Autoxidation of Closed-Shell Organics: An Outer-Sphere Electron Transfer

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In the reaction of singlet organics with $^3O_2$, neither bond formation in the elementary step nor strong orbital overlap in the transition state is spin-allowed:

$$O_2 + X^n \overset{k_{12}}{\underset{k_{-12}}{\leftrightarrow}} O_2^- + X^{(n+1)} \qquad K_{12} = k_{12}/k_{-12} \qquad (1)$$

The reaction is therefore expected to be an outer-sphere electron transfer. As such, its kinetics should be quantitatively described by the simple Marcus equation,[1] where small work terms are neglected, Z is set to 10^{11} M^{-1} s^{-1}, and $\lambda°$ denotes the reorganization energy:

$$\ln(k_{12}) = \ln(Z) - \frac{\lambda°}{4RT}\left(1 - \frac{RT}{\lambda°}\ln(K_{12})\right)^2 \qquad (2)$$

Under the assumption of additivity,

$$\lambda° = 0.5(\lambda°_{11} + \lambda°_{22}) = 4RT\ln(Z) - 2RT\ln(k_{11}k_{22}) \qquad (3)$$

where k_{11} and k_{22} are the self-exchange rates of the participating couples. The nature of reaction 1 was first examined by Marcus,[2] but no firm conclusions were reached because of the lack of available data for the $O_2/O_2^{\bullet-}$ couple at that time. More recently, the outer-sphere hypothesis was substantiated for the reaction of O_2 with a number of metal complexes[3,4] as well as for a limited set of organic autoxidations.[5] The present work will provide kinetic data for reaction 1, covering a range of 23 orders of magnitude in K_{12}.

Table I presents the kinetic and thermodynamic data, and these are plotted in Figure 1. As can be seen, an excellent fit to the Marcus plot is obtained with $\lambda° = 37.4 \pm 2.5$ kcal/mol. Utilizing the experimental[6] $k_{11} = k_{ex}(O_2/O_2^{\bullet-}) = 450$ M^{-1} s^{-1} and an average[7,8] $k_{22} = k_{ex}(\text{organics}) = 10^8$ M^{-1} s^{-1}, eq 3 yields a $\lambda°$ value of only 31 kcal/mol. Put in another way, the experimental $\lambda°$ corresponds to an apparent k_{11} of ca. 2 M^{-1} s^{-1}. However, as was first pointed out in ref 9 and more thoroughly discussed in ref 5, the outer-sphere contribution to $\lambda°$, $\lambda°_{out}$, is not strictly $0.5((\lambda°_{11})_{out} + (\lambda°_{22})_{out})$ if the effective radii r_{11} and r_{22} are very different. In the present case, $r_{22}/r_{11} > 2.5$ can be assumed, which is sufficient to quantitatively account for the discrepancy of ca. 6 kcal/mol.[10] We wish to point out that in ref 4, where the $O_2/O_2^{\bullet-}$ couple was reacted with a number of substitution-inert organic Cr complexes of size similar to the present substrates, the apparent k_{11} derived was almost identical to the one found in the present work. This observation along with Figure 1 reveals the following important features. 1. Reaction 1 is an outer-sphere electron transfer. 2. In the transition state of the self-exchange reaction between O_2 and $O_2^{\bullet-}$, characterized by the experimental rate constant[6] $k_{11} = 450$ M^{-1} s^{-1}, orbital overlap should be negligible. 3. Orbital overlap should also be

Table I. Parameters of Reaction 1

entry no.	X^n	$E°(X^{(n+1)}/X^n)$, V vs NHE	k_{12} (ref), M^{-1} s^{-1}
		Phenolates	
1	4-CN	1.12(12)	9.7×10^{-13} (13)
2	2,4,6-tri-Cl	0.88(14)	7.0×10^{-8} (13)
3	2,4,6-tri-Br	0.88(14)	3.5×10^{-8} (13)
4	2,4,6-tri-I	0.85(14)	7.7×10^{-8} (13)
5	4-*tert*-butyl	0.76(14)	1.1×10^{-6} (13)
6	4-Me	0.68(12)	5.2×10^{-5} (13)
7	4-OMe	0.54(12)	3.1×10^{-3} (13)
7	4-OMe		2.1×10^{-3} (15)
8	2-OMe-4-Me	0.54(14)	5.7×10^{-4} (13)
9	2,6-di-OMe-4-CO_2^-	0.54(14)	9.4×10^{-4} (13)
10	2,4,6-tri-Me	0.49(14)	7.6×10^{-3} (13)
11	4-NH_2	0.22(16)	7.9 (17)
12	4-$(CH_3)_2N$	0.17(16)	2.0×10^1 (17)
		Indophenolates	
13	indophenolate	0.12(18)	8.7×10^1 (19)
14	2-Cl	0.19(18)	1.2×10^1 (19)
15	2-Br	0.18(18)	1.4×10^1 (19)
16	2,6-di-Br	0.28(18)	1.0 (19)
		Others	
17	trolox	0.19(16)	5.5×10^1 (13)
18	S[a]	0.25(20)	0.5 (21)
19	luminol anion	0.87(5)	1.1×10^{-8} (5)
20	luminol dianion	0.43(5)	10^{-2} (5)
21	TMPD[b]	0.27(16)	0.7 (17)
22	Q^{2-} [c]	0.023(22)	9.0×10^1 (23)
23	DQ^{2-} [d]	−0.24(24)	7.8×10^4 (25)
24	ascorbate dianion	0.015(26)	2.2×10^2 (27)
25	$FMNH^-$ [e]	−0.11(28)	4.6×10^3 (28)

[a] 4,4′-Dihydroxy-3,3′-dimethoxystilbene anion. [b] *N,N,N′,N′*-Tetramethyl-1,4-phenylenediamine. [c] 1,4-Hydroquinone dianion. [d] Tetramethyl-1,4-hydroquinone dianion. [e] 1,5-Dihydroflavin mononucleotide anion.

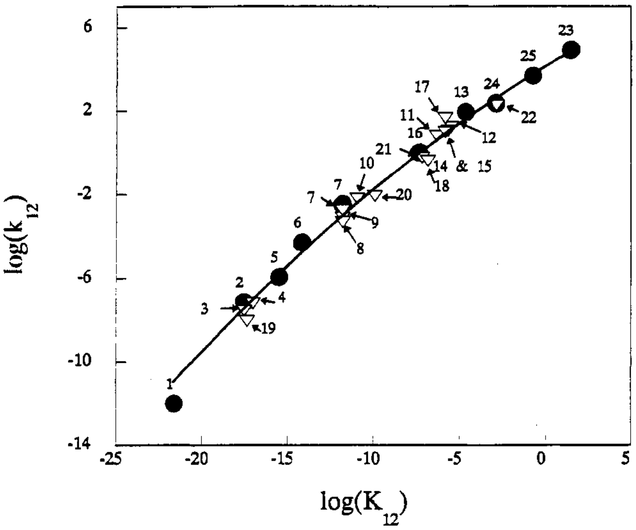

Figure 1. A double logarithmic plot depicting the rate constant k_{12} of O_2 reacting with organic compounds as a function of the equilibrium constant of electron transfer, K_{12}. All substances are numbered according to the first column of Table I. The arrows point to the open triangles. The drawn line was calculated from Marcus' equation with $\lambda° = 37.4$ kcal/mol.

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(10) It can be shown[5,9] that $\Delta = 45.5(q-1)^2/(r_{22}(q+1))$, where Δ is the difference (in kcal/mol) between experimental $\lambda°$ and the one calculated from eq 3, r_{22} is expressed in angstrom units, and $q = r_{22}/r_{11}$. With the reasonable assumption of 5 Å $< r_{22} <$ 7 Å, a Δ of 6.4 kcal/mol is reproduced for $2.6 < q < 3.0$.

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unimportant in the self-exchange rates, k_{22}, of the organics treated here, and their spread around the average of 10^8 M^{-1} s^{-1} appears slight. 4. The mismatch between the sizes of the reacting couples is mainly responsible for the difference between experimental and calculated (from the cross relationship) k_{12}. This difference should not exceed a factor of ca. 10^2.

A further strong argument for the outer-sphere character of organic autoxidations and the role of size mismatch between the participating couples comes from the following consideration. The reaction $O_2^{\bullet-} + HO_2^{\bullet} \leftrightarrow {}^3O_2 + HO_2^-$ was shown to be an outer-sphere electron transfer.[6] As the sizes of the two couples are close, $k_{ex}(HO_2^{\bullet}/HO_2^-) = 17$ M^{-1} s^{-1} was calculated. Now, if the $HO_2^{\bullet}/HO_2^-$ couple were brought to react in an outer-sphere process with substrates of size similar to the present organics or the couples studied in ref 4, the apparent k_{ex} for $HO_2^{\bullet}/HO_2^-$ would be expected to be lower by 2–3 orders of magnitude than the value of 17 M^{-1} s^{-1}, which is believed to be close to the real k_{ex} value. In fact, the findings in ref 11 bear out this expectation, i.e., the derived apparent $k_{ex}(HO_2^{\bullet}/HO_2^-)$ values were found to be 10^{-2}–10^{-1} M^{-1} s^{-1}. In the present work we included all those organics for which reliable kinetic and thermodynamic data were extant or could be obtained. The results attest to the feasibility of predicting the initiation rate of any organic autoxidation within a factor of ca. 10, once the value of K_{12} (and generally k_{22}, which does not always have to be 10^8 M^{-1} s^{-1}) is know. Although we could find no obvious exception in this work, one could envisage reactions that occur via hydrogen transfer or, more likely, via simultaneous[29] electron and proton transfer. Such reactions should occur more rapidly than demanded by the outer-sphere mechanism. The latter then sets a lower limit to the rate of any reaction with O_2. A suitable candidate for concerted electron and proton transfer should be the reaction between O_2 and neutral 1,5-dihydroflavin, $FMNH_2$,[30] which is known to deprotonate at N(1) but to lose its electron at N(5). The experimental rate constant[28] of the $FMNH_2 + O_2$ reaction, $k \approx 200$ M^{-1} s^{-1}, is higher by a factor of merely 10 than the k_{12} value calculated from eq 2. Thus, not even in this favorable case do we have definitive proof of a mechanism other than outer-sphere electron transfer.

Finally, two inorganic couples deserve mention. Both $Fe(CN)_6^{3-}$[31] and $Mo(CN)_8^{3-}$[32] react with $O_2^{\bullet-}$ more slowly, by many orders of magnitude, than would be predicted by the outer-sphere mechanism.[4] While the reason for this anomaly is not yet understood, the present work at least demonstrates that these slow rates should not reflect any property of the $O_2/O_2^{\bullet-}$ couple.

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