Chemical Reactivity of Singlet Sigma Oxygen ($b^1\Sigma_g^+$) in Solution

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Received October 11, 1995⊗

Abstract: Spectroscopic data are presented to indicate that, in solution, chemical reactions of singlet sigma oxygen, $O_2(b^1\Sigma_g^+)$, do not compete effectively with the physical deactivation channels that produce $O_2(a^1\Delta_g)$.

Introduction

The ground state of molecular oxygen, $O_2(X^3\Sigma_g^-)$, is a triplet spin state. The lowest excited electronic state of oxygen, $O_2(a^1\Delta_g)$, is 94 kJ/mol higher in energy than $O_2(X^3\Sigma_g^-)$. This excited state is a singlet spin state, and is commonly called singlet molecular oxygen. Events that result in both the formation and the removal of $O_2(a^1\Delta_g)$ in solution-phase systems have been studied extensively over the past thirty years.[1,2] The importance of $O_2(a^1\Delta_g)$, as documented by this significant body of work, lies in the fact that $O_2(a^1\Delta_g)$ is an intermediate in a host of photooxidation reactions.

The second excited electronic state of oxygen, $O_2(b^1\Sigma_g^+)$, which is 63 kJ/mol more energetic than $O_2(a^1\Delta_g)$, is also a singlet spin state. Given the acknowledged role of $O_2(a^1\Delta_g)$ in a variety of photooxygenations and that $O_2(b^1\Sigma_g^+)$ is more energetic than $O_2(a^1\Delta_g)$, it is not surprising that speculations have risen over the years about the possible intermediacy of $O_2(b^1\Sigma_g^+)$ in photoinduced oxygenation reactions. Unfortunately, data regarding the behavior of $O_2(b^1\Sigma_g^+)$ in solution-phase systems have not been as convincing, and ultimately irrefutable, as the data used to identify $O_2(a^1\Delta_g)$ as a reactive intermediate.

In 1967, Kearns et al.[3−5] published several reports claiming evidence for the intermediacy of $O_2(b^1\Sigma_g^+)$ in a sensitized photooxygenation reaction. The arguments presented by these investigators derived from several key points: (1) On the basis of their own theoretical calculations,[6−8] Kearns et al. assumed that the relative yields of $O_2(b^1\Sigma_g^+)$ and $O_2(a^1\Delta_g)$ in a photosensitized process would depend on the triplet energy E_T of the sensitizer. Specifically, for sensitizers with E_T greater than ∼200 kJ/mol, 10 molecules of $O_2(b^1\Sigma_g^+)$ were expected for each $O_2(a^1\Delta_g)$ molecule produced. The ratio $O_2(b^1\Sigma_g^+)$:$O_2(a^1\Delta_g)$ was predicted to decrease as E_T dropped below 200 kJ/mol, and approach zero as E_T approached 157 kJ/mol, the excitation energy of $O_2(b^1\Sigma_g^+)$. (2) The reaction investigated, the photooxygenation of a cholestenol, yielded two discrete products. As reported previously by Nickon and Mendelson,[9,10] Kearns et al. noted that the relative yields of these two products depended on the sensitizer used for the photooxygenation. More specifically, it was reported by Kearns et al. that the variation in cholestenol product distribution with sensitizer E_T was very similar to the predicted variation of the ratio $O_2(b^1\Sigma_g^+)$:$O_2(a^1\Delta_g)$ with E_T. Kearns et al. thus concluded that one of the products formed in the photooxygenation of the cholestenol derived from a reaction with $O_2(b^1\Sigma_g^+)$, whereas the other product derived from a reaction with $O_2(a^1\Delta_g)$.

These reports by Kearns et al. were later criticized. In 1969, Foote and Wong[11] provided data to indicate that the variation in cholestenol product distribution with the sensitizer (or rather, E_T) was likely due to phenomena other than the reaction of two separate singlet oxygen molecules, $O_2(b^1\Sigma_g^+)$ and $O_2(a^1\Delta_g)$. On the basis of gas-phase data reported by Arnold et al.,[12] Foote and Wong also indicated that the lifetime of $O_2(b^1\Sigma_g^+)$ in the solvent used by Kearns et al. (pyridine) was likely to be so short that a reaction between $O_2(b^1\Sigma_g^+)$ and another solute was highly improbable. On the basis of a separate series of photooxygenation experiments performed as a function of sensitizer E_T, Gollnick et al.[13] likewise concluded that there was no evidence for the reaction of two separate singlet oxygen molecules. Although not directly critical of the Kearns et al. conclusion that $O_2(b^1\Sigma_g^+)$ can be a reactive intermediate, Wang and Ogilby[14] as well as Bodesheim et al.[15] recently showed that the key premise of the Kearns et al. argument was incorrect. Using spectroscopic experiments in which $O_2(b^1\Sigma_g^+)$ and $O_2(a^1\Delta_g)$ were directly monitored, these investigators provided data to indicate that, in a photosensitized reaction, the relative yield of $O_2(b^1\Sigma_g^+)$ does not depend on E_T in the manner predicted by Kearns et al.

In 1978, Reddy and Berry[16] irradiated oxygenated samples of 2,3-dimethyl-2-butene at a wavelength (761 nm) resonant with the transition $O_2(X^3\Sigma_g^-)_{\upsilon=0} \rightarrow O_2(b^1\Sigma_g^+)_{\upsilon=0}$. These authors

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⊗ Abstract published in *Advance ACS Abstracts,* January 1, 1996.

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Table 1. $O_2(b^1\Sigma_g^+)$ Quenching Data

quencher	$\tau_0 k_{tot}^{\Sigma}$ (M^{-1})[a]	k_{tot}^{Σ} (s^{-1} M^{-1})	$k_{e\text{-}v}^{\Sigma}$(calc) (s^{-1} M^{-1})	$[Q]_{max}$ (M)	% $O_2(b^1\Sigma_g^+)$ quenched at $[Q]_{max}$	k_{rxn}^{Σ} (max) (s^{-1} M^{-1})
furan	48	3.7×10^8	4×10^8	0.034	62	6.6×10^7
furan-d_4	13	1.0×10^8	1×10^8	0.060	44	2.5×10^7
dichlorothiophene	15	1.2×10^8	2×10^8	0.184	74	1.8×10^7
tetrachlorothiophene	0[b]	0	0	0.59	0	1.4×10^6
$Cl_2C{=}CCl_2$	−0.04	0	0	4.0	0	2.1×10^5
$Cl_2C{=}CHCH_2Cl$	17	1.3×10^8	3×10^8	0.3	84	1.7×10^7
CH_2Ph_2	110	8.5×10^8	12×10^8	0.046	84	1.1×10^8
$N(CF_2CF_3)_3$	2.3	0.18×10^8	0	0.347	45	4.5×10^6 [c]
$P(C_6F_5)_3$	12	0.9×10^8	0	0.04	32	3.1×10^7 [c]
DABCO	178	14×10^8	12×10^8	0.0039	42	3.7×10^8 [c]

[a] Errors on the Stern−Volmer quenching constants are ±5% of the value indicated (one standard deviation obtained from the linear least-squares analysis). [b] The slope of the Stern−Volmer plot was zero, see text. [c] The designation k_{bypass}^{Σ}(max) is likely to be more accurate than k_{rxn}^{Σ}(max) for these molecules. See text.

concluded that, because $O_2(b^1\Sigma_g^+)$ was directly formed upon irradiation of the sample, any oxygenated product thus formed must derive from a reaction between the olefin and $O_2(b^1\Sigma_g^+)$. The possibility that the olefin might deactivate $O_2(b^1\Sigma_g^+)$ to $O_2(a^1\Delta_g)$ prior to reaction was not considered. In a subsequent report, Hammond[17] used the same technique to study the oxygenation of 2,3-dimethyl-2-butene and concluded that either (a) $O_2(b^1\Sigma_g^+)$ and $O_2(a^1\Delta_g)$ give identical reaction products or (b) $O_2(b^1\Sigma_g^+)$ is deactivated to $O_2(a^1\Delta_g)$ prior to the oxygenation reaction with the olefin.

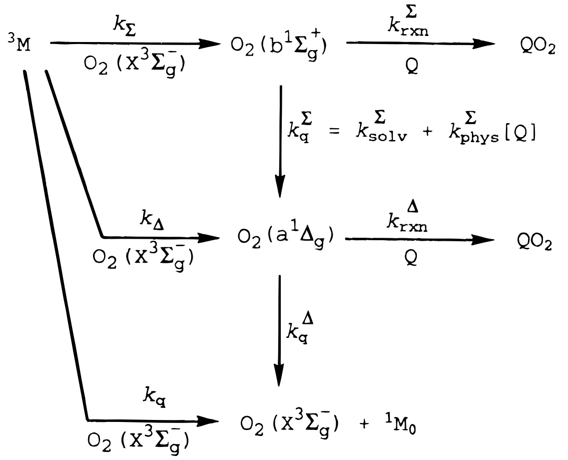
It is now possible to directly detect both $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ in solution-phase emission experiments.[14,15,18−22] We set out to use these spectroscopic techniques to provide a more definitive answer to the question of whether or not $O_2(b^1\Sigma_g^+)$, like $O_2(a^1\Delta_g)$, can react with an organic molecule. The results of this study are presented in this report.

Experimental Section

Details of the techniques and instrumentation we use to monitor $O_2(b^1\Sigma_g^+)$, $O_2(a^1\Delta_g)$, and organic molecule excited states have been published.[14,19,20,23] Briefly, a pulsed Nd:YAG laser was used as the excitation source. The third harmonic (355 nm) of the fundamental lasing wavelength was used in the experiment to obtain $k_\Sigma/(k_\Sigma + k_\Delta)$ for the sensitizer decacyclene. The data in Table 1 were recorded using an excitation wavelength of 416 nm, which was obtained by stimulated Raman scattering of the 355-nm harmonic with H_2 gas and isolating the first Stokes line. The 1270-nm phosphorescence of $O_2(a^1\Delta_g)$ was monitored with a liquid nitrogen cooled germanium detector (North Coast) whose response function was single exponential with a time constant of 400 ns. The 1926-nm fluorescence of $O_2(b^1\Sigma_g^+)$ was monitored with a liquid nitrogen cooled InSb detector (Judson) whose response function was also single exponential, but with a time constant of 2 μs. Under all circumstances, the $O_2(b^1\Sigma_g^+)$ lifetime was less than 2 μs. Thus, we were only able to use the integrated intensity of the InSb detector signal to quantify the behavior of $O_2(b^1\Sigma_g^+)$.[14,19,20]

Tetrachloroethylene, 1,1,3-trichloropropene, 2,5-dichlorothiophene, tetrachlorothiophene, 1,4-diazabicyclo[2.2.2]octane (DABCO), tris(pentafluorophenyl)phosphine, and perfluorotriethylamine were obtained from Aldrich and used as received. Furan and Furan-d_4 (Aldrich) were distilled prior to use in order to remove a stabilizer added by the manufacturer. Diphenylmethane was prepared by catalytic hydrogenation of benzophenone in ethanol. Decacyclene (Aldrich) was recrystallized from benzene/ethanol. CCl_4 (Aldrich) was distilled from P_2O_5 and stored over molecular sieves prior to use.

Scheme 1



Results and Discussion

1. General Background and Methodology. When a triplet state organic molecule of sufficient energy (greater than ~157 kJ/mol) is quenched by $O_2(X^3\Sigma_g^-)$, both $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ can be produced by electronic energy transfer (Scheme 1).[14,15,18,20,22,24,25]

The fraction $k_\Sigma/(k_\Sigma + k_\Delta)$ of excited state oxygen initially formed as $O_2(b^1\Sigma_g^+)$ varies with the sensitizer.[14,15,20,22] Once formed, $O_2(b^1\Sigma_g^+)$ could potentially react with a quencher Q to yield an oxygenated product, QO_2. This reactive quenching channel would compete with both quencher- and solvent-induced physical deactivation channels that produce $O_2(a^1\Delta_g)$ and $O_2(X^3\Sigma_g^-)$ (the latter process is not shown in Scheme 1).

$O_2(b^1\Sigma_g^+)$ physical deactivation occurs via radiative and non-radiative processes. The radiative transitions $O_2(b^1\Sigma_g^+) \rightarrow O_2(X^3\Sigma_g^-)$ and $O_2(b^1\Sigma_g^+) \rightarrow O_2(a^1\Delta_g)$ are very inefficient, and do not contribute significantly to the deactivation of $O_2(b^1\Sigma_g^+)$.[21,26] (Nevertheless, we monitor $O_2(b^1\Sigma_g^+)$ by its fluorescence at 1926 nm.) A great deal of evidence from both gas- and solution-phase studies indicates that collision-induced deactivation of $O_2(b^1\Sigma_g^+)$ results in the non-radiative production of $O_2(a^1\Delta_g)$.[19,22,27−29] Thus, under conditions in which $O_2(b^1\Sigma_g^+)$ interacts with a molecule Q, a quencher-dependent

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decrease in the $O_2(a^1\Delta_g)$ *yield* is evidence for either (1) a chemical reaction between $O_2(b^1\Sigma_g^+)$ and Q that can compete with the non-radiative $O_2(b^1\Sigma_g^+) \rightarrow O_2(a^1\Delta_g)$ transition or (2) quencher-induced deactivation of $O_2(b^1\Sigma_g^+)$ that bypasses $O_2(a^1\Delta_g)$ and directly produces $O_2(X^3\Sigma_g^-)$. Quencher-dependent changes in the yield of $O_2(a^1\Delta_g)$ can be quantified by monitoring changes in the $O_2(a^1\Delta_g)$ phosphorescence intensity at 1270 nm.

Details of this experimental perspective are discussed below:

(A) The Sensitizer. For this particular study, the singlet oxygen sensitizer must meet the following criteria:

(a) E_T must be greater than approximately 157 kJ/mol, the excitation energy of $O_2(b^1\Sigma_g^+)$.

(b) The fraction $k_\Sigma/(k_\Sigma + k_\Delta)$ of excited state oxygen initially formed as $O_2(b^1\Sigma_g^+)$ should be as large as possible.

(c) The compound must be soluble in CCl_4 (*vide infra*).

(d) It must be possible to selectively irradiate the sensitizer without irradiating the singlet oxygen quencher. In a practical sense, this means that the sensitizer must have a discrete absorption band at a comparatively long wavelength.

(e) The sensitizer triplet state should not be susceptible to deactivation by the singlet oxygen quencher, particularly at the high concentrations of the quencher necessary to deactivate a significant fraction of the $O_2(b^1\Sigma_g^+)$ produced.

(f) The sensitizer must be stable over comparatively long periods of irradiation in the presence of both oxygen and the singlet oxygen quencher.

After examining several different molecules, we found that decacyclene best met these criteria. Flash absorption measurements of the decacyclene triplet state at 650 nm indicated that the decay rate of this species was invariant over the concentration range employed for all quenchers Q. Thus, Q did not compete with $O_2(X^3\Sigma_g^-)$ for ^{3}decacyclene, and the amount of both $O_2(b^1\Sigma_g^+)$ and $O_2(a^1\Delta_g)$ produced was independent of added Q. By comparing decacyclene sensitized $O_2(b^1\Sigma_g^+)$ and $O_2(a^1\Delta_g)$ luminescence intensities to the corresponding luminescence intensities observed in a benzophenone sensitized process,[14,20] we determined that the ratio $k_\Sigma/(k_\Sigma + k_\Delta)$ for decacyclene in CCl_4 is ~0.9.

(B) Solvent. In order to have any hope of detecting a bimolecular reaction between $O_2(b^1\Sigma_g^+)$ and a quencher molecule Q, it is imperative that we minimize the solvent-induced deactivation of $O_2(b^1\Sigma_g^+)$. Specifically, we must choose a solvent in which the $O_2(b^1\Sigma_g^+)$ lifetime is comparatively long.

The effect of solvent on the lifetime of $O_2(b^1\Sigma_g^+)$ has recently been examined in a series of direct spectroscopic studies.[19,21] The data indicate that solvent-induced deactivation of $O_2(b^1\Sigma_g^+)$ proceeds almost exclusively by a non-radiative channel to produce $O_2(a^1\Delta_g)$. As with the solvent-dependent, non-radiative deactivation of $O_2(a^1\Delta_g)$, the rate constant for this process depends on the ability of the solvent to accept the electronic excitation energy into vibrational modes. Solvent molecules that contain O−H and C−H bonds are particularly effective at deactivating $O_2(b^1\Sigma_g^+)$.

The work described herein was performed in CCl_4, which clearly lacks C−H and O−H bonds. Given the similarities in the solvent-dependent deactivation mechanisms of $O_2(b^1\Sigma_g^+)$ and $O_2(a^1\Delta_g)$, and that the lifetime of $O_2(a^1\Delta_g)$ in CCl_4 is comparatively long,[30] it is unlikely that one could find a solvent in which the $O_2(b^1\Sigma_g^+)$ lifetime is significantly longer than that in CCl_4.[31] The lifetime of $O_2(b^1\Sigma_g^+)$ in CCl_4 is 130 ± 10 ns,[21] which gives rise to a pseudo-first-order deactivation rate constant k^Σ_{solv} of 7.7×10^6 s^{-1}. Thus, under conditions in which a molecule Q with $k^\Sigma_{rxn} = 5 \times 10^6$ s^{-1} M^{-1} is added to the CCl_4 solution at a concentration of 0.1 M, approximately 6% of the $O_2(b^1\Sigma_g^+)$ molecules produced would be trapped by Q. If Q is also able to deactivate $O_2(b^1\Sigma_g^+)$ via a physical quenching channel, k^Σ_{phys}, the fraction of $O_2(b^1\Sigma_g^+)$ trapped in the chemical reaction will be reduced.

It is important to note that bimolecular rate constants for the interaction between the solvent and $O_2(b^1\Sigma_g^+)$ are approximately 5−6 orders of magnitude larger than corresponding rate constants for the interaction between the solvent and $O_2(a^1\Delta_g)$. Thus, in a solvent such as benzene, $O_2(a^1\Delta_g)$ has a lifetime of 31 μs, whereas $O_2(b^1\Sigma_g^+)$ has a lifetime of 135 ps.[21]

(C) Singlet Oxygen Quenchers. The following points were considered in selecting molecules that might afford us the best chance of detecting a $O_2(b^1\Sigma_g^+)$ reaction.

(a) As discussed in the previous section, it is imperative that we minimize the contribution of physical deactivation channels that will compete with any chemical reaction of $O_2(b^1\Sigma_g^+)$. Thus, when possible, we tried to employ either halogenated or deuterated quenchers that did not have a significant number of C−H and O−H bonds (Table 1). It is unfortunately possible, however, that chlorinated and fluorinated molecules might not be as reactive toward $O_2(b^1\Sigma_g^+)$ as the hydrogen-substituted analog. Although replacing hydrogen with deuterium on the quencher can significantly reduce the rate of $O_2(a^1\Delta_g)$ non-radiative deactivation, a similar substitution unfortunately does not reduce the rate of $O_2(b^1\Sigma_g^+)$ deactivation as much.[19]

(b) We assumed that reactions characteristic of $O_2(a^1\Delta_g)$ might also be observed with $O_2(b^1\Sigma_g^+)$. Thus, molecules capable of undergoing the "ene" reaction as well as $_\pi 2 + _\pi 2$ and $_\pi 2 + _\pi 4$ cycloadditions were chosen.

(c) On the basis of comments by Foote and Wong,[11] where it was noted that $O_2(b^1\Sigma_g^+)$ might react with H-atom donors, diphenylmethane was also examined.

(d) We also wanted to test if $O_2(b^1\Sigma_g^+)$, like $O_2(a^1\Delta_g)$, was sensitive to charge-transfer (CT) interactions. Although such a process would not likely result in the removal of $O_2(b^1\Sigma_g^+)$ by a chemical reaction, we could envision CT-mediated coupling between the $O_2(b^1\Sigma_g^+)$ and $O_2(X^3\Sigma_g^-)$ states[14] which, in turn, would also decrease the yield of $O_2(a^1\Delta_g)$. Several amines and a phosphine were chosen to test for this phenomenon.

(e) Finally, at the high quencher concentrations needed to deactivate a significant portion of the $O_2(b^1\Sigma_g^+)$ produced, the quencher chosen must not deactivate the sensitizer triplet state.

The quenching of solution-phase $O_2(b^1\Sigma_g^+)$ by benzene, cyclohexane, acetone, acetonitrile, chloroform, benzene-d_6, and acetone-d_6 has been studied.[19,21] These molecules deactivate $O_2(b^1\Sigma_g^+)$ to produce $O_2(a^1\Delta_g)$ via a mechanism of electronic-to-vibrational energy transfer. Assuming that $O_2(b^1\Sigma_g^+)$ quenching by these molecules is dominated by the high-frequency C−H and C−D vibrational modes, overall quenching rate constants for each molecule can then be used to obtain average rate constants that reflect the quenching contribution of single C−H and C−D bonds. These single-bond rate constants can then be used to calculate, for each of the quenchers examined in our study, the rate constant k^Σ_{e-v}(calc) expected for the deactivation of $O_2(b^1\Sigma_g^+)$ via electronic-to-vibrational energy transfer. Using $k^\Sigma_{C-H} = 1 \times 10^8$ s^{-1} M^{-1} and $k^\Sigma_{C-D} = 2.5 \times 10^7$ s^{-1} M^{-1}, values of k^Σ_{e-v}(calc) thus obtained are listed in Table 1.

(D) Monitoring the Yield of $O_2(a^1\Delta_g)$. Within 1 μs after pulsed laser excitation (fwhm ~ 5 ns) of the singlet oxygen sensitizer, both the formation and decay of $O_2(b^1\Sigma_g^+)$ are complete: (1) in aerated solutions the lifetime of the sensitizer

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triplet state (i.e., the $O_2(b^1\Sigma_g^+)$ precursor) is 330 ns, and (2) interactions with the quencher Q decrease the $O_2(b^1\Sigma_g^+)$ lifetime below the intrinsic lifetime of 130 ns in CCl_4. The lifetime of $O_2(a^1\Delta_g)$ under our experimental conditions, however, is much longer than 1 μs. Thus, an accurate measure of the total $O_2(a^1\Delta_g)$ yield, produced both by energy transfer from the sensitizer and by the decay of $O_2(b^1\Sigma_g^+)$ (Scheme 1), can be obtained by monitoring the $O_2(a^1\Delta_g)$ phosphorescence intensity approximately 1 μs after pulsed excitation of the sensitizer.[32]

2. Data. Stern−Volmer quenching studies, performed by monitoring the integrated $O_2(b^1\Sigma_g^+)$ fluorescence intensity at 1926 nm,[19] indicated that the $O_2(b^1\Sigma_g^+)$ was being deactivated by the added quencher in all but two cases, tetrachlorothiophene and tetrachloroethylene (Table 1). In fact, the Stern−Volmer plot obtained upon the addition of tetrachloroethylene had a negative slope, which may indicate (1) that the $O_2(b^1\Sigma_g^+)$ lifetime is longer in tetrachloroethylene than in CCl_4 or (2) that $O_2(b^1\Sigma_g^+)$ radiative deactivation is more probable in tetrachloroethylene than in CCl_4.[33,34] Using the $O_2(b^1\Sigma_g^+)$ lifetime τ_0 in CCl_4 of 130 ns reported by Schmidt and Bodesheim,[21] it is possible to obtain the bimolecular rate constant k_{tot}^Σ for the total ($k_{rxn}^\Sigma + k_{phys}^\Sigma$) quencher-induced deactivation of $O_2(b^1\Sigma_g^+)$ by dividing our Stern−Volmer quenching constants by τ_0. Moreover, values of k_{tot}^Σ and τ_0^{-1} can then be used to calculate the percent of $O_2(b^1\Sigma_g^+)$ deactivated by the quencher Q at the maximum concentration of Q used in our experiments, $[Q]_{max}$. These data are listed in Table 1.

For all molecules examined, we did not observe a quencher-dependent decrease in the yield of $O_2(a^1\Delta_g)$. On the basis of the material shown in Scheme 1, we can write an expression for the fractional decrease in the $O_2(a^1\Delta_g)$ phosphorescence intensity due to the presence of a quencher Q that reacts with $O_2(b^1\Sigma_g^+)$

$$\frac{I_\Delta^0 - I_\Delta^Q}{I_\Delta^0} = \frac{k_\Sigma}{k_\Sigma + k_\Delta}\,\frac{k_{rxn}^\Sigma[Q]}{k_{solv}^\Sigma + k_{tot}^\Sigma[Q]} \qquad (1)$$

where I_Δ^0 and I_Δ^Q are the $O_2(a^1\Delta_g)$ phosphorescence intensities in the absence and presence, respectively, of Q. If we assume that a change in the $O_2(a^1\Delta_g)$ phosphorescence intensity of at least 10% is necessary to detect any chemical reaction that depletes the population of $O_2(b^1\Sigma_g^+)$, then we can use eq 1 to establish an upper limit for the rate constant of $O_2(b^1\Sigma_g^+)$ reaction, k_{rxn}^Σ(max), using the values of $[Q]_{max}$ and k_{tot}^Σ determined for each quencher.[35] As already mentioned, $k_\Sigma/(k_\Sigma + k_\Delta) = 0.9$ for decacyclene and $k_{solv}^\Sigma = 7.7 \times 10^6$ s^{-1}. Values of k_{rxn}^Σ(max) thus calculated are shown in Table 1. Note that for the amines and the phosphine, where a chemical reaction is not expected to occur, k_{rxn}^Σ(max) is a misnomer. In these cases, where the phenomenon tested was a $O_2(b^1\Sigma_g^+)$ deactivation channel that bypassed $O_2(a^1\Delta_g)$ to directly produce $O_2(X^3\Sigma_g^-)$, the designation k_{bypass}^Σ(max) is more accurate.

On the basis of the data in Table 1, we make the following observations:

(1) For the unsaturated quenchers as well as diphenylmethane, k_{rxn}^Σ(max) is less than either k_{tot}^Σ or $k_{solv}^\Sigma/[CCl_4]$. In the case of tetrachlorothiophene, where $O_2(b^1\Sigma_g^+)$ quenching was not observed, $k_{rxn}^\Sigma(\text{max}) \sim k_{solv}^\Sigma/[CCl_4]$. Thus, any chemical reaction of $O_2(b^1\Sigma_g^+)$ that might occur with these molecules does not compete effectively with quencher- or solvent-induced deactivation channels that produce $O_2(a^1\Delta_g)$. This conclusion is consistent with the fact that values of k_{tot}^Σ for these quenchers are remarkably similar to the $k_{e\text{-}v}^\Sigma$(calc) values. Indeed, k_{tot}^Σ and $k_{e\text{-}v}^\Sigma$(calc) differ, at most, by a factor of 2.3 (i.e., $k_{tot}^\Sigma = 1.3 \times 10^8$ M^{-1} s^{-1} and $k_{e\text{-}v}^\Sigma(\text{calc}) = 3 \times 10^8$ M^{-1} s^{-1} for 1,1,3-trichloropropene). Because the empirically derived values of k_{C-H}^Σ and k_{C-D}^Σ were obtained from a comparatively small data base (*vide supra*), it is not unreasonable to expect error bars on $k_{e\text{-}v}^\Sigma$(calc) to be as large as ~50% of the value listed in Table 1. Recall that $k_{e\text{-}v}^\Sigma$(calc) was obtained for each quencher assuming that electronic-to-vibrational energy transfer dominates $O_2(b^1\Sigma_g^+)$ deactivation.

(2) In CCl_4, the overall rate constants k_{tot}^Δ for $O_2(a^1\Delta_g)$ removal by furan and furan-*d*$_4$ are 9.0×10^6 and 7.2×10^6 M^{-1} s^{-1}, respectively.[36] These rate constants principally reflect reactive, as opposed to physical, quenching.[37] A dominant reactive channel is consistent with the comparatively small k_{tot}^Δ isotope effect of 1.25; a larger isotope effect would be expected for the electronic-to-vibrational energy transfer process that characterizes $O_2(a^1\Delta_g)$ physical quenching.[19,37] For both furans, k_{rxn}^Σ(max) is significantly less than k_{tot}^Σ indicating that, unlike $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_g^+)$ decays principally via the physical deactivation channel. This observation is consistent with (a) the larger k_{tot}^Σ isotope effect of 3.7 and (b) the coincidence between k_{tot}^Σ and $k_{e\text{-}v}^\Sigma$(calc).

(3) 1,4-Diazabicyclo[2.2.2]octane (DABCO) is a well-known $O_2(a^1\Delta_g)$ quencher, whose mode of action involves CT-mediated coupling between the $O_2(a^1\Delta_g)$ and $O_2(X^3\Sigma_g^-)$ states.[37−39] In CCl_4, the rate constant for the quenching of $O_2(a^1\Delta_g)$ by DABCO is 5.1×10^7 s^{-1} M^{-1},[36] which is much greater, for example, than the rate constant for the quenching of $O_2(a^1\Delta_g)$ by cyclohexane, 4.7×10^3 s^{-1} M^{-1},[37,40] whose mode of action is electronic-to-vibrational energy transfer. The rate constant for the quenching of $O_2(b^1\Sigma_g^+)$ by DABCO is 1.4×10^9 s^{-1} M^{-1}, which is very similar to (a) the rate constant for $O_2(b^1\Sigma_g^+)$ quenching by cyclohexane, 1.3×10^9 s^{-1} M^{-1},[21] and (b) the $k_{e\text{-}v}^\Sigma$(calc) value of 1.2×10^9 s^{-1} M^{-1}. It thus appears that, with DABCO, CT effects are not as important as electronic-to-vibrational energy transfer in the deactivation of $O_2(b^1\Sigma_g^+)$. Nevertheless, because $k_{bypass}^\Sigma(\text{max}) \sim 4 \times 10^8$ s^{-1} M^{-1}, it is still possible that a significant CT component contributes to $O_2(b^1\Sigma_g^+)$ deactivation. Certainly, any CT character that might play a role in $O_2(b^1\Sigma_g^+)$ deactivation does not provide measurable coupling between the $O_2(b^1\Sigma_g^+)$ and $O_2(X^3\Sigma_g^-)$ states;

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(32) In the absence of the quencher Q, the $O_2(a^1\Delta_g)$ lifetime τ_Δ in CCl_4 is in the millisecond domain (ref 30). For most of our quenching experiments, where $\tau_\Delta > 10$ μs, the $O_2(a^1\Delta_g)$ intensity was obtained by extrapolating the single-exponential $O_2(a^1\Delta_g)$ phosphorescence decay function back to time 0. When the comparatively efficient quenchers (e.g., DABCO) were present at their highest concentration, the $O_2(a^1\Delta_g)$ lifetimes recorded were in the range 3−5 μs. Under these conditions, we deconvoluted the detector response function from the time-resolved $O_2(a^1\Delta_g)$ signal to obtain the $O_2(a^1\Delta_g)$ intensity at time 0.

(33) Scurlock, R. D.; Ogilby, P. R. *J. Phys. Chem.* **1987**, *91*, 4599−4602.

(34) Scurlock, R. D.; Nonell, S.; Braslavsky, S. E.; Ogilby, P. R. *J. Phys. Chem.* **1995**, *99*, 3521−3526.

(35) The threshold of a 10% change derives from the worst-case scatter observed from repeated measurements of the $O_2(a^1\Delta_g)$ phosphorescence intensity. This 10% threshold is a conservative estimate, and it is likely that we could accurately detect a 5% change in $O_2(a^1\Delta_g)$ phosphorescence intensity.

(36) Determined in a time-resolved $O_2(a^1\Delta_g)$ phosphorescence experiment by monitoring the change in $O_2(a^1\Delta_g)$ deactivation rate constant as a function of the quencher concentration.

(37) Monroe, B. M. In *Singlet Oxygen*; Frimer, A. A., Ed.; CRC Press: Boca Raton, 1985; Vol. 1, pp 177−224.

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DABCO-induced $O_2(b^1\Sigma_g^+)$ deactivation results principally in the production of $O_2(a^1\Delta_g)$.

(4) Unlike DABCO, $N(CF_2CF_3)_3$ and $P(C_6F_5)_3$ are not effective quenchers of $O_2(a^1\Delta_g)$; we were unable to detect any change in the $O_2(a^1\Delta_g)$ lifetime up to the $[Q]_{max}$ values listed in Table 1. This observation likely reflects a combination of two phenomena: (a) there are no C−H bonds in the molecules, thus the electronic-to-vibrational energy transfer channel is not efficient, and (b) substitution by fluorine may sufficiently increase the quencher ionization potential such that a CT-mediated $O_2(a^1\Delta_g) \rightarrow O_2(X^3\Sigma_g^-)$ deactivation mechanism is no longer competitive. On the basis of $k^{\Sigma}_{e\text{-}v}$(calc) values, $N(CF_2CF_3)_3$ and $P(C_6F_5)_3$ are not expected to be efficient quenchers of $O_2(b^1\Sigma_g^+)$ via a mechanism of electronic-to-vibrational energy transfer (Table 1). Nevertheless, the data show that these two molecules are both reasonably good $O_2(b^1\Sigma_g^+)$ quenchers with $k^{\Sigma}_{tot} \sim 0.2-1.0 \times 10^8\ s^{-1}\ M^{-1}$. *A priori*, one might expect that, when compared to $O_2(a^1\Delta_g)$, the larger excitation energy of $O_2(b^1\Sigma_g^+)$ could make a CT-mediated deactivation process more probable. Specifically, the free-energy change for an electron transfer process should be more exergonic for $O_2(b^1\Sigma_g^+)$ than for $O_2(a^1\Delta_g)$ quenching (ionization potentials for other perfluorinated compounds indicate that $N(CF_2CF_3)_3$ and $P(C_6F_5)_3$ may still be reasonable electron donors). Values of k^{Σ}_{bypass}(max) indicate that, if it occurs, such CT-mediated, $N(CF_2CF_3)_3$- and $P(C_6F_5)_3$-induced $O_2(b^1\Sigma_g^+)$ deactivation must principally result in the formation of $O_2(a^1\Delta_g)$. The values of k^{Σ}_{tot} for $N(CF_2CF_3)_3$ and $P(C_6F_5)_3$ may also reflect, in part, electronic-to-vibrational energy transfer to impurities associated with the fluorinated compounds that contain C−H bonds. Indeed, the supplier of both $N(CF_2CF_3)_3$ and $P(C_6F_5)_3$ specifies 96% and 97% purities, respectively. We assume that the remaining material contains compounds with one or more C−H bonds.

Conclusions

Our data indicate that the removal of $O_2(b^1\Sigma_g^+)$ from a solution-phase system by chemical reaction does not compete effectively with both quencher- and solvent-induced physical deactivation channels that produce $O_2(a^1\Delta_g)$. Thus, one must regard with skepticism published reports in which $O_2(b^1\Sigma_g^+)$ is claimed to be a reactive intermediate in solution-phase photooxygenations.

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE-9402145).

JA953433O