Pulse radiolysis of aryl bromides in aqueous solutions: some properties of aryl and arylperoxyl radicals

Xingwang Fang, Ralf Mertens and Clemens von Sonntag *
Max-Planck-Institut für Strahlenchemie, Stiftstr. 34–36, PO Box 101365, D-45413 Mülheim an der Ruhr, Germany

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Aryl radicals were generated pulse-radiolytically in aqueous solutions by reacting the solvated electron with phenyl bromide and substituted phenyl bromides. The aryl radicals react rapidly ($k \geqslant 2.5 \times 10^9$ dm^3 mol^{-1} s^{-1}) with O_2 giving rise to arylperoxyl radicals which display characteristic absorptions in the visible spectrum (490–600 nm, depending on the substituent). Aryl radicals react with alcohols by H-abstraction. Making use of the strong absorptions of the arylperoxyl radicals in the visible spectrum, rate constants of the reaction of the aryl radicals with various alcohols have been determined by competition kinetics [*e.g.* 4-methoxyphenyl: 1.1×10^7 (2-PrOH), 5.8×10^6 (EtOH), 1.1×10^6 (MeOH), 5.2×10^5 dm^3 mol^{-1} s^{-1} (Bu^{t}OH)]. The temperature dependence of the reaction of the 4-CN-phenyl radical was studied and reaction parameters of its reaction with O_2 ($A = 4 \times 10^{11}$ s^{-1}; $E_a = 12$ kJ mol^{-1}), propan-2-ol ($A = 1.5 \times 10^9$ s^{-1}; $E_a = 13$ kJ mol^{-1}) and *tert*-butanol ($A = 6 \times 10^9$ s^{-1}; $E_a = 25$ kJ mol^{-1}) determined.

While most of the arylperoxyl radicals decay by second-order processes by reacting with one another and other peroxyl radicals present ($k \geqslant 3 \times 10^9$ dm^3 mol^{-1} s^{-1}) HO- and H_2N-substituted arylperoxyl radicals also decay by first-order processes.

It has been noted that the reaction of 4-nitrobromobenzene with the solvated electron does not lead to the formation of an aryl radical by halide elimination.

Aryl radicals may be formed in the photolysis of aryl halides,[1,2] the thermal decomposition of labile compounds such as arylazotriphenylmethanes,[3] (substituted) dibenzoylperoxides,[4] or nitrosobenzenes,[5] or by reacting sodium with aryl iodides at low temperatures.[6] An alternative route to these intermediates, also used in the present study, is the reaction of these arylhalogenides with the solvated electron [from the radiolysis of water, reactions (1)–(3)].[7–10]

$$H_2O \xrightarrow[\text{radiation}]{\text{Ionizing}} e_{aq}^-, {}^{\bullet}OH, H^{\bullet}, H^+, H_2O_2, H_2 \qquad (1)$$

$$ArBr + e_{aq}^- \longrightarrow ArBr^{\bullet -} \qquad (2)$$

$$ArBr^{\bullet -} \longrightarrow Ar^{\bullet} + Br^- \qquad (3)$$

It has recently been reported that vinylperoxyl[9] and arylperoxyl radicals[2,9,10] which are formed in the reaction of the parent radicals with molecular oxygen [reaction (4)], show

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

strong absorptions in the visible. These absorptions allow determination of the rate constants of reactions such as (5) by

$$Ar^{\bullet} + RH \longrightarrow ArH + R^{\bullet} \qquad (5)$$

competition kinetics in a pulse radiolysis experiment.[9,10]

In the past the reactivity of aryl radicals towards various substrates has been the subject of considerable attention.[2–4,9,10] In the earlier studies it was only possible to measure ratios of rate constants, but the more recent work also yielded absolute rate constants.[2,5,9,10] In the present paper we will report the spectra of a number of arylperoxyl radicals (substituted phenylperoxyl radicals) and will supplement our knowledge concerning the reactivity of the parent aryl radicals toward some alcohols.

Experimental

The aryl bromides and the alcohols were of the highest purity commercially available. Solutions (10^{-4}–10^{-3} mol dm^{-3}) were made up in Milli-Q-filtered (Millipore) water. For pulse radiolysis a 2.7 MeV Van de Graaff electron accelerator delivering 0.4–4 µs pulses was used.[11] Appropriate Ar–O_2-mixtures (10 : 1 v/v) were prepared with the help of a Brooks gas mixer. Thiocyanate was used for dosimetry.[12]

For the determination of bromide ion yields solutions were γ-irradiated at a dose rate of 0.14 Gy s^{-1} (Oris IBL-437C) and the irradiated solutions analysed by ion chromatography (Dionex 2010i). The *G* values of the (substituted) Aryl–H were determined by HPLC.

Results and discussion

Formation of aryl radicals

The radiation-chemical yields (*G* values) of the water radicals formed in reaction (1) are $G(e_{aq}^-) \approx G({}^{\bullet}OH) = 2.8 \times 10^{-7}$ mol J^{-1} and $G(H^{\bullet}) = 0.6 \times 10^{-7}$ mol J^{-1}. In order to eliminate a contribution of the OH-radical *tert*-butanol can be added in excess [*cf.* reaction (6); for rate constants see ref. 13].

$$(CH_3)_3COH + {}^{\bullet}OH \longrightarrow {}^{\bullet}CH_2C(CH_3)_2OH + H_2O \qquad (6)$$

In order to investigate whether reactions (2) and (3) proceed with all aryl bromides, Ar-purged aqueous solutions containing phenyl bromide or substituted phenyl bromides (*cf.* Table 1) at a concentration of 10^{-3} mol dm^{-3} and 0.1 mol dm^{-3} *tert*-butanol to scavenge the OH-radicals were γ-irradiated and the bromide ion yields determined by HPIC. Except for 4-nitrophenyl bromide [$G(Br^-) < 0.1 \times 10^{-7}$ mol J^{-1}], the bromide ion yield corresponds to the yield of the solvated electron in all cases. This result shows that the aryl bromide radical anions [*cf.* reaction (2)] usually decompose by bromide ion release [reaction (3)].

Table 1 $G(Br^-)$ and G(Aryl–H) of irradiated 1×10^{-3} mol dm^{-3} aryl bromides in Ar-saturated solutions containing 0.1 mol dm^{-3} *tert*-butanol

Aryl bromide	$G(Br^-)$/ 10^{-7} mol J^{-1}	G(Aryl–H)/ 10^{-7} mol J^{-1}
4-Bromoanisole	2.8	2.8
4-Bromophenol	2.9	2.7
Bromobenzene	2.7	2.7
4-Bromobenzonitrile	2.9	2.8
4-Bromonitrobenzene	< 0.1	absent

Table 2 Absorption maxima of substituted phenylperoxyl radicals. Short-lived intermediates are indicated by an asterisk

Substituent	λ_{max}/nm	ε/dm^3 mol^{-1} cm^{-1}
H	490	1300
4-CN	490	1300
2-CO_2^-	495	1940
3-CO_2^-	510 (510),[a] (520)[b]	1540 (1600)[b]
3-OH*	520	1400
4-Br	530	650
3-OCH_3	540	1000
4-CH_3	560	600
4-OCH_3	590 (600)[c]	1900 (2100)[c]
4-NH_2*	590	2000
4-$N(CH_3)_2$	600	1200

[a] From ref. 2. [b] From ref. 10; [c] from ref. 9.

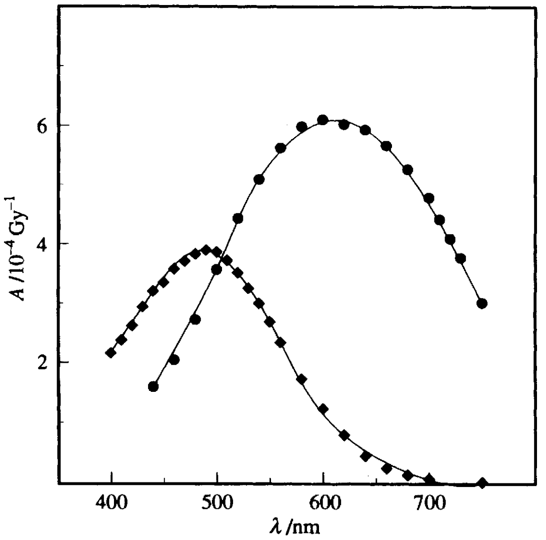

Fig. 1 Absorption spectra of 4-methoxyphenylperoxyl (●) and 4-cyanophenylperoxyl radicals (◆)

This reaction is related to the halogen ion release from 5-halouracil radical anions, where the rate of halogen ion release is indeed very fast; it falls into the nanosecond time range.[14]

The nitro group is known to stabilize very efficiently the electron, and we conclude that this is the reason why the 4-nitrophenyl bromide radical anion is stable with respect to the heterolytic fragmentation of the C–Br bond.

Reaction of aryl radicals with molecular oxygen

In the presence of O_2, the aryl radicals are converted into the corresponding peroxyl radicals [reaction (4)]. These peroxyl radicals have strong absorptions in the visible (Table 2, *cf.* Fig. 1). The rate of formation of the peroxyl radicals depends on the oxygen concentration (*cf.* ref. 9). From the slopes of such plots the rate constant of the addition of O_2 to the aryl radicals has been calculated. They are compiled in Table 3. The rate constant for the reaction of 4-carboxyphenyl with O_2 was found to be 1.6×10^9 dm^3 mol^{-1} s^{-1}.[10]

Table 3 Compilation of the rate constants measured in the present study. Ph = phenyl, MeO-Ph = 4-methoxyphenyl, CN-Ph = 4-cyanophenyl, Br-Ph = 4-bromophenyl, CH_3-Ph = 4-methylphenyl, $N(CH_3)_2$-Ph = 4-dimethylaminophenyl, $RO_2^•$ = arylperoxyl radicals and other peroxyl radicals present in the system

Reaction	Rate constant/dm^3 mol^{-1} s^{-1}
$Ph^• + O_2$	3.3×10^9
$MeO\text{-}Ph^• + O_2$	3.2×10^9
$CN\text{-}Ph^• + O_2$	2.5×10^9
$PhO_2^• + RO_2^•$	1.1×10^9
$MeO\text{-}C_6H_4O_2^• + RO_2^•$	1.2×10^9
$CN\text{-}C_6H_4O_2^• + RO_2^•$	8.6×10^8
$Br\text{-}C_6H_4O_2^• + RO_2^•$	9.6×10^8
$CH_3\text{-}C_6H_4O_2^• + RO_2^•$	8.8×10^8
$N(CH_3)_2\text{-}C_6H_4O_2^• + RO_2^•$	6.6×10^8
$Ph^• + HC(CH_3)_2OH$	1.2×10^7
$Ph^• + CH_3CH_2OH$	4.4×10^6
$Ph^• + CH_3OH$	1.2×10^6
$Ph^• + (CH_3)_3COH$	6.6×10^5
$MeO\text{-}Ph^• + HC(CH_3)_2OH$	1.1×10^7
$MeO\text{-}Ph^• + CH_3CH_2OH$	5.8×10^6
$MeO\text{-}Ph^• + CH_3OH$	1.1×10^6
$MeO\text{-}Ph^• + (CH_3)_3COH$	5.2×10^5
$CN\text{-}Ph^• + HC(CH_3)_2OH$	9.6×10^6
$CN\text{-}Ph^• + CH_3CH_2OH$	2.7×10^6
$CN\text{-}Ph^• + CH_3OH$	6.6×10^5
$CN\text{-}Ph^• + (CH_3)_3COH$	3.3×10^5

Depending on the substituents the maxima of the visible absorption vary between 490 and 600 nm (Table 2). An absorption at 496.4 has been used for the detection of phenylperoxyl radicals in the gas phase.[15] Theoretical calculations of the phenylperoxyl radical transition in the visible will become available.[16] It has been concluded that the phenylperoxyl radical must have a considerable dipole moment. This is expected, since the peroxyl radical function is a strongly electron-withdrawing substituent.[17] There seems to be some solvent dependence of the phenylperoxyl radical absorption, since its maximum in methanol is at 470 nm[18] while in water we find 490–500 nm. The trichlorovinylperoxyl radical undergoes a similar red-shift of 40 nm on going from tetrachloroethene to water.[19]

Many of the arylperoxyl radicals studied only decay by second-order together with the other peroxyl radicals present [H, 4-CH_3, 4-Br, 4-OCH_3, 4-CN, 4-$N(CH_3)_2$] (*cf.* Table 3). However, some (4-NH_2, 3-OH) decay much more rapidly in a first-order reaction (at pH = 7 $k = 6 \times 10^4$ s^{-1} and 3×10^4 s^{-1}, respectively). No significant visible spectra were obtained for the 2-OH- and 4-OH-phenylperoxyl radicals. The lack of their detection may be due to an even faster first-order decay. Details are not yet known, but from the fact that the 4-$N(CH_3)_2$-phenylperoxyl radicals decays by second-order kinetics it seems that the heteroatom-bound hydrogen must be involved in this first-order decay process. Similarly, the vinylperoxyl radical derived from 5-bromouracil decays unimolecularly ($k = 6 \times 10^4$ s^{-1}) while that derived from 5-bromodeoxyuridine only decays in a bimolecular reaction.[9]

H-Abstration by aryl radicals

It is well known that vinyl radicals and their related aryl radicals react readily with hydrogen donors by H-abstration.[7–10] As in the case of the vinyl radicals the rate constant of these reactions can be determined by pulse radiolysis.[9] The H-donor and oxygen compete for the reactive radicals (here the aryl radicals); the absorption of the arylperoxyl radical is the measured entity.

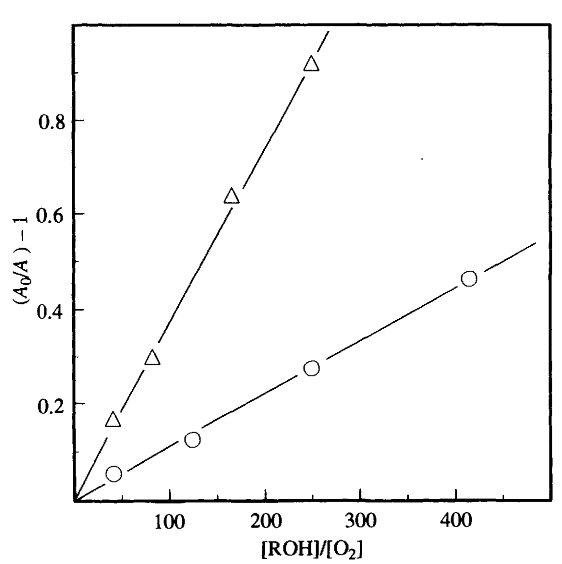

Fig. 2 Stern–Volmer-type plot for the competition of the reaction of 4-cyanophenylperoxyl radicals with oxygen (Ar–O$_2$ = 4:1) and with propan-2-ol (Δ) and ethanol (○). The absorbance at 500 nm of the 4-cyanophenylperoxyl radical 10 μs after the pulse was the measured entity.

The competition is given by eqn. (7) from which eqn. (8) is

$$A = A_0 \frac{k_4[O_2]}{k_4[O_2] + k_5[RH]} \tag{7}$$

$$\frac{A_0}{A} - 1 = \frac{k_5[RH]}{k_4[O_2]} \tag{8}$$

derived (A_0 denotes the measured absorbance in the absence of an H-donor, A the absorbance measured at a given H-donor concentration). Since k_4 is known from the experiments described above k_5 can be calculated from data such as shown in Fig. 2. They are compiled in Table 3.

It can be seen from Table 3 that the rate constants decrease in the series propan-2-ol > ethanol > methanol > *tert*-butanol. This is the expected sequence for the rate constants of H-abstraction reactions of free radicals with these alcohols. It is noted that there is practically no substituent effect. Thus the electron-donating or -withdrawing properties of the substituents seem not to influence much the rate constants for the H-abstraction reaction (*cf.* Table 3). The reported rate constants for the reactions of the 4-carboxyphenyl[10] and the 4-hydroxyphenyl[8] radicals with propan-2-ol ($k = 4 \times 10^6$ and 3×10^7 dm^3 mol^{-1} s^{-1}, respectively) are close to the ones given in Table 3.

The reactivity of the phenyl radical with propan-2-ol (1.2×10^7 dm^3 mol^{-1} s^{-1}) when compared with the reactivity of some vinyl radicals[9] such as trichlorovinyl radical (4×10^7 dm^3 mol^{-1} s^{-1}), 1,2-dichlorovinyl radical (8.4×10^6 dm^3 mol^{-1} s^{-1}), 2-chlorovinyl radical (5.6×10^6 dm^3 mol^{-1} s^{-1}) and the vinyl radical (2×10^5 dm^3 mol^{-1} s^{-1}) shows that the phenyl radical is considerably more reactive than the vinyl radical but not quite as reactive as the trichlorovinyl radical.

The rate constant for H-abstraction from alcohols by the aryl radicals is considerably below diffusion-controlled, even for the rather good H-donor propan-2-ol. The C–H binding energy in benzene is 461 kJ mol^{-1} and that of the tertiary hydrogen in propan-2-ol is 381 kJ mol^{-1}, those of the primary hydrogens in *tert*-butanol is 398 kJ mol^{-1}.[20] Thus reaction (5) is exothermic by 80 kJ mol^{-1} and 63 kJ mol^{-1}, respectively, and there is a considerable driving force for reaction (5) to proceed in both cases. Yet, the reaction of the aryl radicals with the alcohols is rather slow altogether and that with *tert*-butanol is even 20–30 times slower than with propan-2-ol. To shed some light on the reason for this we have determined the kinetic parameters of these reactions by measuring the temperature dependence of the reactions of the 4-CN-phenyl radical with oxygen, as well as with propan-2-ol and *tert*-butanol. Arrhenius plots are shown in Fig. 3. From these data it is calculated that the activation energy of O$_2$ addition ($E_a \approx 12$ kJ mol^{-1}, $A = 4 \times 10^{11}$ s^{-1}) is about the value expected for a diffusion-controlled reaction in water (about 10 kJ mol^{-1}).

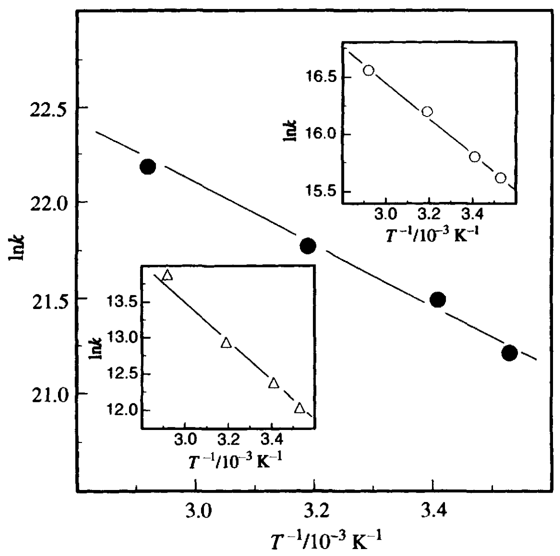

Fig. 3 Arrhenius plots for the reaction of the 4-cyanophenyl radical with oxygen (●), propan-2-ol (○) and *tert*-butanol (△)

The values for the reaction of these radicals with propan-2-ol ($E_a = 13$ kJ mol^{-1}, $A = 1.5 \times 10^9$ s^{-1}) and *tert*-butanol ($E_a = 25$ kJ mol^{-1}, $A = 6 \times 10^9$ s^{-1}) are calculated from the plots shown in Fig. 3. From these data it can be seen that for the reaction with propan-2-ol there is little if any activation energy required beyond that of diffusion. The slowness of the reaction is reflected by the low A factor. In the case of *tert*-butanol there is now a noticeable activation energy involved as well; the A factor not being much different from that found for propan-2-ol. The relative reactivity of phenyl radicals toward primary and tertiary hydrogens has been measured in the gas phase, and a value of k(tertiary C–H)/k(primary C–H) = $0.45\exp(14.6/RT)$ has been obtained.[4] This value compares well with our data [k(propan-2-ol)/k(*tert*-butanol) = $0.5\exp(12/RT)$].

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