

Solvent Effects on Singlet Oxygen Yield from n,π^* and π,π^* Triplet Carbonyl Compounds

Alexander P. Darmany and Christopher S. Foote*

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024-1569

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Quenching of benzophenone (n,π^*) and duroquinone (π,π^*) triplet states by molecular oxygen was studied by time-resolved $O_2(^1\Delta_g)$ phosphorescence and nanosecond laser photolysis in 12 solvents. With the exception of benzophenone in acetonitrile and CCl_4 and of duroquinone in acetonitrile, the quenching rate constant (k_q^T) is independent of the polarity or viscosity of solvents and lies in the range $(2.1\text{--}2.55) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $(1.3\text{--}1.7) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for benzophenone and duroquinone, respectively. The k_q^T values are practically constant when the viscosity of solution increases from 0.3 to 4.2 cP, although the diffusion-controlled rate constant (k_d) decreases by more than a factor of 2. For these carbonyls, the usual observation that $k_q^T \sim 1/\eta k_d$ for quenching by the energy-transfer mechanism does not hold. The efficiency of $O_2(^1\Delta_g)$ formation (S_Δ) is also independent of viscosity or polarity of the solvent and lies in the range 0.31–0.35 for benzophenone and 0.79–0.95 for duroquinone but increases in alcohols, to 0.43–0.60 and 0.87–1.02. Apparently, specific solvation of triplet carbonyls by alcohols results in a decrease in the deactivation rate constant of the triplet encounter complex to the ground state [$^3(S^{\cdots}O_2) \rightarrow (S_0|^3O_2) \rightarrow S_0 + ^3O_2$] and an increase in the contribution of the energy-transfer reaction.

Introduction

It is now well-known that, for ketones with n,π^* triplets, the probability of $O_2(^1\Delta_g)$ generation on collisional quenching of the triplet (S_Δ) in benzene lies in the range 0.3–0.4, while for ketones with π,π^* triplets, $S_\Delta \sim 0.8\text{--}1.0$.^{1–11} The physical reasons for this effect probably have to do with the fact that excitation is localized on the carbonyl group for ketones with n,π^* triplets. In ref 11, it was shown that a heavy atom in sensitizers with π,π^* triplets slightly decreases S_Δ values, whereas in bromo-substituted acetophenones, a sharp decrease in S_Δ values was observed. This effect was explained by taking into account the intersystem crossing between singlet and triplet states in an encounter complex and assuming that, for ketones with n,π^* triplets, the deactivation rate constant of the encounter complex of the triplet carbonyl with oxygen $^3(S^{\cdots}O_2)^*$ to the ground state is much faster than that for reverse intersystem crossing in the complex ($^3(S^{\cdots}O_2)^* \rightarrow ^1(S^{\cdots}O_2)^*$). In this paper, we study the effect of solvent on S_Δ values of ketones with n,π^* and π,π^* triplet states in order to understand the mechanism and main rules governing $O_2(^1\Delta_g)$ generation. The efficiency of $O_2(^1\Delta_g)$ production by benzophenone and duroquinone is determined in 12 different solvents.

Experimental Section

The absorption spectra and decay kinetics of the carbonyl triplet states were investigated by using nanosecond laser transient absorption spectroscopy with 10-ns resolution, as described elsewhere.^{10,11} The solutions were excited by a 355-nm pulse, ≤ 5 mJ, 7 ns from a Quanta Ray Nd-YAG laser; in a few experiments we used a 532-nm pulse, 3 mJ. The yield and decay kinetics of $O_2(^1\Delta_g)$ luminescence at 1.27 μm were recorded by means of an IR laser fluorimeter, described elsewhere.¹² When possible, the decay kinetics were calculated from the average of 30–50 pulses. The yield of $O_2(^1\Delta_g)$ luminescence and the values of T–T sensitizer absorption were linearly proportional to the energy of the laser pulse. The optical densities of solutions were ~ 0.3 at 355 nm, corresponding to duroquinone and benzophenone concentration $\sim 1 \times 10^{-3}$ and $\sim 3 \times 10^{-3}$ M, respectively. All experiments in alcohols were carried out with fresh solutions of benzophenone, which were changed after 1–2 flashes.

Absorption spectra of solutions were recorded on a Beckman Model 25 spectrophotometer. The solutions were degassed by Ar bubbling for 20 min.

The values of singlet oxygen quantum yield ($\Phi_{\Delta}^{\text{obs}}$) and of carbonyl triplet decay rate constant (k^T) were measured in solutions that were air-saturated or bubbled with O_2 or O_2/N_2 (39.8% and 59.6% O_2) mixtures for 20 min.

The determination of $\Phi_{\Delta}^{\text{obs}}$ values was carried out as in ref 10, by comparing the $O_2(^1\Delta_g)$ luminescence intensity extrapolated to the center of the laser pulse for carbonyl and standard. The standard was benzophenone in air-saturated benzene, with the averaged value $\Phi_{\Delta}^{\text{st}} = 0.3$.^{3,6,8} Expression 1 from ref 13 was used to calculate $\Phi_{\Delta}^{\text{obs}}$:

$$\Phi_{\Delta}^{\text{obs}} = \Phi_{\Delta}^{\text{st}} \frac{I_0 (1 - 10^{-OD_{355}^{\text{st}}}) n^2 k_r^{\text{st}}}{I_0^{\text{st}} (1 - 10^{-OD_{355}}) n^2 k_r} \quad (1)$$

where n is the refractive index, k_r is the $O_2(^1\Delta_g)$ radiative rate constant in the solvent investigated, and k_r^{st} is the radiative rate constant in benzene. Equation 1 is correct only for exponential decay of luminescence. In CCl_4 , decay of $O_2(^1\Delta_g)$ luminescence was nonexponential; however, when the laser pulse energy was reduced to ≤ 1 mJ, the decay became exponential with lifetime ~ 4 ms for both sensitizers.

The quantum yield of $O_2(^1\Delta_g)$ production at $[O_2] \rightarrow \infty$ (Φ_{Δ}^{∞}) was obtained from the dependence of $\Phi_{\Delta}^{\text{obs}}$ on the concentration of molecular oxygen.^{10,11} Plots of $1/\Phi_{\Delta}^{\text{obs}}$ against $1/[O_2]$ were linear; the intercept on the ordinate is $1/\Phi_{\Delta}^{\infty}$.^{10,11} Since for benzophenone¹⁴ and duroquinone¹⁵ the quantum yield of triplet is 1.0, $\Phi_{\Delta}^{\infty} = S_\Delta$.

The quenching rate constant of the duroquinone triplet state by oxygen was estimated from eq 2, where k_o^T and k_i^T are the

$$k_q^T = \frac{k_i^T - k_o^T}{[O_2]} \quad (2)$$

decay rate constants of triplet state in degassed and air-saturated solution, respectively, estimated at the T–T absorption maximum at 490 nm.¹⁶

The absorption spectra of triplet and ketyl radical overlap strongly for benzophenone, and the decay rate constant of triplet state in degassed solution was estimated at 525 nm from eq 3,^{17,18} where ΔD_0 is the change in optical density of solution immediately after the laser pulse caused only by the absorption of triplet and ΔD_{∞} is the change in optical density of the solution after the laser

TABLE I: Relative Rate Constants of $O_2(^1\Delta_g)$ Phosphorescence in Various Solvents

solvent	Sens st /Sens ^a	$\Phi_{\Delta}^{\text{air(st)}}$ / $\Phi_{\Delta}^{\text{air}}$	k_r^{st}/k_r	$\langle k_r^{\text{st}}/k_r \rangle^b$
acetone	An/An	1.0 ^c	2.70	2.65
	TPP/TPP	1.0 ^c	2.60	
<i>p</i> -dioxane	An/An	1.0 ^c	2.48	2.4
	TPP/TPP	1.0 ^c	2.36	
ethanol	An/An	0.68 ^d /0.65 ^e	3.66	3.9
	TPP/RB ^h	0.62 ^f /0.78 ^g	4.08	
1-butanol	An/An	1.0 ^c	3.56	3.7
	TPP/RB ^h	0.62 ^f /0.78 ^g	3.89	
2-butanol	An/An	1.0 ^c	3.51	3.6
	TPP/RB ^h	0.62 ^f /0.78 ^h	3.70	
2-propanol	An/An	1.0 ^c	3.86	4.0
	TPP/RB ^h	0.62 ^f /0.76 ⁱ	4.20	

^a Sen = sensitizer; st = standard. ^b Averaged value, error $\pm 20\%$.

^c Assuming $\Phi_{\Delta}^{\text{air}}(\text{benzene}) = \Phi_{\Delta}^{\text{air}}(\text{investigated solvent})$. ^d Reference 7 (by TRTL method). ^e Reference 13 (estimated relative to eosin in ethanol with $\Phi_{\Delta}^{\text{air}} = 0.42^{21}$). ^f Reference 19. ^g Averaged value for RB in CH_3OH and 2-propanol from ref 19. ^h $\lambda_{\text{ex}} = 532 \text{ nm}$.

$$k_o^T = \ln \frac{\Delta D_o - \Delta D_{\infty}}{\Delta D - \Delta D_{\infty}} \quad (3)$$

pulse after a delay time sufficient that the T-T absorption is insignificant and the absorption is caused only by the ketyl radical. The k_q^T values with different oxygen concentrations were estimated at 600 nm where the ketyl radical absorption is insignificant.^{17,18} The quenching rate constants of the benzophenone triplet by oxygen were estimated from the linear dependence of k^T values on the concentration of oxygen by using eq 4:

$$k^T = k_o^T + k_q^T[\text{O}_2] \quad (4)$$

Benzophenone, duroquinone, anthracene (An), tetraphenylporphine (TPP), and rose bengal (RB) were used as received from Aldrich. All solvents were from Fisher and purified by distillation. The experiments were carried out at $22 \pm 1^\circ \text{C}$.

Results

Since the k_r^{rel} values were not known for most of the solvents, we measured these values relative to benzene. The k_r^{st}/k_r value can be estimated from eq 1 to compare the intensity of $O_2(^1\Delta_g)$ luminescence for two sensitizers with known quantum yields of $O_2(^1\Delta_g)$ production. We chose An, TPP, and RB in air-saturated solutions as standards. According to Schmidt and Afshari, $\Phi_{\Delta}^{\text{air}}$ for TPP depends only slightly on solvent, except for Freon 113 and 1-methylnaphthalene, and was 0.64 ± 0.13 in 19 solvents studied.¹⁹ We therefore assumed that $\Phi_{\Delta}^{\text{air}}$ for TPP are identical in benzene, acetone, and dioxane within $\pm 20\%$. Anthracene was

chosen as a standard because its triplet quantum yield is independent of solvent and temperature, except in CCl_4 .²⁰ According to ref 13, the contribution of $O_2(^1\Delta_g)$ formation from the quenching of anthracene fluorescence by oxygen in air-saturated solvents is negligible, because the efficiency of this route is low compared to that of the triplet route. According to ref 13, when the air pressure is 0.2 atm (only triplet quenching) $\Phi_{\Delta} = 0.72$, whereas in air-saturated toluene, $\Phi_{\Delta} = 0.83$. This means that within $\pm 20\%$ we can neglect the contribution of $^1\text{O}_2$ generation from quenching of the anthracene fluorescence by molecular oxygen. Therefore we assumed that $\Phi_{\Delta}^{\text{air}}$ for anthracene is constant in all solvents investigated within $\pm 20\%$. The measured k_r^{st}/k_r values are practically identical within the experimental accuracy, no matter whether the $\Phi_{\Delta}^{\text{air}}$ values for the chosen sensitizers were taken from the literature or we used anthracene as a sensitizer with the above assumption. The results are presented in Table I.

The S_{Δ} values for carbonyls in various solvents (Table II) were measured by using eq 1 and k_r^{st}/k_r values from Table I. We used also the value $k_r^{\text{st}}/k_r = 1.61$ in CCl_4 ,¹⁹ the average of 2.7¹⁹ and 3.2¹³ in acetonitrile, and the average of 0.97¹³ and 1.1²² in toluene; the values 5.6 and 3.67 respectively from ref 23 were used in methanol and 1-propanol. Typical plots of $1/\Phi_{\Delta}^{\text{obs}}$ vs $1/[\text{O}_2]$ for benzophenone are presented in Figures 1 and 2. Duroquinone has a long-lived triplet state (Table II) and the $\Phi_{\Delta}^{\text{obs}}$ values are therefore practically independent of oxygen concentration.

A typical plot of the dependence of the decay rate constant of benzophenone triplet on the oxygen concentration in solution is presented in Figure 3. The values in degassed solution (k_o^T) (Table II) are in agreement with literature values.^{16,17,28}

The lifetimes of singlet oxygen (τ_{Δ}) were in agreement with literature data²⁹ for duroquinone in all investigated solvents and for benzophenone in solvents where hydrogen abstraction is ineffective. However, in toluene, dioxane, and alcohols, the τ_{Δ} values were significantly lower than published data,²⁹ for example, at a laser pulse energy of 2 mJ in air-saturated toluene, dioxane, ethanol, methanol, and 2-butanol, $\tau_{\Delta} = 17.4, 11, 7.8, 6.8$, and $10.4 \mu\text{s}$, respectively. Increased oxygen concentration causes an increase in τ_{Δ} values: in oxygen-saturated toluene, dioxane, ethanol, methanol, and 2-butanol, $\tau_{\Delta} = 24, 13, 9, 8.3$, and $12.6 \mu\text{s}$, while with TPP and RB as sensitizers, values of $\tau_{\Delta} = 30, 26, 15, 11$, and $20 \mu\text{s}$, respectively were obtained.

Gorman et al. have suggested that benzophenone in the ground state is an effective quencher of singlet oxygen.³⁰ We studied the quenching of $O_2(^1\Delta_g)$ luminescence by benzophenone using a 532-nm pulse and TPP and RB as sensitizers and established that the quenching rate constant of singlet oxygen by benzophenone in benzene, acetone, 1-propanol, and ethanol is less than 2×10^3

TABLE II: Photophysical Properties of Benzophenone and Duroquinone in Various Solvents

solvent	η, cP^a	$[\text{O}_2]^{\text{air}}, 10^3 \text{ M}^b$	$k_d \times 10^{-10}, \text{M}^{-1} \text{s}^{-1}$	sensitizer					
				benzophenone			duroquinone		
				$k_o^T \times 10^{-5}, \text{s}^{-1}$	$k_q^T \times 10^{-9}, \text{M}^{-1} \text{s}^{-1}$	S_{Δ}^f	$k_o^T \times 10^{-5}, \text{s}^{-1}$	$k_q^T \times 10^{-9}, \text{M}^{-1} \text{s}^{-1}$	S_{Δ}^f
acetone	0.304	2.4	3.9	5.9	2.1	0.31	1.3	1.6	0.80
acetonitrile	0.345	1.68	3.7 ^g	1.0	3.1	0.35	0.9	2.4	0.80
methanol	0.551	2.12	3.1	39	2.3	0.51	2.1	1.7	0.87
toluene	0.59	1.81	3.1	36	2.2	0.33	1.2	1.5	0.80
benzene	0.649	1.80 ^h	3.0	4.0 ⁱ	2.4 ^j	0.35 ^j	1.2	1.4	0.84
CCl_4	0.969	2.59	2.6 ^g	2.0	1.45	0.36	0.7	1.4	0.95
ethanol	1.078	2.07	2.5	110	2.55	0.43	2.1	1.7	0.92
<i>p</i> -dioxane	1.439	1.51	2.1	100	2.2	0.35	1.2	1.3	0.79
1-propanol	2.256	1.86	2.0 ^g	120	2.3	0.48	1.7	1.6	0.96
2-propanol	2.859	2.12	2.3	260		0.55	2.0	1.6	1.01
1-butanol	2.948	1.85	1.9 ^g	160	2.25	0.60	1.8	1.4	1.02
2-butanol	4.21	1.85 ^k	1.8	91	2.3	0.57	1.6	1.6	1.02

^a Reference 24. ^b References 24–26. ^c Reference 27 (experimental data are averaged for anthracene, perylene, and 9,10-diphenylanthracene). ^d Error, $\pm 20\%$. ^e Error $\pm 15\%$. ^f Error depends mainly on the accuracy of k_r^{rel} definition and is $\pm 20\%$. ^g Evaluated from dependence of k_d on η for anthracene from ref 27. ^h Averaged value from the data on ref 25. ⁱ Reference 16. ^j Reference 7. ^k Assuming that solubility of oxygen in 1- and 2-butanol is identical.

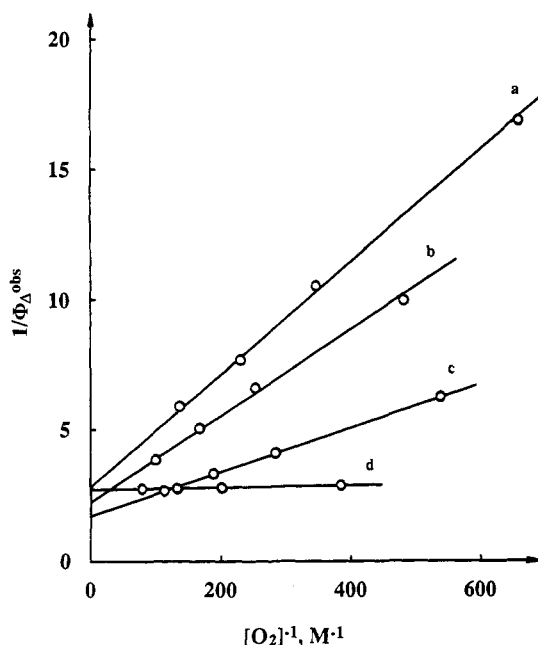


Figure 1. Dependence of $O_2(^1\Delta_g)$ quantum yield from benzophenone on oxygen concentration in (a) *p*-dioxane, (b) ethanol, (c) 2-butanol, and (d) CCl_4 .

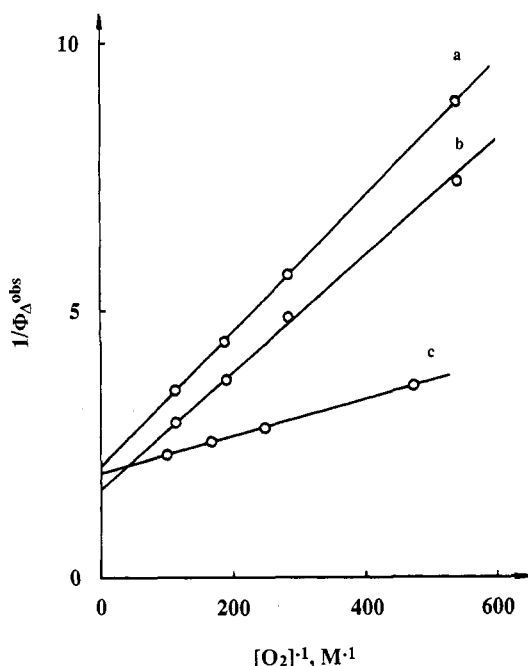
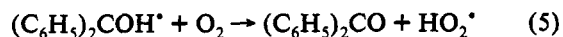


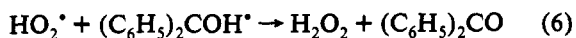
Figure 2. Dependence of $O_2(^1\Delta_g)$ quantum yield from benzophenone on oxygen concentration in (a) 1-propanol, (b) 1-butanol, and (c) methanol.

$M^{-1} s^{-1}$ in all cases. Thus, quenching of singlet oxygen by benzophenone is negligible.

The ketyl radical of benzophenone reacts rapidly with oxygen to give HO_2^{\cdot} .³¹



in the subsequent disproportionation reaction, hydrogen peroxide is formed



Reaction 5 should be more effective for $O_2(^1\Delta_g)$ than for triplet molecular oxygen because the spin-statistical factor is 1, whereas

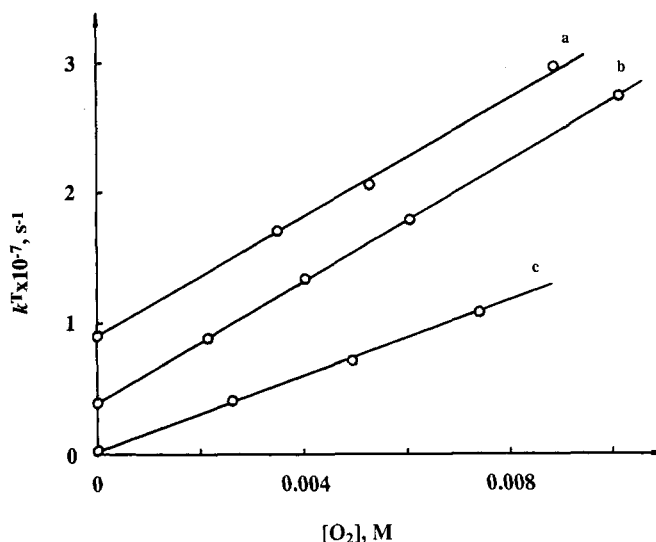


Figure 3. Dependence of benzophenone triplet decay rate constant on oxygen concentration in (a) 2-butanol, (b) methanol, and (c) CCl_4 .

for triplet oxygen it is $1/3$. However, the low τ_{Δ} values in toluene, dioxane, and alcohols cannot be explained by the singlet oxygen interaction with ketyl radical alone, because, for example, the lifetime of ketyl radical in air-saturated solutions is <400 ns. It is possible that the decrease in τ_{Δ} is caused by quenching of singlet oxygen; superoxide ion ($O_2^{\cdot-}$) and probably HO_2^{\cdot} as well are very effective quenchers for 1O_2 .³² This question requires a separate investigation; in any case, low values of $O_2(^1\Delta_g)$ lifetimes in toluene, dioxane, and alcohols do not influence measurement of Φ_{Δ}^{obs} for benzophenone, since eq 1 for dynamic quenching does not contain τ_{Δ} .

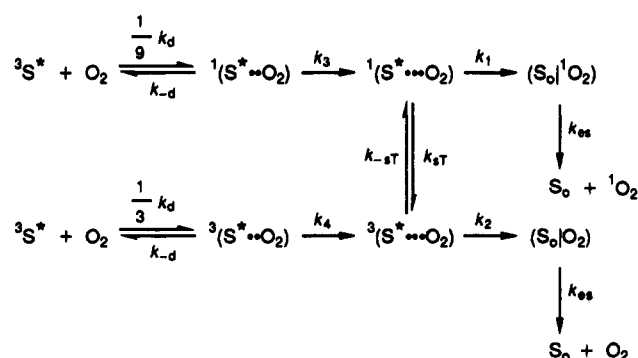
Discussion

The data in Table II show that the quenching rate constant k_q^T for carbonyls is independent of the polarity and viscosity of the solvent, except for benzophenone in acetonitrile and CCl_4 and duroquinone in acetonitrile. The k_q^T values are practically constant when viscosity increases from 0.3 to 4.2 cP even though the diffusion rate constant (k_d) decreases by more than a factor of 2. Since the pioneering work of Porter,³³ it has been believed that quenching of triplet states of oxygen occurs by energy transfer when $k_q^T \sim 1/9k_d$ and this implies that S_{Δ} should be ~ 1 . However, the data in Table II show that this rule is not followed for carbonyls; it may be correct only for electron-donating aromatic in nonpolar solvents of low viscosity³³ such as hexane and benzene.

After this work was submitted, a paper by Wilkinson *et al.* appeared,³⁴ investigating the influence of charge-transfer interactions between substituted naphthalenes and molecular oxygen in benzene on the values of S_{Δ} and k_q^T . The authors established that even for hydrocarbons that are very weak electron donors where CT interactions are energetically unfavorable, the k_q^T values are not equal to $1/9k_d$, and the S_{Δ} values are less than unity. It is interesting to note that Porter's rule also fails for fullerenes: for C_{60} and C_{70} in benzene, the efficiency of $O_2(^1\Delta_g)$ formation is near unity, $S_{\Delta} = 0.96$ ($\lambda_{ex} = 532$ nm)³⁵ and 0.81–0.89,³⁶ whereas the k_q^T values are considerably less than $1/9k_d$: $k_q^T = 1.9 \times 10^9 M^{-1} s^{-1}$ ³⁵ and $7.9 \times 10^8 M^{-1} s^{-1}$,³⁶ respectively. Thus the simplified scheme for triplet-state quenching by molecular oxygen suggested in ref 33 does not describe the experimental data quantitatively.

In a previous paper, we suggested that the intersystem crossing between singlet and triplet states of an encounter complex in quenching of triplet sensitizers by molecular oxygen needs to be taken into account.¹¹

SCHEME I



According to this scheme¹¹

$$k_q^T = \frac{1}{9}k_d - \frac{1/9k_d k_{-d}}{k_3 + k_{-d}} - \frac{1/3k_d k_{-d}}{k_4 + k_{-d}} \quad (7)$$

and

$$S_\Delta = \frac{k_1}{[k_1(k_2 + k_{-sT}) + k_{sT}k_2]} \times \left[\frac{(k_2 + k_{-sT})k_3(k_4 + k_{-d}) + 3k_{-sT}k_4(k_3 + k_{-d})}{k_3(k_4 + k_{-d}) + 3k_4(k_3 + k_{-d})} \right] \quad (8)$$

For the carbonyls in the present study, only the case where $k_3, k_4 < k_{-d}$ applies,¹¹ because, in the first approximation,

$$k_q^T = \frac{1}{9} \frac{k_d}{k_{-d}} (k_3 + k_4) < \frac{1}{9}k_d \quad (9)$$

and since k_d and k_{-d} are both $\sim 1/\eta^{33}$, k_q^T does not depend on viscosity.

The S_Δ values for carbonyls increase in alcohols (Table II). This regularity cannot be explained by the high viscosity of these solvents because this effect is not observed in dioxane, even though it has a viscosity between those of ethanol and 2-propanol. According to Scheme I and eq 8, in any case a decrease in k_2 (the rate constant for radiationless deactivation of the triplet encounter complex to the ground state) should cause an increase in S_Δ . It is likely that the only explanation for the anomalous effect of alcohols is that a specific solvation of triplet carbonyls by alcohols, probable due to hydrogen bonding $[(C_6H_5)_2C=O \cdots (H \cdots O-R)_n]$ results in a decrease in k_2 .

The low probability of $O_2({}^1\Delta_g)$ generation by carbonyls with n, π^* triplets can be explained assuming $k_2 \gg k_{-sT}$.¹¹ If this is true, and if $k_2/k_{-sT} \gg 3k_4(k_3 + k_{-d})/k_3(k_4 + k_{-d})$, then eq 8 becomes

$$S_\Delta = \left(1 + \frac{k_{sT}}{k_1}\right)^{-1} \left[1 + \frac{3k_4(k_3 + k_{-d})}{k_3(k_4 + k_{-d})}\right]^{-1} \quad (10)$$

Probably this case applies for benzophenone in nonalcoholic solvents. In alcohols, k_2 decreases and should be only $> k_{-sT}$, which, according to eq 8, would result in an increase in S_Δ .

For duroquinone, with a π, π^* triplet state, the case $k_2 < k_{-sT}$ is probably realized in nonalcoholic solvents. In alcohols, k_2 decreases and should become $\ll k_{-sT}$. From eq 8 we obtain¹¹

$$S_\Delta = \left[1 + \left(\frac{k_2}{k_{-sT}}\right)\left(\frac{k_{sT}}{k_1}\right)\right]^{-1} \quad (11)$$

and $S_\Delta \rightarrow 1$ when $(k_2/k_{-sT})(k_{sT}/k_1) \ll 1$.

Conclusion

The quenching rate constants of the carbonyl triplet states by oxygen do not depend on solvent, except for benzophenone in acetonitrile and CCl_4 and duroquinone in acetonitrile. For carbonyls, the usual assumption that $k_q^T \sim 1/9k_d$ for estimating quenching by energy-transfer mechanism is not correct. The efficiency of $O_2({}^1\Delta_g)$ generation does not depend on solvent polarity or viscosity and increases in alcohols. Specific solvation of the triplet carbonyls by alcohols results in a decrease of the deactivation rate constant of the triplet encounter complex to the ground state and an increase in the contribution of energy transfer to the quenching.

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