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Electron transfer reactions of singlet molecular oxygen with phenols

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ABSTRACT: The correlation of the reactive component of the bimolecular quenching rate constant, k_r, with ΔG for reactions of singlet molecular oxygen with phenols is interpreted in terms of classical and semiclassical theories of electron transfer. Both treatments indicate a diabatic process with a reorganization energy of about 0.46 eV. The observed diabaticity is in line with a crossing of states with different symmetry. Similar results were obtained for the reactions of singlet molecular oxygen with phenoxide ions in water. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: singlet molecular oxygen; phenols; electron transfer reactions

INTRODUCTION

The quenching of singlet molecular oxygen, $O_2(^1\Delta_g)$, by phenolic compounds has been extensively studied because of the important role of phenols as $O_2(^1\Delta_g)$ scavengers in biological systems, and the potential use of $O_2(^1\Delta_g)$-mediated photo-oxidation of phenolic pesticides in waste water treatment.[1–3]

Scavenging of $O_2(^1\Delta_g)$ by phenols takes place by two main pathways: (*i*) a chemical reaction with rate constant k_r, [Eqn. (1)] and (*ii*) a physical interaction with quenching constant k_q [Eqn. (2)]. The bimolecular rate constant for the overall process, k_t, thus shows the contribution of both reaction channels.

$$O_2(^1\Delta_g) + \text{ phenolic compound (XOH) } \xrightarrow{k_r} \text{products} \qquad (1)$$

$$O_2(^1\Delta_g) + \text{ XOH } \xrightarrow{k_q} O_2(^1\Sigma_g{}^-) + \text{XOH} \qquad (2)$$

Reported values for k_t are strongly dependent on the structural properties of the phenolic substrates and on the solvent. Early work by Thomas and Foote on the quenching of $O_2(^1\Delta_g)$ by substituted 2,6-di-*tert*-butylphenols in methanol showed a linear correlation of log k_t with the half-wave oxidation potentials of the phenols.[4] Scurlock *et al.* observed a similar correlation for substituted phenols in deuterated methanol.[5] The efficiency of the overall quenching process is increased with increasing solvent polarity and the differences in k_t observed for various phenols become more important when the polarity of the media is increased. The previous observations are in agreement with a mechanism involving the formation of charge-transfer intermediates.[1,3 5–8]

Evaluation of the results in terms of charge transfer theories[9] requires the measurement of the overall quenching rate constants under similar experimental conditions, for a set of substituted phenols showing one-electron redox potentials within a wide range. Such conditions are difficult to fulfill for k_t measurements.[3] However, an acceptable set of the reactive component of the bimolecular quenching rate constant, k_r, determined in water at neutral pH is available for substituted phenols showing $XO^{\cdot}/XOH$ one-electron reduction potentials ranging from 0.46 to 1.23 V vs NHE. In this paper, we analyze these data in terms of a classical and a semiclassical treatment of the electron transfer process.[9–11]

CORRELATION OF LOG k_r WITH ONE-ELECTRON REDOX POTENTIALS AND DISCUSSION IN TERMS OF CLASSICAL AND SEMICLASSICAL TREATMENTS

A charge-transfer mechanism was proposed for the $O_2(^1\Delta_g)$-sensitized photo-oxygenation of phenols.[1,6,12] Such a mechanism involves the reactions shown in Scheme 1, where mainly pathways concerning the

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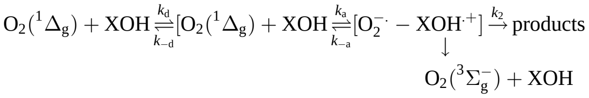
quenching of $O_2(^1\Delta_g)$ by phenol are considered. Deactivation pathways due to the interaction with the solvent molecules are of no significance for the present analysis, as all rate constants were determined in the same solvent.



$$\begin{array}{l} O_2(^1\Delta_g) + XOH \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} [O_2(^1\Delta_g) + XOH \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} [O_2^{-\cdot} - XOH^{\cdot +}] \xrightarrow{k_2} \text{products} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad O_2(^3\Sigma_g^-) + XOH \end{array}$$

Scheme 1

In this scheme k_d and k_{-d} are diffusion-controlled rate constants for the formation and decomposition of the precursor complex, $[O_2(^1\Delta_g)$—XOH]; k_a and k_{-a} are 'activation energy controlled' rate constants of the electron transfer from the phenol to $O_2(^1\Delta_g)$. Decomposition of the charge transfer complex, $[O_2^{-\cdot}$—$XOH^{\cdot +}]$, may take place by a physical and/or chemical process with rate constants k_1 and k_2, respectively. Experimental evidence for the formation of an exciplex has been reported for vitamin E as quencher.[8]

Assuming steady-state conditions for the precursor and charge transfer intermediates,[9,13] the resolution of the differential equation system for the reaction mechanism in Scheme 1 applied to the depletion of $O_2(^1\Delta_g)$ leads to Eqn. (3) for the overall rate constant, k_t:

$$k_t = \frac{k_d}{1 + \frac{k_{-d}}{k_a} + \frac{k_{-d}k_{-a}}{(k_1+k_2)k_a}} \tag{3}$$

Similarly, Eqn. (4) is derived for k_r from the resolution of the differential equations applied to the depletion of phenols and/or formation of products and considering that for relatively efficient quenchers $k_{-a} \ll (k_1 + k_2)$:[9]

$$k_r = f\left(\frac{k_d}{1 + k_{-d}/k_a}\right) \tag{4}$$

with $f = k_2/(k_1 + k_2) = k_r/k_t$.

Table 1 lists the values of k_r obtained in water at pH 7 and the corresponding values of the $XO^{\cdot}$/XOH one-electron reduction potentials vs NHE, $E°(XO^{\cdot}/XOH)$. According to the reaction mechanism shown in Scheme 1, the electron transfer from phenol to $O_2(^1\Delta_g)$ yields phenol radical cations, $XOH^{+\cdot}$, the conjugate acid of the phenoxy radicals $XO^{\cdot}$ [Eqn. (5)]:

$$XOH^{+\cdot} \rightleftharpoons XO^{\cdot} + H^+ \tag{5}$$

Consequently, the $E°(XOH^{+\cdot}/XOH)$ values are the

Table 1. Values of rate constant k_r in water at neutral pH, the one-electron reduction potential of phenoxy radicals vs NHE, $E°$ $(XO^{\cdot}/XOH)$, dissociation pK of the radical cations $XOH^{+\cdot}$ and estimated radii for phenols $X\text{-}C_6H_4OH$

Substituent X	k_r ($l\,mol^{-1}\,s^{-1}$)	$E°$ $(XO^{\cdot}/XOH)$[a]	pK $(XOH^{+\cdot})$	r (Å)[m]
4-OH	2.5×10^{7}[b]	0.46	−1.33[g]	3.08
4-Phenyl	3.8×10^{7}[c]	0.505	−1.38[j]	4.93
2,6-$(OCH_3)_2$	3.6×10^{7}[d]	0.58	−1.43[j]	3.92
4-OCH_3	2.2×10^{7}[d]	0.60	−1.41[g]	3.71
2-OCH_3	6.0×10^{6}[d]	0.77	−1.63[g]	3.47
4-*tert*-Butyl	1.2×10^{7}[d]	0.80	−1.58[j]	3.94
3-OH	2.0×10^{7}[b]	0.81	−1.55[h]	2.81
4-CH_3	1.0×10^{7}[d]	0.87	−1.70[g]	3.29
4-$CH_2CH(NH_2)COOH$[e]	8.0×10^{6}[f]	0.89	−1.64[j]	4.47
4-Cl	6.0×10^{6}[d]	0.94	−1.30[i,k]	3.15
4-H	2.6×10^{6}[d]	0.97	−2.00[g,l]	2.81
4-$COCH_3$	1.5×10^{6}[d]	1.06	−1.86[i]	4.52
3-NO_2	2.6×10^{5}[d]	1.13	−1.78[i]	3.05
4-CN	2.4×10^{5}[d]	1.17	−1.83[i]	3.57
4-NO_2	2.6×10^{5}[d]	1.23	−1.79[i]	3.45

[a] All data from Ref. 14 except for the value for 4-methoxyphenol, which was taken from Ref. 15.
[b] Taken from Ref. 6.
[c] Upper limit from Ref. 16.
[d] Taken from Ref. 17.
[e] Tyrosine.
[f] Taken from Ref. 18.
[g] Taken from Ref. 19.
[h] Taken from Ref. 20.
[i] Taken from Ref. 21.
[j] Calculated from the regression shown in Fig. 1.
[k] The pK value −1.67 from the regression shown in Fig. 1 was used for calculating ΔG.
[l] The value −1.69 V from the regression shown in Fig. 1 was used for calculating ΔG.
[m] Calculated as described in the text.

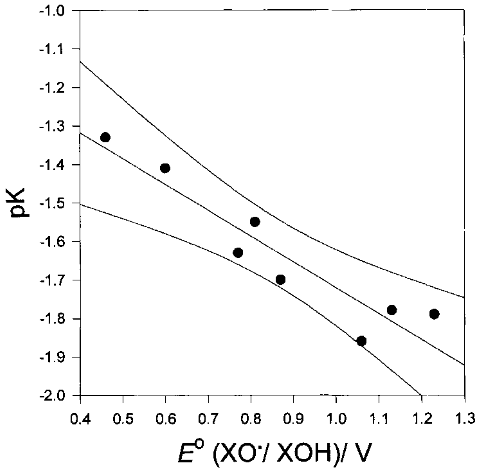


Figure 1. Correlation between pK of XOH$^{+\cdot}$ vs $E°$(XO·/XOH). The intercept and slope of the plot are -1.05 ± 0.09 and -0.67 ± 0.10, respectively. Regression coefficient $r^2 = 0.88$. The solid curves show the 99% confidence interval

reduction potentials required for the application of the charge transfer theories. The latter values may be estimated from the reported $E°$(XO·/XOH) and the corresponding pK of the radical cation.[19–21] However, if $E°$ (XO·/XOH) is used instead of $E°$ (XOH$^{\cdot+}$/XOH) for calculating ΔG, very similar λ and κ values are obtained from the fitting of experimental data with Eqn. (7) (see below).

The pK values are not known for all the radical cations shown in Table 1. However, an acceptable linear correlation of pK vs $E°$(XO·/XOH) (Fig. 1) is observed, from which the unknown pKs can be estimated.

According to the Marcus theory,[10] electron transfer rates are expected to increase as the differences in Gibbs energy for the electron transfer reaction, ΔG, become more negative. ΔG values are calculated with the equation

$$\Delta G = E°(\mathrm{XOH}^{+\cdot}/\mathrm{XOH}) - E°[\mathrm{O_2}(^1\Delta_g)/\mathrm{O_2^{-}}\cdot] - e^2/\varepsilon r \quad (6)$$

where $E°[\mathrm{O_2}(^1\Delta_g)/\mathrm{O_2^{-}}\cdot] = 650\mathrm{mV}$ at pH 7 [22] and $e^2/\epsilon r$ is a small corrective term due to static attraction of the reaction products with $\varepsilon = 80.1$ for the dielectric constant of water at 298 K.[23] The distance r between the donor and acceptor is estimated taking 2 Å as the radius of molecular oxygen in solution (r_{o_2}[19]) and estimating the radii of phenols with a molecular modeling program based on the calculation of the geometry of minimal energy[24] (also shown in Table 1).

Replacing the rate constant k_a in Eqn. (4) by the expression derived as a function of ΔG in the classical Marcus treatment of electron transfer,[10] the following equation is obtained for k_r:

$$k_r = \frac{fk_d}{1 + \frac{k_{-d}}{\kappa\nu}\exp[(\lambda + \Delta G)^2/4\lambda RT]} \quad (7)$$

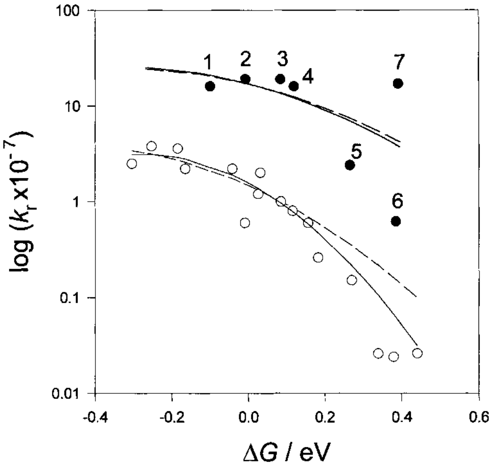


Figure 2. Plot of log k_r vs ΔG for phenols (○) (see Table 1) and the following phenoxide ions (●): phenoxide (1); 4-chlorophenoxide (2); 2-chlorophenoxide (3); 3-chlorophenoxide (4); 4-acetylphenoxide (5); 4-cyanophenoxide (6); and 2,4-dichlorophenoxide (7). The dashed and solid lines show the fitting of the data with Eqn. (7) (classical treatment) and Eqn. (11) (semiclassical treatment), respectively. The fitting of the phenoxide ions data was done without including No. 7

where κ is the transmission coefficient for the electron transfer; ν is the frequency factor and λ/4 is the activation free energy for $\Delta G = 0$ with λ the sum of the inner-sphere and solvent reorganization energies, λ_{in} and λ_{out}, respectively.

The plot of log k_r vs ΔG, shown in Fig. 2, follows the expected trend (see above).

The value $k_d = 1.2 \times 10^{10}\ \mathrm{l\,mol^{-1}\ s^{-1}}$ is estimated from the Smoluchowski equation [Eqn. (8)]:[25]

$$k_d = 4\pi N(D_{o_2} + D_{Ph})(r_{Ph} + r_{o_2})/1000 \quad (8)$$

where N = Avogadro's number, $r_{o_2} = 2$ Å , the average radius of the phenols $r_{Ph} = 3.6$ Å and D_{o_2} and D_{Ph} are, the diffusion coefficients of molecular oxygen [$1.98 \times 10^{-5}\ \mathrm{cm^2\ s^{-1}}$ (Ref. 26)] and phenol in water [$0.89 \times 10^{-5}\ \mathrm{cm^2\ s^{-1}}$ (Ref. 23)], respectively.

The factor $f = k_2/(k_1+k_2) = k_r/k_t$ is known to depend on the solvent and on the nature of the quencher. For the compounds listed in Table 1 values of k_t only for phenol, hydroquinone and resorcinol in neutral aqueous solution are reported.[3] The experimental values of f for the latter phenols are 0.5, 0.1 and 1 respectively. The observed trend does not follow a correlation with the corresponding oxidation potentials (Table 1) and the values of f are thus expected not to affect the log k_r vs ΔG correlation in a systematic way, only the random dispersion of the correlation. Consequently, $f = 0.5$ is a good estimate for this parameter.

Taking $f\,k_d = 6 \times 10^9\ \mathrm{l\,mol^{-1}\ s^{-1}}$ (see above), the best fit of the data (dashed line in Fig. 2) was observed for the values $\lambda = 0.46 \pm 0.04$ eV and $k_{-d}/\kappa\nu = 156 \pm 20$.

In order to estimate the transmission coefficient κ, related to the adiabaticity of the charge transfer process, from the ratio of $k_{-d}/\kappa\nu = 156$, k_{-d} is estimated as the maximum rate for unimolecular dissociation, i.e. $3(D_{o_2} + D_{Ph})/(r_{o_2} + r_{Ph})^2 = 9.0 \times 10^{10}\ s^{-1}$[27,28]. A similar value of k_{-d} ($7 \times 10^{10}\ s^{-1}$) is obtained from the ratio k_d/K_d, where K_d is the equilibrium constant calculated from the Fuoss and Eigen equation.[29]. Hence $\kappa\nu = 6 \times 10^8$ is obtained. As the frequency factor, ν, is in the range 10^{12}–$10^{14}\ s^{-1}$,[30,31] the transmission coefficient, κ, should be lower than 10^{-3}, which indicates a diabatic charge transfer process. This result is in line with the observation that crossing between states of different symmetry results in diabatic electron transfer, as found for electron transfer between excited-state molecules and amines.[9,32]

For the electron transfer reaction of $O_2(^1\Delta_g)$ with the phenoxide ions in water ΔG is calculated as from Eqn. (6) with $E°(XO^{\cdot}/XO^-)$[15] instead of $E°(XOH^{+\cdot}/XOH)$ and without including the static attraction correction term ($e^2/\epsilon r$) because the phenoxy radicals are uncharged species. As several reported k_r values obtained in alkaline medium were measured under pH conditions where the contribution of the corresponding phenols to k_r cannot be neglected, only values calculated for XO^- from experimental pH dependences of the quenching constant are considered.[3] The plot of log k_r vs ΔG for these reactions is also shown in Fig. 2. Following an analysis similar to that described for phenols, a diabatic process (κ of the order of 10^{-3}) with a reorganization energy $\lambda = 0.34$ eV was obtained from the fitting of the data with Eqn. (7) (dashed line in Fig. 2).

In the semiclassical treatment,[33] the rate constant k_a is given by

$$k_a = \kappa Z(4\pi kT\lambda)^{1/2}G \qquad (9)$$

where Z is the collision frequency in solution and G is the thermally weighted Franck–Condon sum given by

$$G = (2\pi\lambda h\nu \coth\gamma)^{-1/2} \exp\left[-(\Delta G + \lambda)^2/(2\pi\lambda h\nu \coth\gamma)\right] \qquad (10)$$

For systems having two or more frequencies, $2\pi\lambda h\nu\coth\gamma$ is the sum over the j vibrational modes of $2\pi\lambda_j h\nu_j \coth\gamma_j$, where $\gamma_j = h\nu_j/2\ kT$ and ν_j are the frequencies of the vibrational modes of the acceptor, donor and solvent. The reorganization energy λ, which is added to ΔG in the exponent, is the sum over j of λ_j.

The rate constant k_t as calculated from the semiclassical treatment is given by $k_t^{-1} = k_a^{-1} + k_d^{-1}$.[9] In the case of a quenching rate limited by the electron transfer process, it can be assumed that $k_t \ll k_d$ and thus $k_r = fk_a$. Hence the following equation is obtained for k_r:

$$k_r = f\kappa Z(4\pi kT\lambda)^{1/2}G \qquad (11)$$

The k_r data shown in Table 1 were fitted with Eqn. (11) (solid line in Fig. 2). In this case, the variables are the values of k_r for every quencher and ν_j are the frequencies of the vibrational modes of the acceptor, donor and solvent associated with the corresponding reorganization energies λ_j. Although several frequencies were included in the fitting function, only the H–O in-plane flexion modes (1300–1400 cm^{-1}) contributed appreciably to the fitting ($\lambda_1 = 0.28$ eV), in addition to the 1 cm^{-1} ($\lambda_2 = 0.18$ eV) usually included in the calculations in order to account for the vibrational modes of water.[33] The frequency associated with O=O vibration in molecular oxygen (1500–1600 cm^{-1}) also did not contribute to the fitting shown in Fig. 2.

As discussed above, if the factor f is taken as 0.5, then the product κZ obtained from the fitting shown in Fig. 2 is of the order of 2×10^8. The collision frequency Z can be estimated by the equation[31]

$$Z \approx 4\pi(r_{Ph} + r_{o2})^2\nu/\alpha \qquad (12)$$

where ν is the frequency factor (see above), $r_{Ph} + r_{o2} = 5.6$ Å and $\alpha \approx 2.6$ Å^{-1}.[31] For $\nu = 10^{12}$–$10^{14}\ s^{-1}$ (see above), Z ranges from 9×10^{10} to $9 \times 10^{12}\ l\ mol^{-1}\ s^{-1}$, and hence κ should be lower than 2×10^{-3}, further confirming the diabaticity of the charge transfer process.

For the electron transfer quenching of $O_2(^1\Delta_g)$ by phenoxide ions in water (Fig. 2), the semiclassical treatment predicts a diabatic reaction with a reorganization energy of about 0.34 eV. In this case, the fitting indicates that only the C–H stretching modes of the phenoxide ions (3000–3100 cm^{-1}) contribute to the charge transfer process. We cannot explain the latter observation, however, as data for only six compounds are available for the fitting the result is questionable. The fitting of the data with Eqn. (11) is shown in Fig. 2 (solid line).

CONCLUSION

The reactions between $O_2(^1\Delta_g)$ and phenols can be interpreted in terms of classical and semiclassical theories of electron transfer. Both treatments indicate a diabatic process with a reorganization energy of about 0.46 eV. The observed diabaticity is in line with a crossing of states with different symmetry. Similar results are obtained for the reactions of $O_2(^1\Delta_g)$ with phenoxide ions in water.

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