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Rate constants for the reaction of halogenated alkylperoxyl radicals with iodide: influence of substituents, solvent polarity, and proton concentration

Igor Štefanić,[1] Klaus-Dieter Asmus[2] and Marija Bonifačić[3]*

[1]Culver Academies, 1300 Academy Road, Culver, Indiana 46511, USA
[2]Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland
[3]Department of Physical Chemistry, Ruđer Bošković Institute, Bijenička c. 54, 10000 Zagreb, Croatia

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ABSTRACT: This pulse radiolysis study deals with the reaction of iodide ions (I^-) with a series of halogenated alkylperoxyl radicals in 2-propanol–water mixtures. Under investigation were $CF_3OO^{\cdot}$, $CFCl_2OO^{\cdot}$, $CCl_3OO^{\cdot}$, $C_2Cl_5OO^{\cdot}$, $CHCl_2OO^{\cdot}$ and $CF_3CHClOO^{\cdot}$. Each of these peroxyl radicals oxidizes a total of three I^- ions in a fast and practically simultaneous reaction sequence. An overall two-electron step, involving a transient peroxyl–iodide adduct radical, results in the oxidation of two iodide ions to yield molecular I_2 and the corresponding halogenated alkoxyl radical, $R(Hal)O^{\cdot}$. The latter is responsible for the oxidation of the third iodide to yield iodine atoms, $I^{\cdot}$. The overall second-order rate constants for these multi-electron oxidation processes were determined by following the formation kinetics of $I_3^-/I_2^{\cdot -}$, the spectrophotometrically accessible forms of I_2 and $I^{\cdot}$ in I^--containing solutions. These rate constants were determined as a function of pH, polarity of solvent mixtures and electronegativity of the substituents at the α-C atom of the peroxyl radicals. They strongly depend on all these variables, with the actual numbers covering a range from 3×10^5 to $7.0 \times 10^8\ M^{-1}\ s^{-1}$. A good linear relationship is obtained between log$k$ and the dielectric constant of the solvent mixture. Within a particular solvent mixture the rate constants depend strongly on the substituents at the alkylperoxyl moiety and correlate with Taft's inductive substituent constants σ^*. The overall multi-electron oxidation mechanism of alkylperoxyl radicals is discussed in the light of the new results. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: multi-electron oxidation; peroxyl radical; pH effect; pulse radiolysis; rate constants; solvent polarity effect; substituent effect

INTRODUCTION

Organic peroxyl radicals, particularly rather strongly oxidizing halogenated alkylperoxyl radicals, are important reactive intermediates in many organic and biological processes. There have been many studies on the effects which the solvent, the nature of the substituents and the temperature exert on their reactions with electron donors.[1–20] Rate constants for the oxidation of chlorpromazine,[10,16] trolox[14,16] and ascorbate ions[13,14] by peroxyl radicals in different solvents were found to be strongly dependent on solvent polarity. Generally, the rate constants increased with increasing dielectric constant of the solvent. Also, the reactivity of the halogenated peroxyl radicals was found to increase with the degree of halogen substitution at the central carbon, with a linear correlation between log$k$ and Taft's inductive substitution constant, σ^*.[10,13] Activation energies covered a range from 1 to 30 kJ mol^{-1}, while pre-exponential factors varied from log$A = 7$ to 14.[15] The rate constants did not directly relate to the reduction potential of the reacting electron donors and, in many cases, stayed well below the diffusion limit in spite of very low activation energies. The increase in the rate constants correlated, however, with an increase in the pre-exponential factor. This suggests that the underlying mechanism is not likely to be an outer-sphere electron transfer but rather involves the formation of an intermediate adduct with subsequent electron transfer.[15] Proton donation by a solvent molecule in this process was also discussed as a contributing parameter.[15,16]

Such an inner-sphere electron transfer had been considered, for example, for a reaction between $CCl_3OO^{\cdot}$ radicals and zinc tetraphenylporphyrin.[7] A similar complex reaction mechanism had been invoked for the $CCl_3OO^{\cdot}$ radical-induced oxidation of organic sulfides.[21–23] The detailed study of this system revealed that halogenated alkylperoxyl radicals may, in fact, act as multi-electron transfer agents.

A most instructive example of a multi-electron transfer mechanism, especially from the quantitative point of

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**Correspondence to:* M. Bonifačić, Department of Physical Chemistry, Ruđer Bošković Institute, Bijenička c. 54, 10000 Zagreb, Croatia.
E-mail: bonifacic@irb.hr

view, is the $CCl_3OO^{\cdot}$ radical-induced oxidation of iodide.[24,25] As demonstrated in a pulse radiolysis study of a 2-propanol–water mixture, using conductivity and optical detection, each equivalent of $CCl_3OO^{\cdot}$ leads to the simultaneous formation of one equivalent of the two-elecron oxidation product I_2 (detectable as I_3^-) and one equivalent of the one-electron oxidation product $I^{\cdot}$ (detectable as $I_2^{\cdot-}$).[24] The proposed mechanism involves addition of the peroxyl radical to an iodide ion to yield a radical anion adduct as primary intermediate product. The second iodide ion then attacks at the first iodine atom which, within the protonated adduct, is made slightly positive by the influence of the peroxyl group. Based on a Fenton-type electron transfer into the hydroperoxide moiety, this leads to the formation of molecular I_2 and a $CCl_3O^{\cdot}$ radical[24] [for stoichiometric details, see Eqns (7)–(14) in the Reaction mechanism section]. The $CCl_3O^{\cdot}$ radical generated in this way is responsible for the oxidation of the third iodide ion to yield an $I^{\cdot}$ atom.

An important piece of evidence in support for the suggested mechanism is the experimentally proven fact that the formation of molecular iodine occurs independently of and practically as fast as the sequential generation of $I^{\cdot}$.[24] Furthermore, a transient species, suggested to be the adduct radical anion, $(CCl_3OOI)^{\cdot-}$, has been identified by its optical spectrum.[23] Also, phosgene (Cl_2CO), a decay product of $CCl_3O^{\cdot}$ after its reaction with I^-, was found to be formed in full stoichiometric yield.[26] The same holds for the other stable product, I_3^-, which accounts for the molecular iodine (I_2) formed directly in the primary two-electron oxidation and as the result of the bimolecular disproportionation of $I_2^{\cdot-}$. The total radiation chemical yield of I_3^- amounts to $G \approx 0.9\ \mu mol\ J^{-1}$ as required for the oxidation of three iodide ions per peroxide radical.[25]

Although the overall reaction mechanism could formally also be considered to involve an oxygen atom transfer as the first step, leading to the formation of hypoiodic acid and a $CCl_3O^{\cdot}$ radical, iodine being then produced via the reaction

$$HIO + I^- + H^+/H_2O \rightarrow I_2 + H_2O/OH^- \qquad (1)$$

this possibility had to be discarded since the rate of this reaction is too slow to account for the experimentally observed fast formation of I_2.[24] A possible oxygen atom transfer had, incidentally, also been dismissed in the case of the $CCl_3OO^{\cdot}$ reaction with sulfides, where the corresponding sulfoxide product results from a similarly fast two-electron oxidation.[21,22] In this system, an investigation with ^{18}O-labeled oxygen had shown that the sulfoxide oxygen originated from the solvent water molecule and not from the peroxyl radical.[22]

Certain questions concerning the details of this complex reaction mechanism, nevertheless, remained open. In particular, it is of interest to verify the suggested dependences of the rate constants on the pH, and to investigate the influence of the solvent composition and the degree of halogenation of the alkylperoxyl radicals. All these aspects will be dealt with in the present paper.

EXPERIMENTAL

All halogenated organic compounds were of the highest grade commercially available. $CHCl_3$, $CFCl_3$ (Merck), CF_3Br and CHF_2Br (DuPont) were used without further purification. CCl_4, $CF_3CH(Cl)Br$, and CCl_3CCl_3 (Merck) were purified by fractional distillation. 2-Propanol (Merck) was subjected to the same procedure but in the presence of $SnCl_2$ (Merck) to eliminate hydroperoxides.[27] Other chemicals, i.e. KI, KSCN and $HClO_4$ (Merck), were of analytical grade. All solutions were prepared freshly before each experiment using water from a Millipore Milli-Q UV system. Samples for the study of $CF_3OO^{\cdot}$ radicals were purged with a mixture of CF_3Br and O_2 (4:1, v/v). The respective pH of the solutions was adjusted with $HClO_4$.

The pulse radiolysis experiments were performed with the Van de Graaff accelerator of the Hahn-Meitner Institute in Berlin, made by High Voltage Corporation (USA). This accelerator produced pulses of 1.5 MeV electrons, typically of 0.5–1 μs duration. The dose per 1 μs pulse was ca 7 Gy. The irradiation cell was connected to a flow system to facilitate the exchange of the solution after each pulse. Dosimetry was based on the thiocyanate system.[28] Analysis of the optical absorption vs time trace was carried out with the help of a computer program that allowed kinetic evaluations. The second-order bimolecular rate constants were derived from plots of k_{obs} (the observed pseudo-first-order rate constant of a product formation) vs concentration of the reactant in excess (I^- in this study). The overall accuracy of ± 10%, characteristic for pulse radiolysis experiments, also applies here. Error limits displayed in Tables 1 and 3 refer solely to the standard deviation of the mean of a series of single measurements. All experiments were carried out at room temperature, $20 \pm 2\,^{\circ}C$.

RESULTS AND DISCUSSION

The rate constants for the reactions of halogenated peroxyl radicals with iodide were measured in air-saturated 2-propanol-water mixtures with the alcohol content ranging from 10 to 90% (v/v). $CF_3OO^{\cdot}$, $CFCl_2OO^{\cdot}$, $CCl_3OO^{\cdot}$, $C_2Cl_5OO^{\cdot}$, $CF_3CHClOO^{\cdot}$ and $CHCl_2OO^{\cdot}$ radicals were produced via radiolysis [for main primary processes, see Eqns (2) and (3)] by dissociative one-electron reduction of the respective halogen compounds (CF_3Br, $CFCl_3$, CCl_4, C_2Cl_6, $CF_3CHClBr$ and $CHCl_3$) in their reaction with solvated electrons and $^{\cdot}C(CH_3)_2OH$ radicals [reactions (4) and (5)]. Subsequently, the thus formed C-centered halogenated alkyl radicals reacted with oxygen [reaction (6)].[29,30] The concentration of alkyl halides was always 30 mM (the exception was gaseous CF_3Br, for which the final concentration in the solution was not known), ensuring practically quantitative conversion of all primary radicals into the respective halogenated alkylperoxyl radicals within the pulse duration.

In the presence of iodide (concentrations 1–10 mM), halogenated alkylperoxyl radicals were further converted into I_3^- and $I_2^{\cdot -}$. The radiation chemical yield of about 0.6 μmol J^{-1} each was determined by the same methods as described already in detail for the iodide oxidation by $CCl_3OO^{\cdot}$ radicals.[24] This was taken as strong evidence that the same reaction mechanism was valid for all peroxyl radicals investigated in this study and that scavenging of the respective radicals occurred quantitatively in all systems, including that containing CF_3Br.

$$H_2O/(CH_3)_2CHOH \rightsquigarrow e^-_{solv}, {}^{\cdot}OH, H^{\cdot}, {}^{\cdot}C(CH_3)_2OH, \ldots \tag{2}$$

$${}^{\cdot}OH/H^{\cdot} + (CH_3)_2CHOH \rightarrow H_2O/H_2 + {}^{\cdot}C(CH_3)_2OH \tag{3}$$

$$RX + e^-_{solv} \rightarrow R^{\cdot} + X^- \tag{4}$$

$$RX + {}^{\cdot}C(CH_3)_2OH \rightarrow R^{\cdot} + X^- + (CH_3)_2CO + H^+ \tag{5}$$

$$R^{\cdot} + O_2 \rightarrow ROO^{\cdot} \tag{6}$$

The rates of halogenated peroxyl radicals oxidation of iodide were measured by following the $I_2^{\cdot -}/I_3^-$ formation kinetics. As previously observed[24] for $CCl_3OO^{\cdot}$, the observable growth kinetics were practically identical and of pseudo-first order. They could not be time-resolved any further at any wavelength throughout the accessible spectral range. Figure 1 shows representative plots of k_{obs} measured at 360 nm as a function of iodide concentration. The slopes of the lines give second-order rate constants for the oxidation of iodide by various peroxyl radicals under conditions where the rate-limiting step is the reaction of the peroxyl radical with iodide (and not the reaction of alkyl radicals with oxygen). (At higher iodide concentrations, the formation of the peroxyl radicals limits the rate of the subsequent oxidation of iodide, and the plot of k_{obs} vs $[I^-]$ will curve and eventually approach a plateau. In these cases the second-order rate constant were calculated from the initial slopes of the k_{obs} vs $[I^-]$ plots.)

For each peroxyl radical, the second-order reaction rate constants were derived from experiments with at least four different iodide concentrations in different 2-propanol–water mixtures as solvent and at different proton concentrations (pHs). (In the context of this investigation, 'pH' always refers to the actual $HClO_4$ concentration added (as negative logarithm of $[HClO_4]$). It can be assumed that the perchloric acid is quantitatively dissociated under all our experimental conditions. Not specifically considered are, however, any effects of the solvent composition on the activity of the protons.) Within experimental error limits, all straight lines passed through the origin without any noticeable intercept. The exceptions are the pH-dependence data shown in Figs 2 and 3, where rate constants were determined from measurements at only one concentration of iodide (1×10^{-3} M for $CF_3OO^{\cdot}$ and $CCl_3OO^{\cdot}$ and 1×10^{-2} M for the much slower reacting $CHCl_2OO^{\cdot}$).

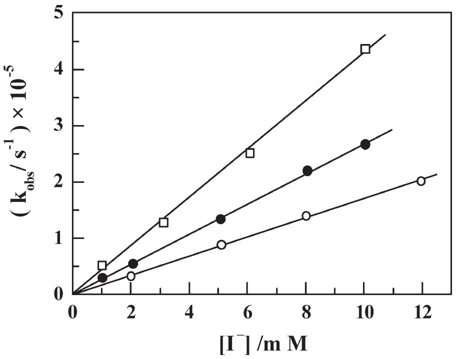

Figure 1. Plots of the observed first-order rate constants (k_{obs}) for the reaction of peroxyl radicals with iodide as a function of iodide concentration for $CF_2Cl_2OO^{\cdot}$ (□), $CF_3CHClOO^{\cdot}$ (●) and $CHCl_2OO^{\cdot}$ (○) in an air-saturated 2-propanol–water mixture (3:7, v/v) at neutral pH

Table 1 summarizes the rate constants obtained for neutral solutions and at pH 3.0. The data reveal very clearly a significant influence of the solvent composition, the substituents and the pH on the reaction rate constant.

Effects of proton concentration

Figure 2 shows the second-order rate constants for the reaction between $CCl_3OO^{\cdot}$ radicals and iodide in different 2-propanol–water mixtures vs pH. All curves exhibit a sigmoidal character. Qualitatively, the strong dependence on the pH of the mixture is absolutely in line with our earlier report in a single solvent system.[24] From the present data, it becomes evident that the pH effect is very much influenced by the solvent composition. Thus, at lower pHs the rate constant decreases with increasing solvent polarity, i.e. with increasing water content. However, in the neutral pH region an opposite trend is observed, in that the rate constant now increases with increasing water content. Consequently, systems with higher water content show less pronounced pH dependences of the rate constants. For example, at neutral pH, upon increasing the 2-propanol content from 1:9 to 4:1 (v/v), the rate constants decrease from 7.4×10^7 to $1.8 \times 10^7\ M^{-1}\,s^{-1}$, whereas at pH 3.0 they increase from 1.8×10^8 to $3.3 \times 10^8\ M^{-1}\,s^{-1}$. The plateau values, taken from the curves at neutral pH and at pH 3.0, are listed in

Table 1. Second-order rate constants for the reaction of halogenated alkylperoxyl radicals with iodide in different 2-propanol–water mixtures at neutral pH and pH 3.0

Radical	2-Propanol: water (v/v)	k(M^{-1} s^{-1})	
		Neutral pH	pH 3.0
$CF_3OO^{\cdot}$	1:9	$(7.1 \pm 0.3) \times 10^7$	$(2.9 \pm 0.2) \times 10^8$
	3:7	$(5.0 \pm 0.3) \times 10^7$	$(4.4 \pm 0.3) \times 10^8$
	2:3	$(4.3 \pm 0.2) \times 10^7$	$(5.3 \pm 0.3) \times 10^8$
	4:1	$(3.3 \pm 0.2 \times 10^7$	$(7.0 \pm 0.3) \times 10^8$
$CFCl_2OO^{\cdot}$	1:9	$(5.9 \pm 0.2) \times 10^7$	$(2.1 \pm 0.1) \times 10^8$
	3:7	$(4.3 \pm 0.1) \times 10^7$	$(2.5 \pm 0.1) \times 10^8$
	3:2	$(2.6 \pm 0.2) \times 10^7$	$(3.4 \pm 0.1) \times 10^8$
	4:1	$(2.0 \pm 0.2) \times 10^7$	$(4.0 \pm 0.2) \times 10^8$
$CCl_3OO^{\cdot}$	1:9	7.4×10^7	1.8×10^8
	3:7	5.5×10^7	2.1×10^8
	2:3	3.9×10^7	2.5×10^8
	3:2	2.4×10^7	3.0×10^8
	4:1	1.8×10^7	3.3×10^8
$C_2Cl_5OO^{\cdot}$	1:1	$(6.1 \pm 0.3) \times 10^7$	$(2.2 \pm 0.2) \times 10^8$
	3:2	$(4.8 \pm 0.2) \times 10^7$	$(2.3 \pm 0.2) \times 10^8$
	4:1	$(3.2 \pm 0.2) \times 10^7$	$(2.3 \pm 0.2) \times 10^8$
$CHCl_2OO^{\cdot}$	1:9	$(3.3 \pm 0.2) \times 10^7$	$(7.1 \pm 0.3) \times 10^7$
	3:7	$(1.7 \pm 0.1) \times 10^7$	$(5.4 \pm 0.3) \times 10^7$
	2:3	$(1.5 \pm 0.1) \times 10^7$	$(4.8 \pm 0.2) \times 10^7$
	3:2	$(1.1 \pm 0.1) \times 10^7$	$(3.5 \pm 0.2) \times 10^7$
	4:1	$(8.7 \pm 0.5) \times 10^6$	$(2.7 \pm 0.2) \times 10^7$
$CF_3CHClOO^{\cdot}$	1:9	$(4.1 \pm 0.3) \times 10^7$	$(5.8 \pm 0.3) \times 10^7$
	3:7	$(2.7 \pm 0.2) \times 10^7$	$(4.3 \pm 0.3) \times 10^7$
	2:3	$(2.1 \pm 0.2) \times 10^7$	$(3.7 \pm 0.2) \times 10^7$
	3:2	$(1.4 \pm 0.1) \times 10^7$	$(2.9 \pm 0.2) \times 10^7$
	4:1	$(8.0 \pm 0.4) \times 10^6$	$(2.0 \pm 0.1) \times 10^7$

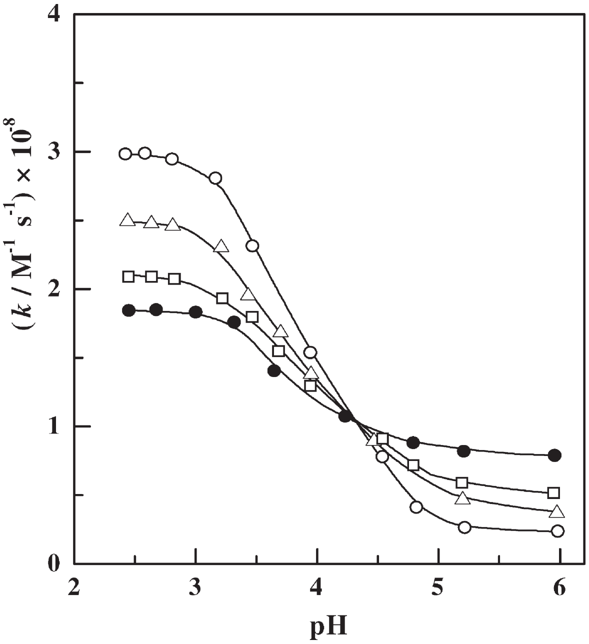

Figure 2. Second-order rate constants for the reaction of $CCl_3OO^{\cdot}$ radicals with iodide as a function of pH in air-saturated 2-propanol–water mixtures [(●) 1:9, v/v; (□) 3:7, v/v; (Δ) 2:3, v/v; (○) 3:2, v/v)] containing 3×10^{-2} M CCl_4 and 1×10^{-3} M KI

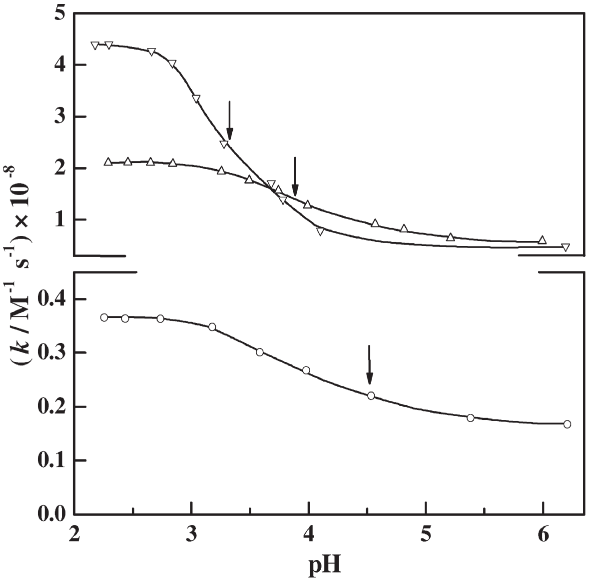

Figure 3. Second-order rate constants for the reaction of peroxyl radicals with iodide as a function of pH for $CF_3OO^{\cdot}$ (∇), $CCl_3OO^{\cdot}$ (Δ) and $CHCl_2OO^{\cdot}$ (○) in an air-saturated 2-propanol–water mixture (3:7, v/v) containing 1×10^{-3} M KI and 3×10^{-2} M RX

Table 1. For 4:1 (v/v) 2-propanol–water mixture experiments were performed only at neutral pH and pH 3.0.

Interestingly, the polarity of the solvent shows no influence on the inflection point of the curves which is at pH 4.0 for all solvent mixtures shown in Fig. 2. However, experiments with different peroxyl radicals have shown that not only the rate constants, but also the position of the inflection point of the curves depend on the degree of the peroxyl radical halogenation. Figure 3 shows the second-order rate constants obtained for the reaction of $CF_3OO^{\cdot}$, $CCl_3OO^{\cdot}$, and $CHCl_2OO^{\cdot}$ radicals with iodide as a function of pH measured in a 3:7 (v/v) 2-propanol–water mixture. It can be seen that the rate constants generally increase with the number of chlorine atoms, and also when chlorine is replaced by the more electronegative fluorine. At the same time, the inflection point of the curves moves to lower pH values (4.5 for $CHCl_2OO^{\cdot}$, 4.4 for $CCl_3OO^{\cdot}$ and 3.9 for $CF_3OO^{\cdot}$).

Solvent effects

The influence of the medium can, in principle, be approached by comparing the rate constants in different solvents. For instance, for reactions where the transition state is of more polar character than are the reactants, log$k$ should increase proportionally to the solvent dielectric constant.[31] For the solvent mixtures used in this work, dielectric constants were calculated by assuming additivity of this property,[10,31,32] i.e.

$$\varepsilon_{\text{mix}} = \sum_i \chi_i \varepsilon_i$$

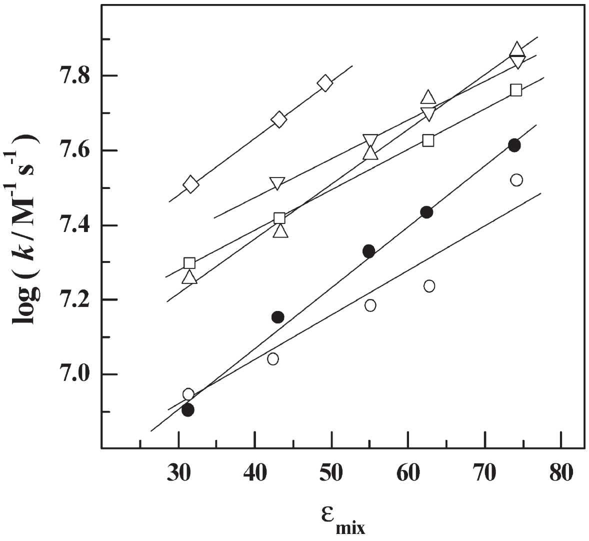

Figure 4. Plots of second-order rate constants for the reaction of peroxyl radicals with iodide (log*k*) as a function of the dielectric constant of the solvent mixture (ε_{mix}) for CF$_3$OO$^{\cdot}$ (▽), CF$_2$Cl$_2$OO$^{\cdot}$ (□), CCl$_3$OO$^{\cdot}$ (△), C$_2$Cl$_5$OO$^{\cdot}$ (◇), CF$_3$CHClOO$^{\cdot}$ (●) and CHCl$_2$OO$^{\cdot}$ (○) radicals at neutral pH

where χ_i is the volume fraction and ε_i the dielectric constant of the component i ($\varepsilon_{\text{2-propanol}} = 18.3$ and $\varepsilon_{\text{water}} = 80.1$).[33] Any contribution by the solute halogenated alkanes, which were present in relatively low concentration, was considered negligible.

The values listed in Table 1 for neutral pH are displayed in Fig. 4 as log*k* versus the dielectric constant of the solvent mixture, ε_{mix}. The rate constants for all peroxyl radicals are seen to increase with increasing solvent polarity and the data points fit straight lines reasonably well. The correlations, which describe log*k* as a function of the solvent dielectric constant, are given in Table 2. Although the differences in slopes are relatively small (0.010ε for CF$_3$OO$^{\cdot}$ to 0.017ε for CF$_3$CHClOO$^{\cdot}$, Fig. 4), it seems that the solvent effect becomes more pronounced for less halogenated radicals. At the same time, the intercepts (extrapolation to $\varepsilon = 0$) decrease. Thus, on going from CF$_3$OO$^{\cdot}$ to CHCl$_2$OO$^{\cdot}$, as representatives with substituents of highest and lowest overall electronegativity, the value of $k_{(\varepsilon=0)}$ decreases by a factor of about four (from 7.05 to 6.47 on a logarithmic scale).

Table 2. Correlations between second-order rate constant for the reaction of peroxyl radicals with iodide (log*k*) and dielectric constant of the solvent mixture (ε_{mix}) at neutral pH and pH 3.0

	Log*k* vs ε_{mix}	
Radical	Neutral pH	pH 3.0
CF$_3$OO$^{\cdot}$	$7.05 + 0.010\varepsilon$	$9.46 - 0.013\varepsilon$
CFCl$_2$OO$^{\cdot}$	$6.96 + 0.011\varepsilon$	$8.83 - 0.007\varepsilon$
CCl$_3$OO$^{\cdot}$	$6.77 + 0.015\varepsilon$	$8.72 - 0.006\varepsilon$
C$_2$Cl$_5$OO$^{\cdot}$	$7.01 + 0.015\varepsilon$	$8.36 - 0.001\varepsilon$
CHCl$_2$OO$^{\cdot}$	$6.47 + 0.015\varepsilon$	$6.99 + 0.010\varepsilon$
CF$_3$CHClOO$^{\cdot}$	$6.41 + 0.017\varepsilon$	$6.98 + 0.011\varepsilon$

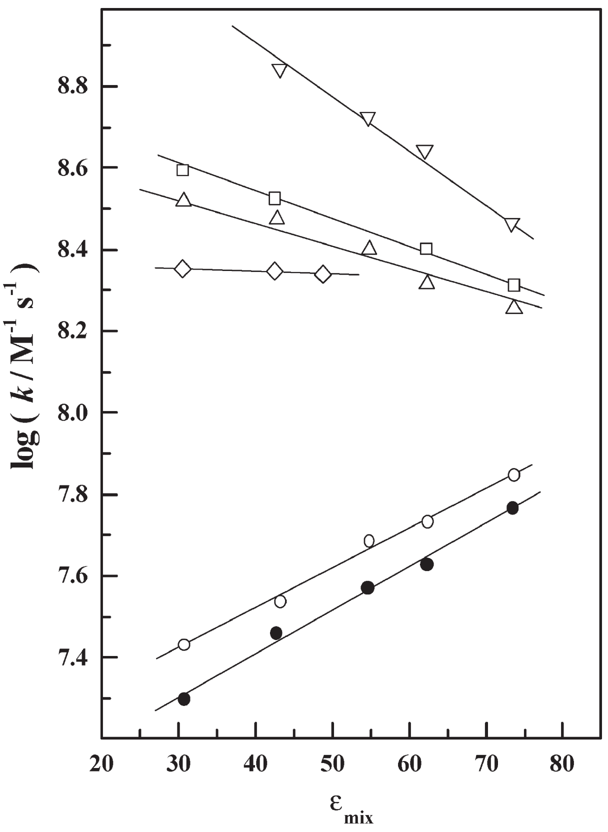

Figure 5. Plots of second-order rate constants for the reaction of peroxyl radicals with iodide (log*k*) as a function of dielectric constant of the solvent mixture (ε_{mix}) for CF$_3$OO$^{\cdot}$ (▽), CF$_2$Cl$_2$OO$^{\cdot}$ (□), CCl$_3$OO$^{\cdot}$ (△), C$_2$Cl$_5$OO$^{\cdot}$ (◇), CF$_3$CHClOO$^{\cdot}$ (●) and CHCl$_2$OO$^{\cdot}$ (○) radicals at pH 3.0

The same treatment was applied for the pH 3.0 data in Table 1. The results are shown in Fig. 5. Again, the data points fit straight lines fairly well. However, compared with neutral pH, the correlations obtained show now a distinctly different behavior. The numerical correlation values at pH 3.0 are also listed in Table 2. They vary from $\log k = 9.46 - 0.013\varepsilon$ for CF$_3$OO$^{\cdot}$ to $\log k = 6.98 + 0.011\varepsilon$ for CF$_3$CHClOO$^{\cdot}$ in their respective reactions with iodide. The observed 'weakening' of the solvent effect by increasing the degree of halogenation is even more pronounced at this lower pH. In fact, for highly halogenated radicals the slope even becomes negative. Thus, the correlations for CF$_3$CHClOO$^{\cdot}$ and CHCl$_2$OO$^{\cdot}$ show the same trend as correlations at neutral pH, i.e. the rate constants increase with increasing solvent polarity. The CCl$_3$CCl$_2$OO$^{\cdot}$ radical shows no particular dependence, whereas those at α-C more heavily halogenated peroxyl radicals CF$_3$OO$^{\cdot}$, CFCl$_2$OO$^{\cdot}$ and CCl$_3$OO$^{\cdot}$ now exhibit a decrease in the rate constant with increasing solvent polarity. Numerically, at acidic pH all rate constants are higher than those at neutral pH. As a result of that and because of the changes in the above-mentioned slope direction (turnover from positive to negative), the differences in intercepts are now huge compared with those at neutral pH. They increase by more than two orders of magnitude on going from $CF_3CHClOO^{\cdot}$ to $CF_3OO^{\cdot}$ (6.98 and 9.46, respectively, on a logarithmic scale). Clearly, the highest intercept, i.e. the highest rate constant extrapolated to $\varepsilon = 0$, is obtained for $CF_3OO^{\cdot}$. This hints at the exceptional oxidative power of the $CF_3OO^{\cdot}$ peroxyl radical and the capability to accept an electron independent of any assistance from a polar environment. It is noted that this appears to be particularly true for the acid system, where $k_{(\varepsilon=0)}$ exceeds the corresponding neutral value by two orders of magnitude, a finding for which we cannot provide any conclusive rationale.

The solvent effect on the reaction rate constant of halogenated alkylperoxyl radicals with different organic reductants has already been extensively investigated in various solvent systems.[20] Generally, the rate constants have been found to increase with increasing dielectric constant of the solvent. The only case reported so far where the rate constants decreased with increasing solvent polarity was for the electron transfer from zinc tetraphenylporphyrin (ZnTPP) to $CCl_3OO^{\cdot}$,[7] where complexation of ZnTPP with the solvent and the reaction of $CCl_3OO^{\cdot}$ with the complex were suggested to precede an inner-sphere electron transfer.

Our present data at neutral pH fall into the above-mentioned 'regular' category. However, the effect of solvent on both parameters, namely the slope and the intercept of the log$k$ vs ε relationship, is smaller than in previous investigations. For example, for the oxidation of chlorpromazine by $CCl_3OO^{\cdot}$ and $CHCl_2OO^{\cdot}$, these correlations were $\log k = 6.9 + 0.030\varepsilon$ and $5.7 + 0.033\varepsilon$, respectively,[10] (to be compared with $6.77 + 0.015\varepsilon$ and $6.47 + 0.014\varepsilon$ for the reaction of the same radicals with iodide obtained here, Table 2).

The solvent effect observed in acidic systems could be explained as the result of at least two compensating effects. A possible explanation could be found in the Hughes–Ingold rules on the influence of solvent polarity on the rate constant.[34] They consider polar interactions, based on a simple qualitative solvation model which considers only pure electrostatic interactions between ions or dipolar molecules and solvent molecules in initial and transition states. The reaction mechanism in our present system involves both dispersion and destruction of electrical charges in the initial steps of the peroxyl radical reaction with iodide [as formulated in general terms in reactions (7), (8a) or (10a), see the later Reaction mechanism section]. The changeover in the log$k$ vs ε correlations from positive to negative slopes at pH 3 (Fig. 5) can reasonably be rationalized by the pH dependence of equilibrium (8a) or (10a). With increasing acidity both equilibria are pushed in the direction of products. The protons also neutralize the OH^- generated in the process. The back-reactions should have a comparatively smaller influence on the overall rate constants in the acidic systems, hence the importance of the water content on the stabilization of the precursor complexes becomes smaller. This diminished influence of the water content is even apparent for $CF_3CHClOO^{\cdot}$ and $CHCl_2OO^{\cdot}$. At neutral pH, the respective correlations are 0.017ε and 0.014ε, as opposed to 0.011ε and 0.010 at pH 3. By increasing the degree of halogenation (σ^* value), the stability of the precursor complex(es) seems to be increased and, finally, the solvation effect becomes less important than the effect of the dispersion/destruction of electrical charges. According to the Hughes–Ingold rules, charge dispersion will cause a small decrease in rate constant as the polarity of the solvent increases. This is, in fact, the case for most of the investigated peroxyl radicals at acidic pH. For the $C_2Cl_5OO^{\cdot}$ radical, which shows no particular dependence on the dielectric constant, it seems that the two opposite effects are approximately of the same intensity.

Substituent effects

The rate constants listed in Table 1 clearly show a significant influence of various alkylperoxyl radical substituents. They increase with the number of halogen atoms and on going from chlorine to the more electronegative fluorine atom. This is a well-known effect, generally associated with the increase in the oxidation potentials of the respective peroxyl radicals.[20] Accordingly, the reactivities of the peroxyl radicals towards iodide studied here are expected to correlate with Taft's inductive substituent constants σ^*.[10,35] Some σ^* constants were available from the literature (for CCl_3 and $CHCl_2$).[36,37] To determine the values for the CF_3, $CFCl_2$ and CF_3CHCl groups, additivity was assumed with the respective contributions being derived from comparison with other values, as recommended by Alfassi *et al.*[10] In the case of $CFCl_2$, for example, the difference between the σ^* values for Cl and F was added to the known σ^* value for CCl_3.

Figure 6 shows the experimentally obtained correlation between log$k$ and Taft's σ^* constants for the reaction of various peroxyl radicals with iodide in three 2-propanol–water mixtures at neutral pH. Although the data points are rather scattered, all correlations exhibit, nevertheless, the same trend, i.e. the rate constant increases with increasing σ^*. In other words, electron-withdrawing substituents in the alkylperoxyl radicals increase the reactivity of these radicals as oxidants. Numerically, this materializes in the slopes of the correlations listed in Table 3. They vary from $\rho = 0.53$ ($\pm$0.04) to 0.29 ($\pm$0.06) for 4:1 and 1:9 (v/v) 2-propanol–water mixtures, respectively, i.e. they increase with increasing alcohol content in the solvent mixture. In view of the scatter of the data, the differences should, however, only conditionally be

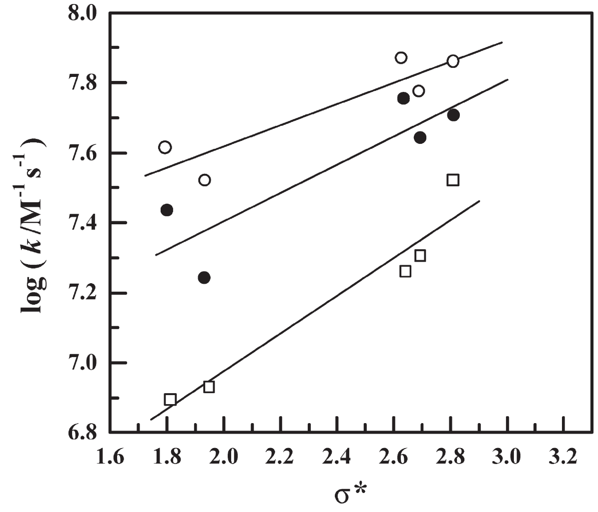

Figure 6. Plots of second-order rate constants for the reaction of peroxyl radicals with iodide (log*k*) as a function of Taft's inductive substituent constants (σ^*) for 2-propanol–water mixtures [(○) 1:9, v/v; (●) 3:7, v/v; (□) 4:1, v/v] at neutral pH

considered as real. The correlations are, in fact, almost parallel but the absolute values of the rate constants are clearly grouped for each solvent, being higher for solvents of higher polarity.

The same correlation was established for the rate constants measured at pH 3.0 (Table 1) and shown in Fig. 7. In this case the data points fit straight lines very well. Also, the effect of the substituent's electron-withdrawing power and the solvent influence is more pronounced than under neutral conditions. The slopes now vary from $\rho = 1.52$ (± 0.02) to 0.65 (± 0.01) for 4:1 and 1:9 (v/v) 2-propanol–water mixtures, respectively. These ρ values are also listed in Table 3. Compared with the neutral pH systems, the slopes at pH 3 are higher by a factor of 2.2 for 1:9 (v/v), 2.4 for 3:7 (v/v), and 2.9 for 4:1 (v/v) 2-propanol–water mixtures. It is also noteworthy that the solvent composition appears to influence the substituent effect much more strongly in the acidic solution. For example, at pH 3 the reactivity ratio $CF_3OO^{\cdot}$:$CCl_3OO^{\cdot}$:$CHCl_2OO^{\cdot}$ = 1:0.47:0.04 decreases to 1:0.62:0.24 as the water content of the solvent mixture increases from 20% to 90% (v/v), respectively. Under the same conditions, but in neutral systems, the respective values vary much less (1:0.5:0.3 and 1:1:0.5).

Table 3. Correlation values (ρ) obtained from the plot of second-order rate constants (log*k*) and Taft's inductive substituent constants (σ^*) for the reaction of halogenated alkylperoxyl radicals with iodide in different 2-propanol–water mixtures at neutral pH and pH 3.0

2-Propanol: water (v/v)	ρ	
	Neutral pH	pH 3.0
1:9	0.29 (±0.06)	0.65 (±0.01)
3:7	0.4 (±0.1)	0.92 (±0.02)
4:1	0.53 (±0.04)	1.52 (±0.02)

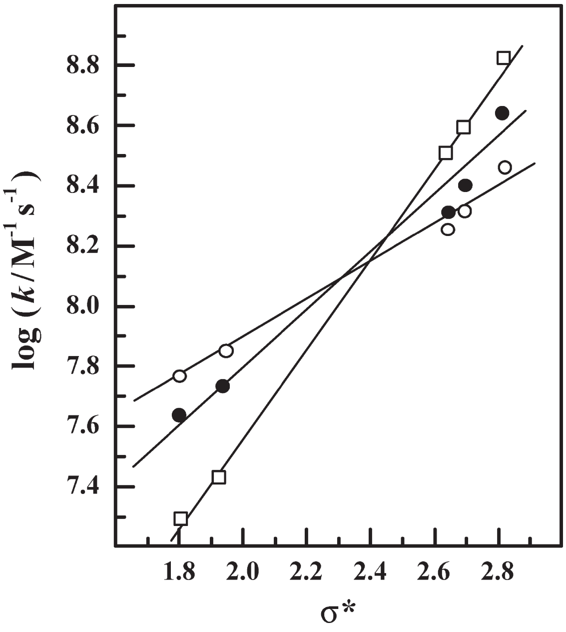

Figure 7. Plots of second-order rate constants for the reaction of peroxyl radicals with iodide (log*k*) as a function of Taft's inductive substituent constants (σ^*) for 2-propanol–water mixtures [(○) 1:9, v/v; (●) 3:7, v/v; (□) 4:1, v/v] at pH 3.0

Irrespective of pH, the rate constants increase with the inductive substituent constant σ^*, in accordance with previous findings for the oxidation of chlorpromazine,[10] ascorbate[13] and TMPD[13] by several halogenated alkylperoxyl radicals. For example, the correlation parameter between log*k* and σ^* was found to be $\rho = 0.41$ for ascorbate and 0.38 for TMPD.[13] The solvent influence on ρ has also been investigated before,[10] and qualitatively the same effect was found in this work, namely, a decrease in ρ with increasing solvent polarity.

Reaction mechanism

In the discussion of the reaction mechanism, it is important to note that all parameters investigated, namely pH, solvent polarity and peroxyl radical substituents, did not affect either the type of iodide oxidation products or their yield. Under all experimental conditions, I_3^- and $I_2^{\cdot-}$ were produced practically simultaneously and in equal yields. Numerically, the yields matched those published for $CCl_3OO^{\cdot}$ in our recent paper.[25] What were influenced by the above parameters, however, were the kinetics of the $I_3^-/I_2^{\cdot-}$ formation. Mechanistically, this is consistent with the multi-electron transfer mechanism, originally postulated for $CCl_3OO^{\cdot}$-induced oxidation of iodide.[24,25]

Our present results now allow us some further insight into the details of the initial steps in this mechanism. The relevant processes are summarized in reactions (7)–(14).

$$\mathrm{ROO}^{\cdot} + \mathrm{I}^{-} \rightleftharpoons [\mathrm{R{-}O{-}O{-}I}]^{\cdot -} \tag{7}$$

$$[\mathrm{R{-}O{-}O{-}I}]^{\cdot -} + \mathrm{H}^{+} \rightleftharpoons [\mathrm{R{-}O{-}O(H){-}I}]^{\cdot} \tag{8a}$$

$$[\mathrm{R{-}O{-}O{-}I}]^{\cdot -} + \mathrm{H_2O} \rightleftharpoons [\mathrm{R{-}O{-}O(H){-}I}]^{\cdot} + \mathrm{OH}^{-} \tag{8b}$$

$$[\mathrm{R{-}O{-}O(H){-}I}]^{\cdot} + \mathrm{I}^{-} \rightarrow \mathrm{RO}^{\cdot} + \mathrm{OH}^{-} + \mathrm{I_2} \tag{9}$$

$$[\mathrm{R{-}O{-}O{-}I}]^{\cdot -} + \mathrm{I}^{-} + \mathrm{H}^{+} \rightarrow \mathrm{RO}^{\cdot} + \mathrm{I_2} + \mathrm{OH}^{-} \tag{10a}$$

$$[\mathrm{R{-}O{-}O{-}I}]^{\cdot -} + \mathrm{I}^{-} + \mathrm{H_2O} \rightarrow \mathrm{RO}^{\cdot} + \mathrm{I_2} + 2\mathrm{OH}^{-} \tag{10b}$$

$$\mathrm{RO}^{\cdot} + \mathrm{I}^{-} \rightarrow \mathrm{I}^{\cdot} + \mathrm{RO}^{-} \tag{11}$$

$$\mathrm{I_2} + \mathrm{I}^{-} \rightleftharpoons \mathrm{I_3^{-}} \tag{12}$$

$$\mathrm{I}^{\cdot} + \mathrm{I}^{-} \rightleftharpoons \mathrm{I_2^{\cdot -}} \tag{13}$$

$$2\,\mathrm{I_2^{\cdot -}} \rightarrow \mathrm{I_3^{-}} + \mathrm{I}^{-} \tag{14}$$

The first step, reaction (7), is considered to be the addition of iodide to the peroxyl group and formation of the adduct radical anion. Protonation [reactions (8a) and (8b)] leads to the neutral species $[\mathrm{R{—}O{—}O(H){—}I}]^{\cdot}$, which then reacts with the second iodide as formulated in reaction (9). This reaction can be viewed as a nucleophilic S_N2 attack of the second iodide ion at the iodine atom of the protonated adduct.[24] The latter is considered to assume a slightly positive charge owing to the influence of the neighboring electronegative oxygen. Such an electronic situation is favorable for the formation of molecular $\mathrm{I_2}$, with simultaneous release of OH^- and $\mathrm{RO}^{\cdot}$. Mechanistically, the process includes an electron transfer into the hydroperoxide moiety, resembling typical Fenton chemistry features. Since it is not possible to time-resolve the initial peroxyl radical addition to I^- or the involvement of the protons, these two steps can be combined and, in fact, may well occur as a concerted process, as formulated in reactions (10a) and (10b)].

The alkoxyl radicals liberated in reactions (9) and (10) are responsible for the oxidation of the third iodide ion to iodine atoms [reaction (11)]. Reactions (12) and (13) represent the respective complexation of $\mathrm{I_2}$ and $\mathrm{I}^{\cdot}$ into $\mathrm{I_3}^-$ and $\mathrm{I_2}^{\cdot -}$. The last three processes are known to be very fast, and practically controlled only by diffusion.[38] They can, therefore, be excluded as overall rate determining. Finally, on a much longer time-scale (several tenths of a millisecond under the experimental condition of a relatively low dose per pulse), the $\mathrm{I_2}^{\cdot -}$ terminate by disproportionation [reaction (14)] to yield the remaining amount of $\mathrm{I_3}^-$.

In one specifically investigated system, namely the $\mathrm{CCl_3OO}^{\cdot}$-induced oxidation of iodide in 30% 2-propanol–water, time-resolved evidence has been found for a transient adduct. Its formation occurred about 10 times faster than its subsequent decay into $\mathrm{I_2}$ (observed as formation of $\mathrm{I_3}^-$).[23] Hence the rate-determining steps for the $\mathrm{I_3}^-/\mathrm{I_2}^{\cdot -}$ formation are reactions (9) and (10). Whether the formation of neutral $[\mathrm{ROO(H){—}I}]^{\cdot}$ radical occurs in two consecutive reaction steps or one concerted process also could not be decided in these experiments. Evidence was provided, however, for this protonated species being the reaction partner for the second iodide. This emerged from the kinetics of the $\mathrm{I_3}^-/\mathrm{I_2}^{\cdot -}$ formation, which were not influenced by the ionic strength at any pH.[24] Also, the shift of the inflection point to lower pH, exhibited in Fig. 3 for peroxyl radicals carrying increasingly electronegative substituents, is in accordance with the general influence of substituents on an acid's p*K* value.[34]

The observed acceleration of the overall rate on going to lower pH can reasonably be explained by the formation of the neutral adduct radical, causing the shift of equilibria (8) [and possibly also equilibrium (7)] to the right-hand side. This does not invalidate, however, our earlier explanation[24] on the role of H^+ in accelerating the overall rate constant, namely their assistance in the neutralization of the hydroxide ions liberated in reaction (9) [or reaction (10)]. Furthermore, both equilibria (7) and (8) may affect the observed reaction rate constant, i.e. under conditions where the respective forward processes become rate determining for the $\mathrm{I_2}$ formation. In our case, the proposed inner-sphere electron transfer occurs within a complex reaction mechanism which includes several reaction steps and equilibria. The observed overall reaction rate constant thus depends on all three parameters (pH, solvent polarity and electronegativity of the substituents) investigated in this study. In particular, the observed pH dependence may not directly reflect the true p*K* value of the adduct radical.

In conclusion, the results obtained in this work on solvent and substituent effects are well in line with previous reports for the one-electron transfer reactions of halogenated alkylperoxyl radicals towards a variety of reductants like chlorpromazine,[11] ascorbate,[13,14] trolox[14] and TMPD.[13,14] It has now become clear that the initial transient adduct radicals are the common base for the one-electron and multi-electron reactions. There are, indeed, convincing reports that also other presumed one-electron oxidations by peroxyl radicals proceed via such adduct intermediates, with subsequent electron transfers taking place by an inner-sphere mechanism.[10,13] A striking example of the simultaneous formation of one- and two-electron transfer reaction products is the reaction of $CCl_3OO^{\cdot}$ radicals with dimethyl sulfide.[21–23] These studies clearly revealed that two-electron transfers are possible and, in fact, fairly common between peroxyl radicals and suitable molecules containing heteroatoms as radical docking sites. In particular, it is important to note that the formation of a typical one-electron transfer product does not preclude the occurrence of an immediately preceding two-electron transfer process. In the case of iodide, the stable two-electron transfer product (I_3^-) and the transient one-electron product ($I_2^{\cdot -}$) exhibit very strong absorption bands, making them particularly suitable markers for direct investigation. For many other, particularly two-electron, oxidation products, this is, unfortunately, not the case, making an unambiguous identification and unraveling of mechanistic details more challenging. However, the results obtained in this work, and also some previous observations,[21–25] generate some new perceptions about the role of peroxyl radicals and, in particular, their involvement in fast and efficient multi-electron transfer processes.

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