One- and Two-electron Reduction Potentials of Peroxyl Radicals and Related Species

Gábor Merényi,[a] **Johan Lind**[a] **and Lars Engman**[b]
[a] *Laboratory of Nuclear Chemistry, Royal Institute of Technology, Stockholm, Sweden*
[b] *Institute of Chemistry, Department of Organic Chemistry, University of Uppsala, Uppsala, Sweden*

Utilising gaseous and aqueous thermodynamic quantities, estimates (in water *versus* NHE) have been made of the one-electron reduction potentials of alkyl peroxyl radicals including $CCl_3OO^\bullet$, percarboxyl and carboxyl radicals, and alkoxyl radicals, including $CCl_3O^\bullet$ and two-electron reduction potentials of alkyl hydroperoxides including CCl_3OOH, alkyl peroxyl radicals including $CCl_3OO^\bullet$ and of percarboxyl radicals.

Peroxyl radicals are important intermediates occurring in a number of processes, *e.g.*, lipid peroxidation, combustion, autoxidation, and photoinduced oxidation in the presence of oxygen. More often than not these processes also produce alkoxyl radicals and typical end-products are peroxides and hydroperoxides. For a reliable assessment of reaction mechanism as well as for successful modelling of, *e.g.*, autoxidations, good knowledge of thermochemical data is of the essence. Experimentally, these are not always easy to come by. For instance, the usual method of measuring redox equilibria is hampered by several factors. Thus, hydroperoxides are relatively unstable, especially when deprotonated. Furthermore, alkoxyl radicals rapidly rearrange to form more stable radicals *via* β-scission[1-4] or 1,2-hydrogen shifts.[5,6] In actual fact, only for H_2O_2 and its oxidised and reduced homologues in water are there complete experimental data available.[7] Consequently, thermodynamic data have to be estimated for most other hydroperoxide/hydroxide species. In ref. 8 tentative redox potentials for some alkyl peroxyl radicals have been suggested on kinetic grounds. This kinetic screening was later extended to include more substrates and an improved redox estimate of 1.02–1.11 V (*vs.* NHE) for the $CH_3OO^\bullet/CH_3OOH$ couple at pH 7 has been derived.[9] Recently, a fair number of one-electron reduction potentials for certain biologically important redox couples have been estimated[10] from gas phase data. In particular, estimates of 1.0 V for $ROO^\bullet/ROOH$ and 1.6 V for $RO^\bullet/ROH$ at pH 7 have been arrived at.[10] By judicious combination of gas-phase thermochemical data[11,12] with reasonable solvation free energies we have refined these estimates and extended them to include data for percarboxyl radicals and $CCl_3OO^\bullet$ as well. In addition, the two-electron reduction potentials of peroxyl radicals and their parent hydroperoxides have also been estimated, providing a measure of the oxygen-atom transfer capacity of these species. Our values referenced to NHE are presented in Table 1.

Two-electron Reduction Potentials of ROOH *and* RC(O)OOH.—We now demonstrate how we estimated two-electron reduction potentials of hydroperoxides and peracids in water. This quantity for, *e.g.*, an alkyl hydroperoxide, ROOH, can be calculated from gas-phase data and free energies of hydration as shown in eqn. (1).

$$\begin{aligned}2 \times 96.48 \times {}^2E^\circ(\mathrm{ROOH, 2\,H^+/ROH, H_2O}) ={} & \Delta_f H^\circ(\mathrm{ROOH})_g - \Delta_f H^\circ(\mathrm{ROH})_g - \\ & 298 \times [S^\circ(\mathrm{ROOH})_g - S^\circ(\mathrm{ROH})_g - \tfrac{1}{2} \times S^\circ(\mathrm{O_2})_g] + \\ & \Delta G^\circ_{g\text{-}aq}(\mathrm{ROOH}) - \Delta G^\circ_{g\text{-}aq}(\mathrm{ROH}) - \Delta_f G^\circ(\mathrm{H_2O})_{aq} \quad (1)\end{aligned}$$

Here, $\Delta_f H^\circ$ and S° denote, respectively, standard enthalpies of formation and molar entropies at 298 K. The subscripts g and aq symbolise the gaseous and aqueous phases. $\Delta G^\circ_{g\text{-}aq}$ signifies the free energy of transfer from standard gaseous to standard aqueous state. $\Delta_f G^\circ(H_2O)_{aq}$ is the standard free energy of formation at 298 K of liquid water, its numerical value being −237.15 kJ mol^{-1}. As the experimental $\Delta G^\circ_{g\text{-}aq}$ values of CH_3OH and CH_3OOH are the same,[16,17] *i.e.*, $\Delta\Delta G^\circ_{g\text{-}aq} = 0$, we assume this identity to hold for all ROOH/ROH couples, including RC(O)OOH/RC(O)OH and CCl_3OOH/CCl_3OH.

The values for ${}^2E^\circ(CH_3OOH) = 1.70$ V and ${}^2E^\circ[(CH_3)_3COOH] = 1.68$ V were calculated from data in refs. 11, 12 and 18. Based on this finding we assume ${}^2E^\circ$(ROOH) for all non-halogenated alkyl hydroperoxides, ROOH, to be *ca.* 1.69 V.

In ref. 19 the equilibrium constants, *K*, for the reaction $\mathrm{RC(O)OH + H_2O_2 \rightleftharpoons RC(O)OOH + H_2O}$ were shown to be essentially independent of R, where R denotes an alkyl group. In water $K \approx 2.2$. After changing the standard state of H_2O from 1 mol dm^{-3} to mole fraction $x = 1$ and utilising ${}^2E^\circ(\mathrm{H_2O_2, 2\,H^+/2\,H_2O}) = 1.76$, we obtain ${}^2E^\circ[\mathrm{RC(O)OOH, 2\,H^+/RC(O)OH, H_2O}] = 1.80$ V. The same type of calculation applied to data in ref. 20 yields ${}^2E^\circ[\mathrm{HC(O)OOH, 2\,H^+/HC(O)OH, H_2O}] = 1.82$ V for performic acid. By means of quantum chemical calculations using the PM3[21] program we reproduced the experimental difference in $\Delta_f H^\circ$ of several alkyl alcohol/hydroperoxide and carboxylic acid/peracid couples within 4 kJ mol^{-1}. The calculated value for the CCl_3OH/CCl_3OOH couple was found identical with that of $CH_3C(O)OH/CH_3C(O)OOH$. Since the entropy differences are assumed to be small and similar, we made the assumption given in eqn. (2).

$$\begin{aligned}E^\circ(\mathrm{CCl_3OOH, 2\,H^+/CCl_3OH, H_2O}) ={} & \\ E^\circ[\mathrm{CH_3C(O)OOH, 2\,H^+/CH_3C(O)OH, H_2O}] ={} & 1.80\ \mathrm{V} \quad (2)\end{aligned}$$

Comparison of the figures in Table 1 reveals that, on a molar basis, H_2O_2, peracids and perchlorinated methyl hydroperoxide are equally strong two-electron oxidants. On the other hand, non-halogenated alkyl hydroperoxides are about 10 000 times weaker. While this is a thermodynamic comparison, it is noted that, usually, hydrogen peroxide and peracids oxidise substrates faster than, *e.g.*, *tert*-butyl hydroperoxide.

One-electron Reduction Potentials of Peroxyl and Percarboxyl Radicals.—This quantity is calculated according to eqn. (3). Here, E_{bd} denotes the bond dissociation enthalpy at

$$\begin{aligned}96.48 \times E^\circ(\mathrm{ROO^\bullet, H^+/ROOH})_{aq} ={} & E_{bd}(\mathrm{ROO{-}H})_g - 298 \times [S^\circ(\mathrm{H^\bullet})_g + S^\circ(\mathrm{ROO^\bullet})_g - \\ & S^\circ(\mathrm{ROOH})_g] - \Delta_f G^\circ(\mathrm{H^\bullet})_g + \Delta\Delta G^\circ_{g\text{-}aq}(\mathrm{ROO^\bullet}) \quad (3)\end{aligned}$$

Table 1 Reduction potentials in water characterising peroxyl and oxyl groups

Reaction	Redox potential $E°$/V *vs.* NHE[a]	$E°_7$/V[c]
$H_2O_2 + 2e^- + 2H^+ \longrightarrow 2H_2O$	1.76[7]	1.35
$HO_2^{\bullet} + e^- + H^+ \longrightarrow H_2O_2$	1.44[7]	0.90
$HO_2^{\bullet} + e^- \longrightarrow HO_2^-$	0.75[7]	
$OH^{\bullet} + e^- + H^+ \longrightarrow H_2O$	2.73[13,14]	2.32
$OH^{\bullet} + e^- \longrightarrow OH^-$	1.90[13,14]	
$HO_2^{\bullet} + 2e^- + 2H^+ \longrightarrow OH^{\bullet} + H_2O$	1.12[b]	0.64
$ROOH + 2e^- + 2H^+ \longrightarrow ROH + H_2O$	1.69 ± 0.02	1.28
$ROO^{\bullet} + e^- + H^+ \longrightarrow ROOH$	1.47 ± 0.04	1.06
$ROO^{\bullet} + e^- \longrightarrow ROO^-$	0.77 ± 0.06	
$RO^{\bullet} + e^- + H^+ \longrightarrow ROH$	2.18 ± 0.04	1.77
$RO^{\bullet} + e^- \longrightarrow RO^-$	1.23 ± 0.07	
$ROO^{\bullet} + 2e^- + 2H^+ \longrightarrow RO^{\bullet} + H_2O$	1.34 ± 0.07	0.93
$RC(O)OOH + 2e^- + 2H^+ \longrightarrow RC(O)OH + H_2O$	1.80 ± 0.01	1.45
$RC(O)OO^{\bullet} + e^- + H^+ \longrightarrow RC(O)OOH$	1.60 ± 0.06	1.19
$RC(O)OO^{\bullet} + e^- \longrightarrow RC(O)OO^-$	1.12 ± 0.07	
$RC(O)O^{\bullet} + e^- + H^+ \longrightarrow RC(O)OH$	2.24 ± 0.08	1.96
$RC(O)O^{\bullet} + e^- \longrightarrow RC(O)O^-$	1.96 ± 0.09	
$RC(O)OO^{\bullet} + 2e^- + 2H^+ \longrightarrow RC(O)O^{\bullet} + H_2O$	1.48 ± 0.05	1.07
$CCl_3OOH + 2e^- + 2H^+ \longrightarrow CCl_3OH + H_2O$	1.80 ± 0.03	1.48
$CCl_3OO^{\bullet} + e^- + H^+ \longrightarrow CCl_3OOH$	1.60 ± 0.10	1.19
$CCl_3OO^{\bullet} + e^- \longrightarrow CCl_3OO^-$	1.15 ± 0.16	
$CCl_3O^{\bullet} + e^- + H^+ \longrightarrow CCl_3OH$	2.5 ± 0.2	2.3
$CCl_3O^{\bullet} + e^- \longrightarrow CCl_3O^-$	2.3 ± 0.3	
$CCl_3OO^{\bullet} + 2e^- + 2H^+ \longrightarrow CCl_3O^{\bullet} + H_2O$	1.35 ± 0.18	0.93

[a] For the R-oxygen species the error margins were based on the uncertainty in the thermodynamic data. In the case of the CCl_3-oxygen species allowance was also made for the uncertainties inherent in estimations based on free energy relationships (see below). [b] The two-electron reduction potential of the ($HOO^{\bullet}$, $2H^+/OH^{\bullet}$, H_2O) couple is given by: ${}^2E°(HOO^{\bullet}, 2H^+/OH^{\bullet}, H_2O) = {}^2E°(H_2O_2, 2H^+/2H_2O) + 0.5E°(HO_2^{\bullet}, H^+/H_2O_2) - 0.5E°(OH^{\bullet}, H^+/H_2O)$. [c] For the calculation of $E°$ at pH 7 we utilise, apart from the pK_a values mentioned in the text, p$K_a(HO_2^{\bullet}) = 4.8$.[15]

298 K and $\Delta_fG°(H^{\bullet})_g = 843.3$ kJ mol^{-1}, is the gaseous standard free energy of formation of the hydrogen atom at 298 K. For all primary alkyl hydroperoxides the O–H bond strength[11,18,22] is set to 368 ± 4 kJ mol^{-1}. In ref. 23 the O–H bond strength in $CH_3C(O)OO$–H was derived to be *ca.* 381 kJ mol^{-1}. Comparing the electron-withdrawing abilities of the $CH_3C(O)$ and CCl_3 groups we believe the O–H bond strength in CCl_3OO–H to be 381 ± 8 kJ mol^{-1}. The free energy of transfer of $ROO^{\bullet}$ from gas to water, $\Delta\Delta G°_{g\text{-}aq}(ROO^{\bullet})$, is given by eqn. (4).

$$\Delta\Delta G°_{g\text{-}aq}(ROO^{\bullet}) = \Delta G°_{g\text{-}aq}(ROO^{\bullet}) - \Delta G°_{g\text{-}aq}(ROOH) \quad (4)$$

The experimentally obtained value of $\Delta\Delta G°_{g\text{-}aq}(HOO^{\bullet})$[13,24] is 7.9 kJ mol^{-1} and the corresponding $\Delta\Delta G°_{g\text{-}aq}(OH^{\bullet}) = \Delta G°_{g\text{-}aq}(OH^{\bullet}) - \Delta G°_{g\text{-}aq}(H_2O)$ is[13] 9.2 kJ mol^{-1} (with the aqueous standard state of H_2O taken as 1 mol dm^{-3}). These values correspond to *ca.* half the average strength of a hydrogen bond between a solute and a water molecule.[13] Based on these findings we set both $\Delta\Delta G°_{g\text{-}aq}(ROO^{\bullet})$ and $\Delta\Delta G°_{g\text{-}aq}(RO^{\bullet}) = \Delta G°_{g\text{-}aq}(RO^{\bullet}) - \Delta G°_{g\text{-}aq}(ROH)$ equal to 8.5 kJ mol^{-1}. This should hold for R = CCl_3 as well.

Although somewhat less certain, we assume this difference also to hold between RC(O)OOH and $RC(O)OO^{\bullet}$, as well as between RC(O)OH and $RC(O)O^{\bullet}$.

The pH-independent redox potentials are calculated as from eqn. (5). The pK_a values[25,26] of primary and secondary alkyl

$$E°(ROO^{\bullet}/ROO^-) = E°(ROO^{\bullet}, H^+/ROOH) - 0.059 \times pK_a(ROOH) \quad (5)$$

hydroperoxides vary between 11.5 and 12.1. The pK_a of $(CH_3)_3COOH$ is 12.8. Similarly, the average pK_a of percarboxylic acids is 8.2, while that of performic acid is 7.3. From a linear free energy relationship plot[26] correlating the pK_a values of alkyl and acyl hydroperoxides with the Swain–Lupton constant[27] *F*, the pK_a of CCl_3OOH is predicted to be 7.5. We believe this value to be correct to within 1 pH unit. From Table 1 it transpires that, with respect to one-electron oxidising power, percarboxylic radicals and $CCl_3OO^{\bullet}$ are essentially equal and much stronger than $HO_2^{\bullet}$ or alkyl peroxyl radicals, $ROO^{\bullet}$. This is reflected in the finding that the former two radicals react with the same substrates at similar rates and much faster than non-halogenated alkyl peroxyl radicals.[28]

One-electron Reduction Potentials of Alkoxyl and Carboxyl Radicals.—The general equation is given in eqn. (6). $E_{bd}(g)$ for

$$96.48 \times E°(RO^{\bullet}, H^+/ROH)_{aq} = E_{bd}(RO\text{–}H)_g - 298 \times [S°(H^{\bullet})_g + S°(RO^{\bullet})_g - S°(ROH)_g] - \Delta_fG°(H^{\bullet})_g + \Delta\Delta G°_{g\text{-}aq}(RO^{\bullet}) \quad (6)$$

alcohols and carboxylic acids as well as $S°_g$ values were taken from refs. 11, 12 and 29. For $\Delta\Delta G°_{g\text{-}aq}(RO^{\bullet})$ see the discussion above. The O–H bond strength in CCl_3O–H was estimated as follows. There is a remarkable constancy in the difference between the O–H bond strengths of RO–H and the O–O bond strengths[12,29] of the corresponding RO–OR, the difference being 280 ± 4 kJ mol^{-1}. The O–O bond strength[29] in CF_3O–OCF_3 is 193 kJ mol^{-1}. Thus the strength of the O–H bond in CF_3O–H is predicted to be 473 kJ mol^{-1}. As the Swain–Lupton *F* constants for CF_3 and CCl_3 are the same we assume the same O–H bond strength to within *ca.* 8 kJ mol^{-1} in CCl_3O–H.

The pH-independent redox potentials were obtained from eqn. (7). The pK_a values of alkanols range from 15.5 to 16.8.

$$E°(RO^{\bullet}/RO^-) = E°(RO^{\bullet}, H^+/ROH) - 0.059 \times pK_a(ROH) \quad (7)$$

Normal carboxylic acids have pK_a values of *ca.* 4.7, except for formic acid ($pK_a = 3.75$). For CCl_3OH we took $3.5 < pK_a < 4.0$, as estimated in ref. 30. Table 1 reveals that, as reflected by their one-electron reduction potentials referenced to pH 0, alkoxyl and carboxyl radicals should display similar hydrogen-abstracting ability. On the other hand, the former are much weaker one-electron oxidants than the latter, judging by their pH-independent $E°$ values. However, since all of these radicals are very unstable with respect to rearrangement or decarboxylation, these figures reflect potentialities rather than actualities. The same applies to the formally very strong oxidant $CCl_3O^{\bullet}$, which is expected rapidly to expel $Cl^{\bullet}$ by way of β-scission.

Two-electron Reduction Potentials of Peroxyl and Percarboxyl Radicals.—This quantity provides a thermodynamic measure of the ability of a radical to transfer an oxygen atom to a substrate in aqueous solution. Alternatively, it can be taken to be a measure of the homolytic O–O bond strength in the peroxyl or related radical. Eqn. (8) quantifies this definition,

$$\begin{aligned} {}^2E°(ROO^{\bullet}, 2\,H^+/RO^{\bullet}, H_2O) = \\ {}^2E°(ROOH, 2\,H^+/ROH, H_2O) + 0.5 \times \\ E°(ROO^{\bullet}, H^+/ROOH) - 0.5 \times E°(RO^{\bullet}, H^+/ROH) \end{aligned} \quad (8)$$

where all input quantities were as calculated above. As seen from Table 1, $HO_2^{\bullet}$ is the weakest oxygen-transfer agent, while percarboxylic radicals are the most efficient. In addition, it would seem that alkyl peroxyl radicals are equally good two-electron oxidising agents, regardless of whether they are halogenated or not. While, again, this is a thermodynamic analysis, one would expect, at least in certain reactions, this thermodynamic rating to spill over to kinetics as well. This assumption is borne out by observations attesting to percarboxyl radicals attacking double bonds considerably faster than do alkyl peroxyl radicals.[31]

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