

structures which are essentially $\text{H}^+(\text{H}_2\text{O})_n$ so that a gradual deprotonation of the acid will occur. The driving force for this change will be the superior accommodation of the proton in a water cluster, when many water molecules are available.

In analogy with the generally accepted intermediate in acid catalyzed esterification one might argue that the monohydrated, protonated propionic acid should not have the hydrogen bonded structure II but the structure IV. However one cannot be certain that structure IV is of greater stability. Structure IV offers covalent and therefore one might think better bonding. However the carbon atom is burdened by three C-O

single bonds, an unusual situation and is electron density deficient to start with. As mentioned above the present results suggest that the exothermicity for the addition of the first water molecule (i.e., reaction 18) is lower than that for the second (reaction 19). This taken together with the fact that ΔH_{18} is so close to ΔH_{19} argues that at least the dihydrate has the structure III and does not correspond to a monohydrated structure IV.

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Theory of Electron Transfer Generation and Quenching of Singlet Oxygen [$^1\Sigma_g^+$ and $^1\Delta_g$] by Superoxide Anion. The Role of Water in the Dismutation of O_2^-

Ahsan U. Khan

Contribution from the Departments of Chemistry and Biophysics, Michigan State University, East Lansing, Michigan 48824. Received March 23, 1976

Abstract: A critical dependence on the number of water molecules present has been found in a theoretical analysis applying the electron transfer theory of Marcus to the generation of singlet oxygen in the dismutation reaction of ion clusters of the superoxide ion O_2^- of the form $\text{O}_2^-(\text{H}_2\text{O})_n$. For the $n \geq 5$, excited oxygen is produced from the reaction. There is a narrow H_2O concentration range for the production of $\text{O}_2(^1\Delta_g)$, beyond which $\text{O}_2(^1\Sigma_g^+)$ becomes the dominant product. The theoretical analysis also predicts that singlet oxygen can be efficiently quenched by the O_2^- ion in solution through electron transfer reactions.

Experimental evidence is accumulating that singlet oxygen is generated in electron transfer reactions of the superoxide anion.¹⁻³ Failure to improve singlet oxygen $\text{O}_2(^1\Delta)$ yields from potassium superoxide in dimethyl sulfoxide (DMSO)^{1,4} solution suggests O_2^- plays a dual role in these solutions: generating singlet oxygen in a dismutation reaction and, at higher O_2^- concentration, quenching singlet oxygen. Moisture is necessary for the solution and gas phase dismutation reaction. We have used the theory of Marcus on adiabatic electron transfer⁵⁻⁷ to study the reactions: (i) $\text{O}_2^-(\text{H}_2\text{O})_n + \text{O}_2^-(\text{H}_2\text{O})_n \rightarrow \text{O}_2^{2-}(\text{H}_2\text{O})_n + \text{O}_2(\text{H}_2\text{O})_n$ and (ii) $\text{O}_2^- + \text{O}_2(^1\Sigma_g^+, ^1\Delta_g) \rightarrow \text{O}_2(^3\Sigma_g^-) + \text{O}_2^-$. The results show for reaction (i) singlet oxygen is generated from hydrated superoxide ions with $n \geq 5$ and for reaction (ii) quenching of singlet oxygen is very efficient.

To construct potential energy surfaces for the electron

transfer reaction, Marcus has developed an empirical formula $G_d = m^2\lambda$, where $-1 \leq m \leq +1$ is the fraction of charge transferred. λ can be evaluated from the theoretical expression $\lambda = \Delta e^2/2(1/2a_1 + 1/2a_2 - 1/R)(1/\epsilon_{op} - 1/\epsilon_s)$ where Δe is the total electronic charge transferred; a_1 and a_2 are the ionic radii, including the inner coordination shell; R is the interionic separation; and ϵ_{op} and ϵ_s are the optical and static dielectric constants of the surrounding solvent. An $R = 10 \text{ \AA}$ is a reasonable limiting distance. As the reaction proceeds, a crossing point is reached where spatial configurations of the nuclei, including solvent orientation, are the same for both reactants and products. This intersection represents the activation barrier ΔG_d^* . Once ΔG_d^* is evaluated, the rate can be estimated from $k = Z\kappa\rho \exp(-\Delta G_d^*/kT)$ where Z is approximately $10^{11} \text{ l. mol}^{-1} \text{ s}^{-1}$ and κ and ρ are approximately unity.⁵⁻⁷

ΔG for reaction (i) was estimated using: (1) Mass spectro-

Table I

Solvent	Axial orientation	$(1/2a_1 + 1/2a_2 - 1/R)$	O_2^- quenching of 1O_2 (k , l. mol $^{-1}$ s $^{-1}$)			Solvent quenching, (k , s $^{-1}$) ^{4,11}	
			I $^1\Sigma_g^+ \rightarrow ^3\Sigma_g^-$	II $^1\Sigma_g^+ \rightarrow ^1\Delta_g$	III $^1\Delta_g \rightarrow ^3\Sigma_g^-$	$^1\Delta_g$	$^1\Sigma_g^+$
DMSO	<i>a</i>	0.65	5×10^{10}	1×10^7	5×10^8	3×10^4	
	<i>b</i>	0.55	1×10^{11}	2×10^8	5×10^9		
	<i>c</i>	0.44	6×10^{10}	3×10^9	3×10^{10}		
H ₂ O	<i>a</i>	1.82	8×10^{10}	7×10^7	2×10^9	5×10^5	2×10^{10}
	<i>b</i>	1.42	7×10^{10}	2×10^9	3×10^{10}		

metric studies of thermal electron attachment to moist molecular oxygen give dissociation energies, D_0 , of $O_2^{\cdot-} \cdot (H_2O)_n \rightarrow O_2^- + nH_2O$ for $n = 1, 2, 3$, and 5 .^{8,9} Values for $n = 4$ and 6 came from a plot of D_0 vs. n . For this analysis $(H_2O)_n$ represents the inner coordination sphere of the ion. (2) Born Haber cycle calculations give $\Delta H_f = 110$ kcal mol $^{-1}$ for $O_2 + 2e = O_2^{2-}$.¹⁰ (3) Hydration energies for O_2^{2-} were taken as four times experimental values of D_0 , $O_2^{\cdot-} \cdot (H_2O)_n$, since hydration energy is directly proportional to the square of the ionic charge. (4) No subsequent reaction of $O_2^{2-} \cdot (H_2O)_n$ was considered. (5) No hydration energy was included for O_2 . (6) $T\Delta S$ is large for $O_2^{\cdot-} \cdot (H_2O)_n$ cluster formation.⁸ The product side includes $T\Delta S$ for $O_2^{2-} \cdot (H_2O)_n$ formation and a large increase in entropy from disruption of the inner coordination shell around neutral O_2 . We have equated $T\Delta S$ terms on both sides, resulting in a conservative estimate of ΔG for the reaction. (7) Solvation energies for reactant and product clusters in DMSO were neglected.

Then for $n = 4$, the ground state dismutation reaction is endothermic by 4 kcal mol $^{-1}$; $n = 5$, exothermic by 22 kcal mol $^{-1}$; and $n = 6$, exothermic by 50 kcal mol $^{-1}$.

Figure 1 shows potential surfaces for reaction (i) with $n = 4, 5$, and 6 H₂O molecules. The estimated ionic radius for both reactants and products, including inner coordination shells, is 3.5 Å. The bottoms of the wells represent ΔG for the complete reaction. The wells intersect at ΔG_d^* . Interactions between electronic states of the same multiplicity cause splitting at the intersection point; for $R = 10$ Å this is small. As ΔG for the dismutation reaction becomes increasingly large and negative, the route to ground state products becomes increasingly inaccessible.⁶ For $n = 6$, only excited oxygen, predominantly $^1\Sigma$, is produced.

Adding a statistical factor to account for state multiplicity, estimated reaction rates are: For $n = 4$, $k(^3\Sigma) = 5 \times 10^6$, $k(^1\Delta) = 10^{-12}$, and $k(^1\Sigma) = 10^{-31}$ l. mol $^{-1}$ s $^{-1}$. For $n = 5$, $k(^3\Sigma) = 8 \times 10^9$, $k(^1\Delta) = 4 \times 10^7$, and $k(^1\Sigma) = 4 \times 10^{-2}$ l. mol $^{-1}$ s $^{-1}$. For $n = 6$, $k(^3\Sigma) = 10^{-8}$, $k(^1\Delta) = 6 \times 10^7$, and $k(^1\Sigma) = 2 \times 10^{10}$ l. mol $^{-1}$ s $^{-1}$. Increasing or decreasing the estimated ionic radii changes the relative ratios of the species produced. However, at $n = 6$ singlet oxygen clearly predominates.

Rates for quenching reaction (ii) were evaluated for two solvents, DMSO and water. Three reactions were considered: (I) quenching of $^1\Sigma$ directly to the ground state, (II) stepwise quenching of $^1\Sigma$ to $^1\Delta$, and (III) quenching of $^1\Delta$. Table I gives the estimated rates. In dry DMSO the species are considered not to have an inner coordination shell. Since $O_2^{\cdot-}$ and neutral O_2 are ellipsoidal, four axial orientations are possible in dry DMSO: (a) minor to minor, (b) minor to major ($O_2^{\cdot-}$, O_2) or (O_2 , $O_2^{\cdot-}$), and (c) major to major. In aqueous solution a spherical radius of 3.5 Å was used for $O_2^{\cdot-} \cdot (H_2O)_n$, and two orientations are possible for neutral, unsolvated molecular oxygen.

Quenching of $^1\Sigma$ directly to $^3\Sigma$ approaches diffusion control in all cases. Stepwise quenching of $^1\Sigma$ by O_2^- to generate $^1\Delta$ is appreciably slower, and quenching directly to the ground state is expected to dominate, in contrast to solvent quenching of $^1\Sigma$, predicted as proceeding stepwise through $^1\Delta$.¹¹ Quenching of $^1\Delta$ by electron transfer is more efficient than

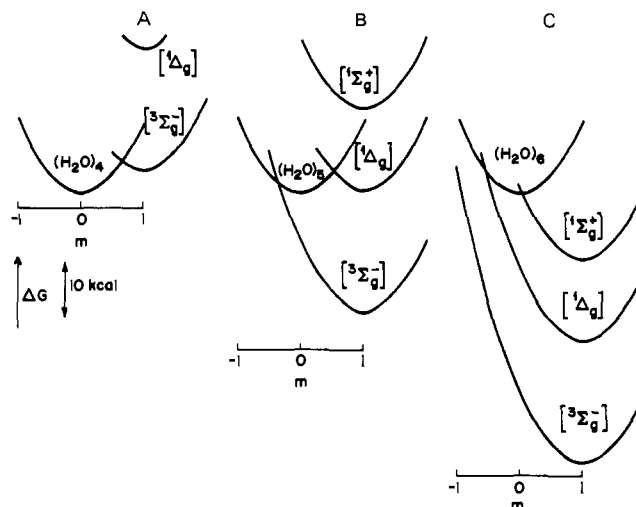


Figure 1. Potential energy diagrams for: (A) $O_2^{\cdot-} \cdot (H_2O)_4 + O_2^{\cdot-} \cdot (H_2O)_4 \rightarrow O_2^{2-} \cdot (H_2O)_4 + O_2 \cdot (H_2O)_4$; (B) $O_2^{\cdot-} \cdot (H_2O)_5 + O_2^{\cdot-} \cdot (H_2O)_5 \rightarrow O_2^{2-} \cdot (H_2O)_5 + O_2 \cdot (H_2O)_5$; and (C) $O_2^{\cdot-} \cdot (H_2O)_6 + O_2^{\cdot-} \cdot (H_2O)_6 \rightarrow O_2^{2-} \cdot (H_2O)_6 + O_2 \cdot (H_2O)_6$. Potential wells for the combined reactants are labeled $(H_2O)_n$, and wells for the combined products are labeled explicitly by the molecular oxygen state.

solvent quenching of $^1\Delta$ (see Table I).¹²

This analysis emphasizes the critical nature of H₂O concentration on the generation of excited oxygen from dismutation of the superoxide anion. At elevated H₂O concentrations production of $^1\Sigma$ predominates. These conditions would be expected to also increase $^1\Delta$ concentration through stepwise quenching of $^1\Sigma$. However, in the presence of O_2^- , quenching of $^1\Sigma$ proceeds directly to the ground state, and $^1\Sigma$ is also efficiently quenched. Singlet oxygen generation is therefore limited to a narrow concentration range.

Enzymatic generation of O_2^- occurs in the hydrophobic environment surrounding the active site. Enzymatic control of water and O_2^- concentration could yield appreciable singlet oxygen generation; in contrast, generation of singlet oxygen in other enzymatic systems could indicate the presence of a few aberrant H₂O molecules.

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