS), chlorpromazine, and 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox C) by one-electron oxidation. The rate constants k for these reactions, determined from the rate of formation of the one-electron oxidation products as a function of substrate concentration, vary between 4×10^6 and 2×10^9 L mol⁻¹ s⁻¹ and increase in the order phenyl-, 4-biphenylyl-, 2-naphthyl-, 1-naphthyl-, and 9-phenanthrylperoxyl, the same order as the absorption peaks of these radicals. Good correlation was found between log k and the energy of the absorption peak.

Introduction

Most kinetic studies on reactions of peroxyl radicals have concentrated on alkylperoxyl radicals.¹ Rate constants for reactions of alkylperoxyl radicals with several organic compounds have been measured by following the formation of the product radical,²⁻⁴ since these peroxyl radicals exhibit optical absorption only in the UV, generally with λ_{max} near 250 nm and relatively low molar absorptivities ($\epsilon \sim 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$). Recent studies have shown that phenylperoxyl radicals exhibit absorptions in the visible range.⁵⁻⁷ Kinetic measurements at these peaks permitted direct determination of the rate constant for formation of phenylperoxyl radicals via reaction 1 ($k_1 =$ 4.6×10^9 for phenyl⁷ and $1.6 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ for 4-carboxyphenyl⁶ in aqueous solutions).

$$C_6H_5 + O_2 \rightarrow C_6H_5O_2$$
(1)

Rate constants for reactions of these peroxyl radicals with other reactants were also determined by following the decay of their absorption, but more often by following the buildup of an oxidation product radical with a higher molar absorptivity.

Among the aliphatic peroxyl radicals studied, much work has focused on halogenated species, which are more reactive than the non-halogenated analogues, and was aimed at understanding the mechanism of their formation and deleterious effects in biochemical systems. Peroxyl radicals are also formed during detoxification of halogenated compounds by ozone or ionizing radiation and play a major role in the mechanism of decomposition. Since the most hazardous halogenated compounds are aromatic, it is important to study the formation and reactions of peroxyl radicals derived from such compounds. Rate constants for oxidation of several organic compounds by phenylperoxyl radicals were found⁶ to be considerably higher than those for methylperoxyl.¹ In the present study, we examine the absorption spectra and reactivities of other arylperoxyl radicals, those derived from biphenyl, 2-naphthyl-, 1-naphthyl-, and 9-phenanthryl, and compare them with those for phenylperoxyl.

Experimental Section

The materials used were of the highest grade commercially available and were used as received. Methanol (MeOH) was obtained from Mallinckrodt⁸ and tert-butyl alcohol (t-BuOH) from Fisher. Chlorpromazine [2-chloro-10-(3-dimethylaminopropyl)phenothiazine hydrochloride] (ClPz) was obtained from Sigma. Trolox C (6-hydroxy-2,5,7,8-tetra-methylchroman-2carboxylic acid, a Vitamin E analogue), ABTS [2,2'-azinobis-(3-ethyl-benzothiazoline-6-sulfonic acid), diammonium salt], and the aryl halides were from Aldrich. Water was purified by a Millipore Super-Q system. Fresh solutions were prepared before each experiment and were irradiated either under air or after deoxygenation by bubbling with N₂. Samples were transferred to the irradiation cell and were irradiated with 50 ns pulses of 2 MeV electrons from a Febetron 705 pulser. Other details of the pulse radiolysis apparatus and data processing were as described before.^{2,4} All measurement were carried out at room temperature, 20 ± 2 °C.

Absorption spectra of the arylperoxyl radicals were monitored in air-saturated solutions, generally in neat MeOH, and using a high dose per pulse (generally in the range of 200 Gy) because the yield (see below) and the molar absorptivities of these radicals were relatively low. Since the absorption bands are fairly broad, we estimate the uncertainty in the position of the peak as ± 10 nm. Rate constants for reactions of arylperoxyl radicals with organic substrates were measured by following the buildup of absorption of the organic radical produced (CIPz at 520 nm, trolox at 430 nm, and ABTS at 415 nm). Because of the higher molar absorptivities of these radicals, as compared with those of the peroxyl radicals, these kinetic measurements were done with a lower dose per pulse (generally between 5 and 20 Gy). To correct for possible competing reactions, the first-order formation rates were measured with at least three different concentrations of the substrate, varying by about a factor of 4, and the second-order rate constants were derived from plots of the first-order rates vs concentration (under

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conditions where the rate-limiting step is not the reaction of the aryl radical with O_2). 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 uncertainties in the measurements of volumes and weights, which we estimate as 10%. The overall estimated standard deviations are given in the tables along with the rate constants.

Results and Discussion

As in previous studies, $2^{-4,6,7}$ we utilize the solvated electron, formed upon radiolysis of water or alcohols, to effect reductive dehalogenation of aryl halides to aryl radicals.

$$H_2O \longrightarrow e_{aq}^- + H^+ + OH + H^+ + H_2 + H_2O_2$$
 (2)

$$ArX + e_{ao} \rightarrow Ar^{\bullet} + X^{-}$$
 (3)

The aryl halides used in this study react with e_{aq}^{-} with diffusioncontrolled rate constants, $k \sim 10^{10}$ L mol⁻¹ s^{-1,9} so that at concentrations >1 × 10⁻² mol L⁻¹ reaction 3 is complete within <50 ns. The other radicals formed upon water radiolysis, H[•] and •OH, were scavenged by the alcohol to prevent their reaction with the aryl halides. The hydroxyalkyl radicals derived from the alcohol do not react rapidly with aryl halides.¹⁰ In the presence of O₂, both the aryl and hydroxyalkyl radicals produced in these solutions react with O₂ to form peroxyl radicals.

$$Ar^{\bullet} + O_2 \rightarrow ArO_2^{\bullet}$$
 (4)

The rate constants for these reactions are $> 1 \times 10^9$ L mol⁻¹ s⁻¹,^{1,6,7} so that in aqueous solutions under air ([O₂] ~ 2.5 × 10⁻⁴ mol L⁻¹) the reaction has a half-life of <3 μ s and in neat MeOH ([O₂] ~ 2.2 × 10⁻³ mol L⁻¹) it has a half-life of <0.3 μ s. In fact, the formation of all the arylperoxyl radicals in neat MeOH was complete within 0.2 μ s. The aliphatic peroxyl radicals, produced along with the arylperoxyl, do not interfere with the measurements of the absorption spectra and reaction kinetics of the arylperoxyl because the aliphatic ones absorb only in the UV and react more slowly than the aromatic radicals.

The optical absorption spectrum of the phenylperoxyl radical was measured by pulse radiolysis of bromobenzene in neat MeOH and in aqueous 10% MeOH solutions. In both solutions, a broad visible band was found with a maximum at 470 nm, close to the value of $\lambda_{max} = 490$ nm reported before,⁷ and only slightly blue-shifted as compared with that reported for the 4-carboxyphenylperoxyl in aqueous solutions (520 nm).⁶ To compare the spectra for the various arylperoxyl radicals, we measured all of them in MeOH solutions because of the limited solubility of the higher bromoarenes in aqueous alcohol solutions. Methanol was chosen rather than 2-propanol because of the lower reactivity of aryl radicals toward the former solvent. In 2-PrOH, phenyl radicals abstract a hydrogen atom from the solvent

$$Ar^{\bullet} + SH \to ArH + S^{\bullet} \tag{5}$$

 $(k_5 = 1.2 \times 10^7 \text{ for phenyl}^7 \text{ and } 4 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1} \text{ for 4-carboxyphenyl}^6)$ and this reaction competes with reaction 4 and lowers the yield of phenylperoxyl radicals considerably. In MeOH, k_5 will be an order of magnitude lower⁷ and, in fact, the yield of arylperoxyl radicals was substantially higher than that in 2-PrOH.

All the arylperoxyl radicals examined exhibit broad absorptions in the visible range (Figure 1). These absorptions were not observed when the solution was deoxygenated by bubbling with N₂, supporting their assignment to peroxyl radicals. Additional absorption below 400 nm was not examined in detail because it may include contributions from other radicals formed in the solution. The higher arylperoxyl radicals exhibit λ_{max} values which are red-shifted compared with phenylperoxyl: 4-biphenylylperoxyl, 550 nm; 2-naphthylperoxyl, 575 nm; 1-naphthylperoxyl, 650 nm; and 9-phenanthrylperoxyl, 700 nm. The molar absorptivities, ϵ , of phenylperoxyl⁷ and 4-carboxyphenylperoxyl⁶ radicals were reported to be 1600 L mol⁻¹ cm⁻¹. By comparing the absorbance at the peak for the various arylperoxyl radicals with that for phenylperoxyl under similar conditions (solvent, dose, and ArBr concentration) we can estimate the following ϵ values at the respective λ_{max} (L mol⁻¹ cm⁻¹): 4-biphenylylperoxyl, 1500; 2-naphthylperoxyl, 1100; 1-naphthylperoxyl, 800; and 9-phenanthrylperoxyl, 750. In these estimates, however, we assume that most aryl radicals react with O₂ to form ArO₂• (reaction 4) rather than abstract H from the solvent (reaction 5). If reaction 5 has a substantial contribution, the extent of this competing process may vary for the different aryl radicals and this will introduce a significant error to the estimate of ϵ . The alternative method for determining ϵ for the peroxyl radical is by reaction with a compound that will produce quantitatively another radical of known ϵ (as has been done for 4-carboxyphenylperoxyl).⁶ This method was attempted with the most reactive compound in the present study, ABTS, but its rate constant became much lower in neat MeOH than in aqueous MeOH solutions and thus quantitative conversion of ArO2[•] to the ABTS radical was not achieved. Full conversion may be achieved in aqueous MeOH, but then the solubility of ArBr is limited, production of the peroxyl radical is much less than quantitative, and the absorbance observed was too low to give a reasonable estimate of ϵ .

In the absence of other additives, the peroxyl radicals decay by reaction with the same radical or with the radicals derived from the alcohol, or by reacting with the alcohol via H abstraction. Addition of organic reductants resulted in increased rate of decay of the peroxyl radical and in formation of transient species from these additives. By following the rate of formation as a function of additive concentration, we determined the rate constants for oxidation of three model reductants, ABTS, trolox, and CIPz, by the arylperoxyl radicals. When the solutions were deoxygenated by bubbling with N_2 , the formation of the transient species from these reductants were not observed, confirming again the involvement of peroxyl radicals.

The reaction of the peroxyl radicals with ABTS and CIPZ is a one-electron oxidation process to yield the radical cation, e.g.

$$ArO_{2}^{\bullet} + ClPz \rightarrow ArO_{2}^{-} + ClPz^{\bullet+}$$
(6)

Oxidation of trolox, however, yields the neutral phenoxyl radical, although the mechanism may involve electron transfer, particularly in polar solvents.

$$ArO_{2}^{\bullet} + Ar^{1}OH \leftarrow ArO_{2}H + Ar^{1}O^{\bullet}$$
(7)

The kinetic measurements were most accurate with ABTS, because of the strong absorption of the radical produced and its very long lifetime. Since ABTS has limited solubility in neat MeOH, which restricted the measurements of low rate constants, and the bromoarenes have limited solubility in water, we used 60% MeOH as a convenient solvent for all these measurements. Furthermore, in neat MeOH, the rate constant for electron transfer was found to be considerably lower than in aqueous solutions. This, in turn, dictates the use of higher ABTS concentrations, beyond the solubility limit, for accurate rate determination. We also measured the rate constants in 30%



Figure 1. Optical absorption spectra of the arylperoxyl radicals in the visible range. Monitored by pulse radiolysis of the aryl bromide $((1-5) \times 10^{-2} \text{ mol } \text{L}^{-1})$ in MeOH under air. The absorbance was determined at $0.1-0.3 \,\mu$ s after the pulse, after the reaction of the aryl radical with O₂ was complete. The absorbance at the lower wavelengths was not determined since it may contain contributions from other radicals. (a) Phenylperoxyl, (b) 4-biphenylylperoxyl, (c) 2-naphthylperoxyl, (d) 1-naphthylperoxyl, and (e) 9-phenanthrylperoxyl.

 TABLE 1:
 Rate Constants for Reactions of Arylperoxy

 Radicals with ABTS in Aqueous Alcohol Solutions and

 Absorption Maxima of the Radicals

| | k, L me | λmax. | Ε. | |
|---|-------------------------------|-------------------------------|-----|------|
| radical | 60% MeOH | 30% t-BuOH | nm | eV |
| $C_6H_5O_2$ | $(3.8 \pm 1.0) \times 10^7$ | $(5.1 \pm 0.8) \times 10^7$ | 470 | 2.64 |
| 4-C6H5-C6H4O2* | $(6.6 \pm 1.1) \times 10^8$ | $(5.9 \pm 0.9) \times 10^8$ | 550 | 2.25 |
| 2-C ₁₀ H ₇ O ₂ • | $(6.0 \pm 1.0) \times 10^{8}$ | $(7.2 \pm 1.1) \times 10^{8}$ | 575 | 2.16 |
| $1-C_{10}H_7O_2^{\bullet}$ | $(1.6 \pm 0.3) \times 10^9$ | $(1.2 \pm 0.2) \times 10^9$ | 650 | 1.91 |
| 9-C ₁₄ H ₉ O ₂ • | $(2.1 \pm 0.3) \times 10^9$ | $(1.2 \pm 0.2) \times 10^9$ | 700 | 1.77 |

t-BuOH and found them to be generally within a factor of 2 similar to those in 60% MeOH (Tables 1 and 2).

Arylperoxyl radicals are found to be much more reactive than alkylperoxyl. For example, the rate constants for the reaction of CH₃O₂^{*} with ABTS and trolox were too low to be measured by pulse radiolysis ($k < 10^5$ L mol⁻¹ s⁻¹).^{11,12} The more reactive ClCH₂O₂^{*} radical reacts with these compounds^{11,13} about as rapidly as does phenylperoxyl. The higher arylperoxyl radicals, however, react more rapidly, and their rate constants for ABTS and trolox are higher than those of the very reactive CCl₃O₂^{*} radical.¹ Clearly, the increased number of halogens as well as the increased number of aromatic rings result in increased electron withdrawal from the peroxyl site and thus in increased reactivity of the peroxyl radical. This effect has been

 TABLE 2:
 Rate Constants for Reactions of Arylperoxy

 Radicals with Trolox and Chlorpromazine in Aqueous
 Alcohol Solutions

| | | $k, L \text{ mol}^{-1} \text{ s}^{-1}$ | | |
|---|---------------------|---|---|--|
| radical | solvent | trolox | ClPz | |
| $C_6H_5O_2^{\bullet}$ 2- $C_{10}H_7O_2^{\bullet}$ 1- $C_{10}H_7O_2^{\bullet}$ | 60% MeOH | $\begin{array}{c} (2.7 \pm 0.5) \times 10^{7} \\ (1.2 \pm 0.3) \times 10^{8} \\ (2.8 \pm 0.4) \times 10^{8} \\ (1.0 \pm 0.2) \times 10^{7} \end{array}$ | $(4.2 \pm 0.6) \times 10^{6}$ | |
| $2-C_{10}H_7O_2^{\bullet}$ $1-C_{10}H_7O_2^{\bullet}$ | 30 <i>% I-</i> ВиОн | $(1.0 \pm 0.2) \times 10^{8}$ $(4.1 \pm 0.6) \times 10^{8}$ $(5.6 \pm 0.8) \times 10^{8}$ | $(4.2 \pm 0.6) \times 10^{3}$ $(1.7 \pm 0.3) \times 10^{7}$ $(1.2 \pm 0.2) \times 10^{8}$ | |

demonstrated for a series of substituted alkylperoxyl radicals, where the rate constant for oxidation of ascorbate was correlated with the polar substituent constant,² and for a series of 4-substituted phenylperoxyl, where k for oxidation of ABTS was correlated with the Hammett σ .⁶ Such substituent constants are not available for the various aryl moieties, but it is reasonable to assume that the increased number of aromatic rings would result in increased electron affinity of the aryl moiety, which would influence the electron acceptor. Among the naphthylperoxyl radicals, 1-naphthyl is consistently more reactive than 2-naphthyl. This finding is in line with the higher electron affinity of position 1, as is evident, for example, from the spin density distribution in the naphthalene radical anion.¹⁴



Figure 2. Correlation of the rate constants for oxidation by the peroxyl radicals with the energies of the absorption maxima for these radicals. (a) Results for ABTS (\bigcirc) and trolox (\triangle) in 60% MeOH; (b) results for ABTS (\bigcirc), trolox (\triangle), and ClPz (\square) in 30% *t*-BuOH.

The rate constants for the arylperoxyl radicals examined show a clear trend of increasing reactivity in the order phenyl, 4-biphenylyl, 2-naphthyl, 1-naphthyl, 9-phenanthryl. This order of reactivity follows the order of their absorption maxima. To attempt a quantitative correlation between these two sets of data, we corrected the experimental rate constants, k_{obs} (Tables 1 and 2), for the effect of the diffusion-controlled limit, k_{diff} , to obtain the activation-controlled value, k_{act} , according the equation $1/k_{act}$ $= 1/k_{obs} - 1/k_{diff}$. The value of k_{diff} was calculated from the viscosity η as $8RT/3\eta$,¹⁵ and was 3.8×10^9 for 60% MeOH and 2.4×10^9 L mol⁻¹ s⁻¹ for 30% *t*-BuOH. The corrections to k_{obs} were negligible for $k \le 10^8$ L mol⁻¹ s⁻¹ and increased up to a factor of 2 for the highest rate constants. Correlations of log $k_{\rm act}$ with the energy $(E = hc/\lambda)$ of the absorption peak show a nearly linear dependence in all cases (Figure 2). Since the Marcus theory relates log k with the driving force (or ΔG°) for the reaction, the lines in Figure 2 suggest that the energy of the absorption peak is inversely related to the driving force for the reaction (i.e., to the redox potential or electron affinity of the peroxyl radical). Possibly, as the π -system becomes more extended, all the energy levels are compressed, and this reduces the distance between the singly occupied molecular orbital (SOMO) and the penultimate occupied molecular orbital¹⁶ (Eof the peak in the visible range) as well as the distance between the SOMO and the continuum level (ionization potential). As the ionization potential decreases, the electron affinity increases and, assuming similar effects of solvation in the whole series, the redox potential will become more positive. This implies strong interaction between the aromatic π -system and the unpaired electron on the terminal oxygen, which affects the absorption spectrum as well as the reactivity.

In summary, the number of aromatic rings and their position relative to the oxyl group have a strong influence on the absorption spectrum of the arylperoxyl radical as well as on its reactivity as an oxidant. Polycyclic arylperoxyl are very reactive species. Such radicals are expected to be produced in the process of detoxification of polycyclic aryl halides by ionizing radiation, and will rapidly oxidize any reductants present in the mixture or abstract a hydrogen atom, leading to formation of hydroperoxides, which will eventually decompose to phenols. If these phenols contain additional halogens, the process will continue until all halogens are removed. The high electron affinity of polycyclic aryl halides also suggests that these compounds may be readily reduced in biological systems and thus produce highly reactive peroxyl radicals, which may initiate lipid peroxidation and result in various deleterious effects.

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