Reduction Potential of the *tert*-Butylperoxyl Radical in Aqueous Solutions

Tomi Nath Das,[†] T. Dhanasekaran, Z. B. Alfassi,[‡] and P. Neta*

Physical and Chemical Properties Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

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Rate constants for oxidation of *tert*-butyl hydroperoxide anion ($t\text{-BuO}_2^-$) by several oxidants were determined by pulse radiolysis. Rapid oxidation was found with $N_3^\bullet$ (4.4×10^8 L mol^{-1} s^{-1}) and $^\bullet O^-$ (2.6×10^8 L mol^{-1} s^{-1}), but others ($Br_2^{\bullet-}$, $I_2^{\bullet-}$, $ClO_2^\bullet$, $CO_3^{\bullet-}$, $C_6H_5N(CH_3)_2^{\bullet+}$) reacted much more slowly. Since the reduction potentials of these oxidants are much higher than that estimated for $t\text{-BuO}_2^\bullet$, the observed rate constants suggest that the self-exchange rate for $t\text{-BuO}_2^\bullet/t\text{-BuO}_2^-$ is very slow and that it would be difficult to establish rapid equilibrium by pulse radiolysis with a suitable redox pair. Therefore, to determine the reduction potential for this peroxyl radical, the forward and reverse rate constants for reaction 6, $t\text{-BuO}_2^\bullet + Fe(CN)_6^{4-} \rightleftarrows t\text{-BuO}_2^- + Fe(CN)_6^{3-}$, were measured independently. The forward rate constant was measured by kinetic spectrophotometric pulse radiolysis in N_2O-saturated solutions containing high concentrations of N_3^- (1 mol L^{-1}), $t\text{-BuO}_2^-$ (0.4 mol L^{-1}), and varying concentrations of $Fe(CN)_6^{4-}$ (0.012−0.036 mol L^{-1}) at pH 13.7. The rate constant k_6 was found to be 2.5×10^2 L mol^{-1} s^{-1}. Such a low rate constant was possible to measure by pulse radiolysis only because the self-decay of $t\text{-BuO}_2^\bullet$ is very slow compared to those of other peroxyl radicals. The reverse reaction rate constant was measured by mixing the reactants and following the disappearance of $Fe(CN)_6^{3-}$ in the presence of spin traps to remove the peroxyl radicals from the equilibrium. A rate constant of $k_{-6} = 1.4 \times 10^{-2}$ L mol^{-1} s^{-1} was derived. By taking the reduction potential of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ as 0.459 V vs NHE for the conditions used in these experiments, we calculate $E(t\text{-BuO}_2^\bullet/t\text{-BuO}_2^-) = 0.71$ V and $E(t\text{-BuO}_2^\bullet/t\text{-BuO}_2H) = 1.05$ V at pH 7 and 1.47 V at pH 0. The rate constants for oxidation of $Fe(CN)_6^{4-}$ and other compounds by various peroxyl radicals were then utilized for the estimation of the reduction potentials of these peroxyl radicals.

Introduction

Organic peroxyl radicals react with various compounds by several possible mechanisms, mainly hydrogen abstraction, addition to unsaturated bonds, and oxidation.[1,2] The most important mechanism in aqueous solutions is that of electron transfer to peroxyl radicals from various reductants (such as antioxidants). Rate constants for electron transfer to peroxyl radicals vary widely;[3] they were shown to be strongly affected by substituents on the radical, by the reduction potential of the other reactant, and by the solvent composition. Knowledge of the reduction potentials of peroxyl radicals will permit prediction of their electron-transfer rate constants based on the Marcus theory.[4] Reduction potentials have been estimated and calculated for a number of organic peroxyl radicals,[5−7] but no direct experimental measurements of these potentials have been reported. A value for the methylperoxyl radical ($E_7 = 1.05$ V vs NHE)[8] has been derived from the rate constants for oxidation of several ferrocenes by $CH_3O_2^\bullet$ by using the Marcus relation. The reduction potentials for a series of peroxyl radicals have been estimated from their rate constants with various reductants by using as reference the reduction potentials estimated for $CH_3O_2^\bullet$ and other simple peroxyl radicals. These estimates, in turn, were based on the reduction potential of $HO_2^\bullet$, which is the only measured value available. However, estimations of values for $RO_2^\bullet$ on the basis of results for $HO_2^\bullet$ may suffer from uncertainties due to the much stronger hydrogen bonding in $HO_2^\bullet$ as compared with $RO_2^\bullet$. This difference is reflected in the anomalously high boiling point of H_2O_2 and the discrepancy between its enthalpy of formation and that calculated by group additivity values based on data for alkyl hydroperoxides.[9]

To measure a reduction potential for an $RO_2^\bullet/RO_2^-$ redox pair by equilibration with a reference redox pair, it is important to have a stable hydroperoxide. One of the few stable hydroperoxides known is the *tert*-butyl hydroperoxide. This compound is used in the present study to determine the reduction potential of the *tert*-butylperoxyl radical. The estimated value for this radical was reported to be ∼0.35 V lower than that estimated for the methylperoxyl.[7] The present study is aimed at measuring the reduction potential of $t\text{-BuO}_2^\bullet$ directly and using this value for estimating the potentials of other organic peroxyl radicals. Various approaches have been attempted, and the combination of several kinetic measurements permitted determination of the potential of $t\text{-BuO}_2^\bullet$.

Experimental Section

The organic compounds *tert*-butyl hydroperoxide, *N*,*N*-dimethylaniline (DMA), *N*,*N*-dimethyl-4-toluidine (DMT), and the spin traps *N*-*tert*-butyl-α-phenylnitrone (PBN) and nitromethane (NM) were obtained from Aldrich.[10] The inorganic compounds were mostly from Mallinckrodt and were of the purest grade available. Water was purified by a Millipore Super-Q system. Changes in the concentrations of $Fe(CN)_6^{3-}$ upon thermal and radiolytic reactions were determined spectrophotometrically. The molar absorptivity of $Fe(CN)_6^{3-}$ was measured to be 1070 L mol^{-1} cm^{-1} at 420 nm, whereas that of $Fe(CN)_6^{4-}$ at the same wavelength was only <5 L mol^{-1} cm^{-1}.

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* To whom correspondence should be addressed.

[†] On leave from the Bhabha Atomic Research Centre, Trombay, Mumbai, India.

[‡] Permanent address: Ben-Gurion University of the Negev, Beer Sheva, Israel.

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The rate constants of thermal reactions were determined from the kinetics of either the disappearance or the formation of $Fe(CN)_6^{3-}$. The reactants were placed in separate compartments in a divided quartz cell, and the absorbance was measured before mixing and was then followed for 10−30 min after mixing, until it reached a steady value. Fast kinetic experiments were carried out by pulse radiolysis. Two independent facilities were used; one based on a Febetron 705 pulser providing single 50 ns pulses of 2 MeV electrons and the other on a Varian linear accelerator providing multiple pulses of 5 MeV electrons with variable pulse duration from 20 ns to 2 μs. The detection in both systems is based on optical absorption in the UV and visible range. Second-order rate constants were derived from the concentration dependence of the observed first-order rate constants. The relative standard uncertainties of these rate constants are estimated to be ±10−15%. All measurements were carried out at room temperature (20 ± 2 °C).

Results and Discussion

The reduction potential of $t\text{-BuO}_2^\bullet$ may be determined by establishing equilibrium 1 with a reference redox pair (A/A^-),

$$A + t\text{-BuO}_2^- \rightleftarrows A^- + t\text{-BuO}_2^\bullet \tag{1}$$

and determining the equilibrium constant, K_1, either from the equilibrium concentrations of the four components or from the rate constants of the forward and reverse reactions, k_1 and k_{-1}. To assess the possibility of reaching such an equilibrium, we began by studying the oxidation of $t\text{-BuO}_2^-$ at high pH ($pK_a(t\text{-BuO}_2H) = 12.8$)[11] with various oxidants.

Kinetic spectrophotometric pulse radiolysis was utilized for production of various oxidizing species and for measuring the kinetics of their reactions with $t\text{-BuO}_2^-$. The oxidants listed in Table 1 were produced in N_2O-saturated solutions containing the appropriate precursor, as indicated. For example, the azidyl radical was formed by the following reactions.

$$H_2O \rightsquigarrow e_{aq}^- + H^\bullet + {}^\bullet OH + H_2 + H_2O_2 \tag{2}$$

$$e_{aq}^- + N_2O \rightarrow N_2 + OH^- + {}^\bullet OH \tag{3}$$

$${}^\bullet OH + N_3^- \rightarrow OH^- + N_3^\bullet \tag{4}$$

The rate constant for oxidation of $t\text{-BuO}_2^-$ by the azidyl radical

$$N_3^\bullet + t\text{-BuO}_2^- \rightarrow N_3^- + t\text{-BuO}_2^\bullet \tag{5}$$

and by the other oxidants were determined by following the decay of the optical absorption of the oxidizing radical, since the absorption of the peroxyl radical formed is generally weaker and at lower wavelength. For the case of ${}^\bullet O^-$, however, because the absorbances of both reactants and products are fairly low, we used competition with the reaction ${}^\bullet O^- + O_2 \rightarrow {}^\bullet O_3^-$ and followed the production of the ozonide anion at 430 nm. The second-order rate constants were determined from the dependence of the first-order rate constants on the concentration of the hydroperoxide anion, calculated from the total concentration of the hydroperoxide added and the pH of the solution by taking $pK_a = 12.8$ for $t\text{-BuO}_2H$.[11] In this calculation we assume that the reactivity of the neutral $t\text{-BuO}_2H$ is very small compared to that of the anion. This was confirmed to be the case for the reaction of $N_3^\bullet$, where the rate constant was measured to be 4.4×10^8 L mol^{-1} s^{-1} for the anion but only $<5 \times 10^4$ L mol^{-1} s^{-1} for the neutral form at pH 7.

TABLE 1: Rate Constants for Oxidation of *tert*-Butyl Hydroperoxide Anion by Various Radicals

radical	E^a (V)	precursors^b	λ (nm)	pH	k (L mol^{-1} s^{-1})
$N_3^\bullet$	1.33^c	N_3^- (0.1)	278	13.4	$(4.4 \pm 0.4) \times 10^8$
${}^\bullet O^-$	1.77^c	H_2O^d	430	14	$(2.6 \pm 0.3) \times 10^8$
$Br_2^{\bullet -}$	1.62^c	Br^- (0.1)	360	13.0	$(5.0 \pm 0.5) \times 10^6$
$I_2^{\bullet -}$	1.03^c	I^- (0.1)	380	13.7	$(1.6 \pm 0.2) \times 10^6$
$CO_3^{\bullet -}$	1.59^e	CO_3^{2-} (0.2)	600	13.3	$(1.1 \pm 0.1) \times 10^6$
$ClO_2^\bullet$	0.934^c	ClO_2^- (0.025)	360	13.3	$(4.8 \pm 0.5) \times 10^5$
$Mo(CN)_8^{3-}$	0.84^f	$Mo(CN)_8^{4-}$ (0.03)	385	13.6	$<10^5$
$DMA^{\bullet +}$	0.86^g	DMA (0.005)^h	450	13.1	$(2.1 \pm 0.2) \times 10^6$
$DMT^{\bullet +}$		DMT (0.035)^h	425	13.0	$(3.9 \pm 0.4) \times 10^6$
$PhO^\bullet$	0.79^i	PhO^- (0.08)	400	13.5	$<3 \times 10^4$

[a] One-electron reduction potential of the oxidizing species used, taken from the literature as indicated. [b] The values in parentheses are the concentrations in mol L^{-1}. All solutions were saturated with N_2O and were examined by the Febetron based pulse radiolysis system at room temperature. [c] From Stanbury, D. M. *Adv. Inorg. Chem.* **1989**, *33*, 69. [d] Saturated with $N_2O/O_2 = 9/1$. [e] From Huie, R. E.; Clifton, C. L.; Neta, P. *Radiat. Phys. Chem.* **1991**, *38*, 477. [f] From ref 18. [g] From Huie, R. E.; Neta, P. *J. Phys. Chem.* **1986**, *90*, 1193. [h] DMA = *N*,*N*-dimethylaniline, DMT = *N*,*N*-dimethyl-4-toluidine; these solutions also contained 0.1 mol L^{-1} N_3^-. [i] From Lind, J.; Shen, X.; Eriksen, T. E.; Merenyi, G. *J. Am. Chem. Soc.* **1990**, *112*, 479.

The rate constant for oxidation of $t\text{-BuO}_2^-$ by $N_3^\bullet$ is only 4.4×10^8 L mol^{-1} s^{-1} (Table 1) despite the large driving force for this reaction, i.e., an expected difference in reduction potential greater than 0.5 V. The rate constants for $Br_2^{\bullet -}$ and $CO_3^{\bullet -}$ are only 5×10^6 and 1.1×10^6 L mol^{-1} s^{-1}, respectively, despite their high reduction potentials. $I_2^{\bullet -}$ and the radical cations of *N*,*N*-dimethylaniline and *N*,*N*-dimethyl-4-toluidine also oxidize $t\text{-BuO}_2^-$ with relatively low rate constants (Table 1). All these rate constants are much lower, for example, than those for oxidation of phenoxide by the same species. These findings suggest that the self exchange rate for the couple $t\text{-BuO}_2^\bullet/t\text{-BuO}_2^-$ is very low. As a result, any electron-transfer involving this couple that may lead to a measurable equilibrium can be expected to have a very low rate constant that may not be measurable by the pulse radiolysis technique, due to the limited lifetimes of the radicals involved.

By comparison with primary and secondary alkylperoxyl radicals, the self-decay of $t\text{-BuO}_2^\bullet$ is relatively slow ($2k = 2 \times 10^4$ L mol^{-1} s^{-1}).[3] We searched for a reference redox pair that also involves long-lived or stable species. We examined several ferrocenes, substituted phenols, *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine, and various metal complexes and found the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ system to be the only suitable pair for use as the reference for the $t\text{-BuO}_2^\bullet/t\text{-BuO}_2^-$ pair.

$$t\text{-BuO}_2^\bullet + Fe(CN)_6^{4-} \rightleftarrows t\text{-BuO}_2^- + Fe(CN)_6^{3-} \tag{6}$$

The rate constant k_6 was measured by the pulse radiolysis technique. The peroxyl radical, $t\text{-BuO}_2^\bullet$, was generated by the rapid reaction 5 of the azidyl radical with the hydroperoxide. To maximize the formation of this radical, we used high concentrations of $t\text{-BuO}_2^-$ (0.4 mol L^{-1}). In turn, to maximize the precursor reaction 4, we used very high concentrations of azide (1 mol L^{-1}). Despite this, some of the oxidizing radicals reacted directly with the $Fe(CN)_6^{4-}$, since this reactant had to be added at relatively high concentrations for the slow reaction 6 to take place before significant decay of the radicals. Fortunately, the $t\text{-BuO}_2^\bullet$ radicals undergo a very slow second-order decay, with a first half-life of ∼10 s at the radical concentrations used in these experiments (radiation dose of ∼16 Gy per pulse). The kinetic traces show a rapid step of oxidation of $Fe(CN)_6^{4-}$, mainly by $N_3^\bullet$ radicals, and a much slower step of oxidation by the $t\text{-BuO}_2^\bullet$ radical extending over 0.5−1.5 s. Figure 1a shows an example of such a kinetic trace; eight such

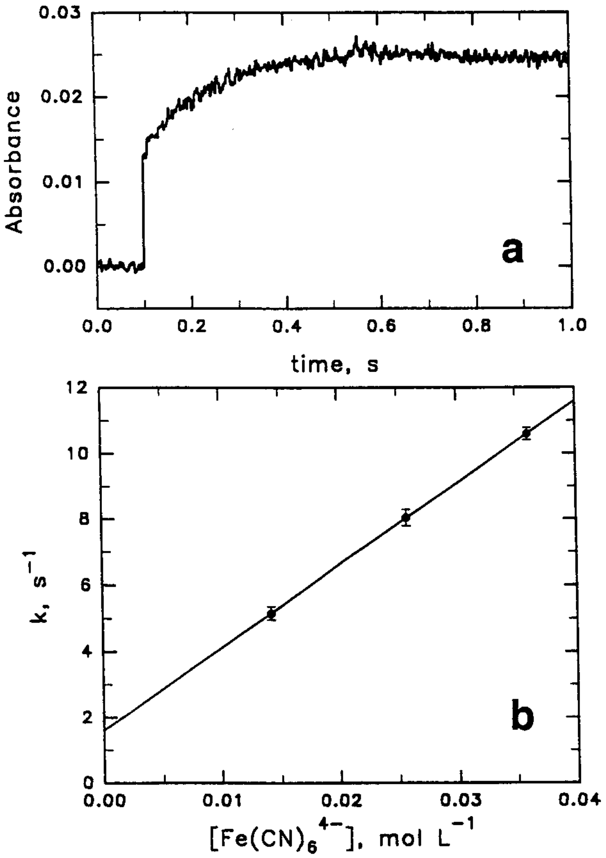

Figure 1. Oxidation of $Fe(CN)_6^{4-}$ by t-$BuO_2^\bullet$. (a) Kinetic trace showing formation of absorbance at 430 nm, due to $Fe(CN)_6^{3-}$, in a fast step followed by a much slower step. (b) Rate constant of the slow formation reaction as a function of $[Fe(CN)_6^{4-}]$. The solutions contained 1 mol L^{-1} NaOH, 1 mol L^{-1} NaN_3, 0.4 mol L^{-1} *tert*-butyl hydroperoxide, and various concentrations of $Fe(CN)_6^{4-}$, were saturated with N_2O, and irradiated with an electron pulse that provided a dose of 16 Gy. In general, seven traces were averaged to obtain the trace shown in (a), and eight such averages were run for each concentration of $Fe(CN)_6^{4-}$.

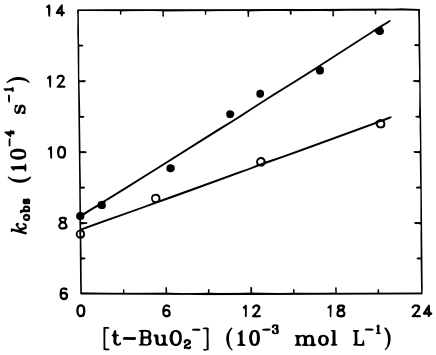

Figure 2. Rate constants for oxidation of t-BuO_2^- by $Fe(CN)_6^{3-}$ in the presence of spin traps. Solutions containing 1×10^{-4} mol L^{-1} $Fe(CN)_6^{3-}$, 0.2 mol L^{-1} KOH, 0.02 mol L^{-1} spin trap (○, PBN; ●, NM), and the indicated concentration of t-BuO_2^- were prepared by rapid mixing in a spectrophotometer cell, and the absorbance at 420 nm was followed over time.

traces were recorded for each concentration of $Fe(CN)_6^{4-}$. From the dependence of the rate constant of the slow step on $[Fe(CN)_6^{4-}]$ between 0.014 and 0.036 mol L^{-1} (Figure 1b), we calculate a rate constant of $(2.5 \pm 0.3) \times 10^2$ L mol^{-1} s^{-1} for reaction 6. The concentration of $Fe(CN)_6^{4-}$ was restricted to the above range because at lower concentrations the self-decay of the peroxyl radicals competes considerably with reaction 6 whereas at higher concentrations the rapid direct oxidation of the ferrocyanide competes with reaction 5; thus, the contribution of the slow reaction 6 becomes very small, and the traces do not provide accurate rate constants. It should be pointed out that the above measurements were done over a long time scale, and thus the solution in the cell, which was exposed to the analyzing light for >1 s, underwent considerable photooxidation of $Fe(CN)_6^{4-}$ to $Fe(CN)_6^{3-}$ if it was not protected. To avoid this interfering process, we protected the cell from light at $\lambda <$ 420 nm and measured the formation kinetics at 430 nm. Under these conditions there was no detectable photochemistry in the solution by the analyzing light.

The G value for the total yield of $Fe(CN)_6^{3-}$ produced by the radiation pulse was estimated from the kinetic traces, such as that in Figure 1a. Taking into account the intercept of the plot in Figure 1b, we calculate a limiting G value of 0.6 μmol J^{-1}. This value indicates that most of the primary radicals produced by the radiolysis of the solution lead to eventual oxidation of $Fe(CN)_6^{4-}$. This implies that most of the e_{aq}^- also result in eventual oxidation. In the above treatment we took into account reactions 2−6 and the partial direct oxidation of ferrocyanide by $N_3^\bullet$ radicals and assumed that all e_{aq}^- react with N_2O (reaction 3). However, the high concentrations of *tert*-butyl hydroperoxide used in these experiments compete with reaction 3 to form the *tert*-butoxyl radical (and its subsequent products). Our results show, however, that despite this competition, most of the radicals formed by the reaction of e_{aq}^- with the hydroperoxide also lead to eventual oxidation of ferrocyanide. This is not surprising since t-$BuO^\bullet$ has been shown to oxidize a number of other compounds quite rapidly.[12]

The reverse reaction 6 is observed to occur over minutes, and thus it cannot reach equilibrium since the t-$BuO_2^\bullet$ radicals decay by radical−radical reactions. The disappearance of $Fe(CN)_6^{3-}$ is controlled mainly by this decay. To measure the rate constant for this reaction (k_{-6}) while suppressing the forward reaction (k_6), we adapted the spin trapping method utilized by Ram and Stanbury.[13] The spin traps react rapidly with the peroxyl radicals but not with the other species involved in equilibrium 6. The decay of $Fe(CN)_6^{3-}$ in the absence of spin traps, controlled by the decay of t-$BuO_2^\bullet$, is relatively slow. Addition of spin traps, to scavenge the peroxyl radicals and prevent the back-reaction, accelerates the decay of $Fe(CN)_6^{3-}$ until it becomes limited by the rate of reaction −6. Two spin traps were utilized for this purpose, *N*-*tert*-butyl-α-phenylnitrone (PBN)[14] and the aci-anion of nitromethane ($CH_2{=}NO_2^-$).[15] A concentration of 0.02 mol L^{-1} of either one of the spin traps was sufficient to give the highest experimental rate constant for decay of $Fe(CN)_6^{3-}$. From the dependence of the observed decay rate constant on $[t\text{-}BuO_2^-]$, under conditions of $[t\text{-}BuO_2^-] \gg [Fe(CN)_6^{3-}]$, we derived a second-order rate constant $k_{-6} = 1.4 \times 10^{-2}$ L mol^{-1} s^{-1} (Figure 2) from the experiments with PBN. Similar results were obtained by using the nitromethane anion as the spin trap, with $k = 2.6 \times 10^{-2}$ L mol^{-1} s^{-1} (Figure 2). This higher value is due to the fact that the species formed by spin trapping, t-$BuOO{-}CH_2{-}NO_2^{\bullet-}$, is a nitro radical anion which also reduces $Fe(CN)_6^{3-}$,[16] so that reaction −6 results in the overall reduction of two $Fe(CN)_6^{3-}$ ions. By taking this stoichiometric factor into account, the value of k_{-6} is 1.3×10^{-2} L mol^{-1} s^{-1}, in good agreement with the value derived from the experiments with PBN. The linear plots in Figure 2 show large intercepts, which are due to the decay of $Fe(CN)_6^{3-}$ in the presence of the spin traps alone (without hydroperoxide) under the same alkaline conditions.

The reduction potential of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ was reported to increase from 0.356 V at zero ionic strength to 0.459 V at 0.1 mol L^{-1} total $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ concentration.[17,18] This increase leads to a lower driving force for the oxidation of ferrocyanide by the peroxyl radical and thus to a decrease in the rate constant. For calculation of the equilibrium constant K_6 we used conditions of high ferrocyanide concentrations or high ionic strength, which are consistent with the higher reduction potentials. The rate constants under these conditions are $k_6 = 2.5 \times 10^2$ L mol^{-1} s^{-1} and $k_{-6} = 1.4 \times 10^{-2}$ L mol^{-1} s^{-1}, and thus $K_6 = 1.8 \times 10^4$. By taking the reduction potential of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ as 0.459 V vs NHE for the conditions used in these experiments, we calculate $E(t\text{-}BuO_2^{\bullet}/t\text{-}BuO_2^-) = 0.71$ V. From the pH dependence of E $\{E_{pH} = E_0 + 0.059 \log(K_a + [H^+])\}$, by using the p$K_a$ value of t-BuO$_2$H, we calculate $E(t\text{-}BuO_2^{\bullet},H^+/t\text{-}BuO_2H) = 1.05$ V at pH 7 and 1.47 V at pH 0.

The Marcus equation[4] for adiabatic electron transfer relates the rate constant, k, with the free energy of the reaction, $\Delta G°$, the reorganization energy, λ, and the work required to bring the reactants together, w_R, and to pull the products apart, w_P:

$$k = Ze^{-\Delta G^{\ddagger}/RT} \tag{7}$$

$$\Delta G^{\ddagger} = w_R + \frac{\lambda}{4}\left(1 + \frac{\Delta G° + w_P - w_R}{\lambda}\right)^2 \tag{8}$$

The work term can be reduced to the form

$$w_{ab} = \frac{4.23 \times 10^{-8} z_a z_b}{r(1 + 3.28 \times 10^7 r(\mu^{1/2}))} \tag{9}$$

where z_a and z_b are the ionic charges of the species involved, r is the reaction distance, and μ is the ionic strength. By taking the collision frequency $Z = 1 \times 10^{11}$ s^{-1} and the value of $K_6 = 1.8 \times 10^4$ calculated above, we derive $\lambda = 238$ kJ mol^{-1} for reaction of t-BuO$_2^{\bullet}$ with $Fe(CN)_6^{4-}$.

If we assume that the reorganization energy λ is the same for similar reactions of other peroxyl radicals, we can utilize the experimental rate constants for oxidation of $Fe(CN)_6^{4-}$ by various peroxyl radicals to estimate the reduction potentials for these radicals. These reduction potentials were derived in this manner because it is not possible to determine them more accurately by experimental measurements, similar to those described above for t-BuO$_2^{\bullet}$, due to the instability of the corresponding hydroperoxides. The rate constants for oxidation of $Fe(CN)_6^{4-}$ by various peroxyl radicals, summarized in Table 2, were partly measured in this study and partly taken from the literature.[19] From these rate constants and eqs 7 and 8, assuming the same λ and w_P as above, we calculate the reduction potentials for the various $RO_2^{\bullet}/RO_2^-$ pairs (Table 2).

Rate constants have been reported also for the reactions of t-BuO$_2^{\bullet}$ and several other peroxyl radicals with TMPD (N,N,N',N'-tetramethyl-p-phenylenediamine).[20] By taking those rate constants, the value for the reduction potential of $t\text{-}BuO_2^{\bullet}/t\text{-}BuO_2^- = 0.71$ V, and the reduction potential for $TMPD^{\bullet+}/TMPD = 0.265$ V[21] and by assuming the same λ value for all the peroxyl radicals, we calculate another set of reduction potentials (Table 2). The value of λ for these reactions was 162 kJ mol^{-1}, considerably lower than that for the reaction with ferrocyanide. Because some of the rate constants used in these calculations are relatively high, they were corrected for the effect of diffusion ($k_{act}^{-1} = k_{obs}^{-1} - k_{diff}^{-1}$). Nevertheless, the reduction potentials calculated for $Cl_2CHO_2^{\bullet}$ and $Cl_3CO_2^{\bullet}$ are substantially lower than those calculated on the basis of the ferrocyanide results. This discrepancy may be due to experimental uncertainties in the reported rate constants or may indicate that the assumption of constant λ for all radicals reacting with the same reductant is not completely correct.

TABLE 2: Calculated Reduction Potentials of Peroxyl Radicals

	from $Fe(CN)_6^{4-}$		from TMPD		from ascorbate	
radical	k^a	E^b	k^a	E^b	k^a	E^b
$(CH_3)_3CO_2^{\bullet}$	2.5×10^2	0.71	1.1×10^6	0.71		
$CH_3O_2^{\bullet}$	8×10^3 [c]	0.92	4.3×10^7	0.96	1.7×10^6	0.94
$HOCH_2O_2^{\bullet}$	9×10^4	1.07	7.2×10^7	1.00	4.7×10^6	1.01
$NCCH_2O_2^{\bullet}$	2.0×10^6	1.29	2.9×10^8	1.11	5.0×10^7	1.19
$ClCH_2O_2^{\bullet}$	1.8×10^6 [d]	1.28	4.2×10^8	1.15	1.2×10^8	1.26
$Cl_2CHCO_2^{\bullet}$	2.9×10^7 [d]	1.51	7.4×10^8	1.20	7.0×10^8	1.43
$Cl_3CO_2^{\bullet}$	4.6×10^7 [d]	1.55	1.7×10^9	1.31	9.1×10^8	1.47
$C_6H_5O_2^{\bullet}$	3.1×10^6 [d]	1.33				
$CH_3CH_2O_2^{\bullet}$			3.3×10^7	0.94		
$(CH_3)_2CHO_2^{\bullet}$			9.2×10^6	0.85		

[a] Rate constants, in L mol^{-1} s^{-1}, for reaction of $RO_2^{\bullet}$ with $Fe(CN)_6^{4-}$ (measured in this study or taken from ref 19 as noted) and with ascorbate (from ref 20) were measured at pH 7 and those for TMPD (from ref 20) were measured at pH 8. [b] Reduction potentials for $RO_2^{\bullet}/RO_2^-$, in V vs NHE, calculated as discussed in the text. [c] This value was remeasured in this study since the reported values (in refs 8 and 19) differ considerably. The present value was measured at low dose per pulse and supports that reported in ref 8. [d] From ref 19.

TABLE 3: Calculated Reduction Potentials of Peroxyl Radicals and O−H Bond Dissociation Energies of Hydroperoxides

radical	$E(RO_2/RO_2^-)^a$ (V)	p$K_a(RO_2H/RO_2^-)^b$	$E(RO_2/RO_2H)$ at pH 0 (V)	$E_{bd}(ROO{-}H)_g^c$ (kJ mol^{-1})
$(CH_3)_3CO_2^{\bullet}$	0.71	12.8	1.47	369
$(CH_3)_2CHO_2^{\bullet}$	0.81	(11.9)	1.51	372
$CH_3CH_2O_2^{\bullet}$	0.91	(11.2)	1.57	379
$CH_3O_2^{\bullet}$	0.94	11.5	1.62	383
$HOCH_2O_2^{\bullet}$	1.02	(10.7)	1.65	388
$NCCH_2O_2^{\bullet}$	1.20	(9.8)	1.78	400
$ClCH_2O_2^{\bullet}$	1.23	(9.5)	1.79	401
$Cl_2CHCO_2^{\bullet}$	1.38	(9.0)	1.91	413
$Cl_3CO_2^{\bullet}$	1.44	(8.7)	1.95	418
$C_6H_5O_2^{\bullet}$	1.33	(8.9)	1.80	402

[a] Average of the values in Table 2, except for the values for ethyl and isopropyl, which were calculated from the difference, given in Table 1 of ref 7, with respect to methyl. [b] pK_a values of the hydroperoxides from ref 11 or estimated values (in parentheses) from ref 7. [c] Bond dissociation energy in the gas phase for the hydroperoxide O−H bond, calculated as described in the text (eq 10).

Rate constants were also reported for the reactions of various peroxyl radicals with ascorbate ions,[20] but the value for t-BuO$_2^{\bullet}$ was not measured. Therefore, we used the value for methylperoxyl as the reference, taking the average reduction potential for this radical from the other two sets of calculations and taking the reduction potential for ascorbate at pH 7 as 0.30 V.[21] From similar calculations we derived another set of reduction potentials (Table 2). The value of λ for reaction with ascorbate was calculated to be 187 kJ mol^{-1}. From a comparison of the three sets of results in Table 2, it is apparent that relative reduction potentials can be determined by this method with a standard uncertainty of about ±0.05 V in most cases.

The values of $E(CCl_3O_2^{\bullet}/CCl_3O_2^-)$ calculated in Table 2 are significantly higher than the value of 1.15 V calculated before.[6,7] Further support for our value can be derived from recent reports that $CCl_3O_2^{\bullet}$ radicals oxidize thioanisole ($E = 1.45$ V)[22] with a rate constant of 9×10^7 L mol^{-1} s^{-1},[23] whereas the $N_3^{\bullet}$ radicals ($E = 1.33$ V) do not.[23,24] These findings indicate that the reduction potential of $CCl_3O_2^{\bullet}$ is higher than that of $N_3^{\bullet}$, i.e., >1.33 V, and that it is close to that of thioanisole, in agreement with our estimate.

Rate constants and reduction potentials are also known for $HO_2^\bullet$ radicals.[21,25] However, the reorganization energy for its reactions with the same reductants may be substantially different than that for the organic peroxyl radicals, and therefore, it was not included in the comparative calculations discussed above. In fact, from the data available for its reaction with ferrocyanide we calculate a λ value of 206 kJ mol^{-1}, as compared with 238 kJ mol^{-1} found for $t\text{-}BuO_2^\bullet$. Conversely, if we assume the same λ and calculate the reduction potential for $HO_2^\bullet$ by the same comparative method, we obtain a value that is about 0.2 V too high.

The reduction potentials for $RO_2^\bullet/RO_2^-$ can be used to derive the reduction potentials for $RO_2^\bullet,H^+/RO_2H$ if the pK_a values for RO_2^-/RO_2H are known. The reduction potentials at pH 0 can then be utilized to calculate the bond dissociation energies of the O−H bond in the various hydroperoxide by using eq 10.[6]

$$E_{bd}(ROO-H)_g = 96.48E°(RO_2^\bullet,H^+/RO_2H)_{aq} + 298[S°(H^\bullet)_g + S°(RO_2^\bullet)_g - S°(RO_2H)_g] + \Delta_f G°(H^\bullet)_g - \Delta\Delta G°_{g-aq}(RO_2^\bullet) \quad (10)$$

These calculations were done by taking the known pK_a values[11] or those estimated before.[7] The values of the molar entropies ($S°$) at 298 K (−2.04 kJ mol^{-1}) were estimated by taking methyl hydroperoxide as the reference. The free energy of transfer of $RO_2^\bullet$ from gas to water, $\Delta\Delta G°_{g-aq}(RO_2^\bullet)$, and the gaseous standard free energy of formation of $H^\bullet$ at 298 K, $\Delta_f G°(H^\bullet)_g$, were taken as 8.5 kJ mol^{-1} and 843.3 kJ mol^{-1}, respectively. The calculated bond energies are summarized in Table 3. The value calculated for $t\text{-}BuO_2H$ is 369 kJ mol^{-1} as compared with the value of 359 kJ mol^{-1} reported before.[26] The value for $Cl_2CHO_2^\bullet$ is 413 kJ mol^{-1} as compared with the value of 407 kJ mol^{-1} estimated before.[27] Although these values are approximations based on kinetics, their derivation relies heavily on the pK_a values of the hydroperoxides, which were obtained mostly from correlations. More reliable bond energies must await further measurements of these pK_a values as well as more direct kinetic determinations.

The rate constants for oxidation of various reductants by the *tert*-butylperoxyl radical are much lower than the rate constants for oxidation of the same reductants by the phenoxyl radical, despite the similarity of the reduction potentials of these two radicals. For example, the rate constants for oxidation of TMPD by phenoxyl and 4-methoxyphenoxyl radicals are[28] 2 orders of magnitude higher than that for oxidation by the *tert*-butylperoxyl radical (Table 2). This difference is expressed in the values of the reorganization energy λ, which are considerably higher for peroxyl radical (of the order of 200 kJ mol^{-1}, see above discussion) than for phenoxyl radical reactions (of the order of 80 kJ mol^{-1}).[29] This difference implies that the self-exchange rate constant for $RO_2^\bullet/RO_2^-$ is much lower than that for $PhO^\bullet/PhO^-$, which was reported to be $\sim 2 \times 10^8$ L mol^{-1} s^{-1}.[30]

An attempt to calculate the self-exchange rate constant for $t\text{-}BuO_2^\bullet/t\text{-}BuO_2^-$ from the reduction potential and the rate constants for reactions of the peroxyl radical with ferrocyanide or the rate constants for reaction of the hydroperoxide anion with some of the oxidants in Table 1, on the basis of the Marcus cross-reaction equation, gave very scattered results. Part of the scatter may be due to uncertainties in the self-exchange rates of the other couples chosen for this comparison, but the wide scatter may suggest that the intimate details of the overall oxidation reactions include more parameters than those expressed in the basic outer-sphere electron-transfer process. Such details probably include the protonation of the incipient hydroperoxide anion, which has been suggested[31] to be concerted with the electron-transfer step and to affect the overall observed rate constant. This protonation process may play a more crucial role in the reactions of the weakly oxidizing alkylperoxyl radicals than in those of the stronger oxidants like the chlorinated peroxyl radicals. In fact, as the polarity of the solvent decreases, alkylperoxyl radicals may be more likely to react by a hydrogen-abstraction process, whereas the stronger oxidants may continue to react via electron transfer even at low polarity,[31,32] if there is a significant difference between the reduction potentials of the peroxyl radical and the substrate.

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