Singlet Oxygen Production from Excited Azoalkanes

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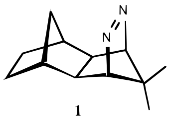
The mechanisms for the photosensitized production of singlet oxygen ($^1\Delta_g$) from excited organic molecules are of great interest in organic, physical, and biological chemistry. During the past few years the research in this field has reached a new level of intensity and sophistication,[1−9] where the relationships between the singlet oxygen efficiency (S_Δ) and sensitizer properties have been examined, namely, their electronic configuration,[2,3] oxidation potential,[4,5] spin multiplicity,[6,7] and energy.[3,8] It is generally accepted that n,π* triplet states show low singlet oxygen efficiencies (S_Δ *ca.* 0.3−0.4) whereas most π,π*-excited triplets are significantly more efficient (S_Δ *ca.* 0.8−1.0).[1−9] This dichotomy has been suggested as an experimental criterion for the differentiation between an n,π* or π,π* configuration.[2b,5,9b]

We felt that the examination of n,π* chromophores other than ketones was desirable to demonstrate the limitations of the proposed generalization and have examined the oxygen quenching of azoalkanes. We now find a singlet oxygen efficiency approaching unity for the n,π* triplet state of azoalkane **1**, which demonstrates that low values for S_Δ are not related to the n,π* configuration of the sensitizer but rather to its specific chemical constitution. A high S_Δ value of 0.7 ± 0.1 has also been estimated for azoalkane **2**.



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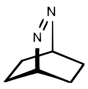

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In contrast to aromatic ketones,[2b,5,9b] there is no doubt that the lowest excited triplet state of azoalkanes possesses an n,π* configuration; this is corroborated by their phosphorescence properties, the absence of heavy-atom effects, and their propensity to undergo hydrogen abstraction reactions.[10] For 2,3-diazabicyclo[2.2.1]hept-2-ene, the parent structure of **1**, the π,π* triplet state has been proposed to lie 42 kcal/mol above the n,π* triplet.[11] The photophysical properties of azoalkanes **1** and **2** are shown in Table 1. Azoalkane **1** is a member of the rare class which exhibits T−T absorption (λ_{max} = 290/450 nm) and a long triplet lifetime (τ_T *ca.* 600 ns).[10] The singlet-excited azoalkane **2** (τ_S *ca.* 450 ns in benzene) fluoresces strongly, but does not undergo efficient intersystem crossing (ISC) like **1**.[12]

Table 1. Photophysical Properties and Oxygen Quenching Parameters for Azoalkanes **1** and **2** in CCl_4 and Benzene

	azoalkane **1**		azoalkane **2**
	CCl_4	benzene	benzene
E_S/kcal mol^{-1} [a]	79		76.1
E_T/kcal mol^{-1}	63[b]		53−56.5[c]
ΔE_{ST}/kcal mol^{-1}	16		20−23
τ_S/ns[d]	4.1	2.8	450[e]
τ_T/ns[d]	620	580	25[f]
$^1k_q/10^9$ M^{-1} s^{-1} [d,g]	2.1	8.1	8.7[h]
$^3k_q/10^9$ M^{-1} s^{-1} [d,g]	0.30	0.31	5−6[i]
Φ_T[d,j]	0.77	0.59	0.0[c]
Φ_T^{ox} [g,k,l]	0.79	0.66	0.97
F_S[g,l,m]	0.10	0.18	0.97
F_T[g,l,m]	0.69	0.63	0.55
Φ_Δ[g,l]	0.51	0.40	0.41
S_Δ	0.94	0.96	0.7

[a] From 0−0 fluorescence band. [b] From 0−0 phosphorescence band (ref 10c). [c] Reference 12. [d] Obtained by time-resolved transient absorption or fluorescence spectroscopy (355 nm excitation). [e] Reference 12c: 434 ns. [f] Determined in cyclohexane by time-resolved photoacoustic calorimetry; R. A. Caldwell, personal communication; see also ref 12d. [g] Oxygen concentrations of saturated benzene and CCl_4 taken as 9.3 and 12.1 mM. [h] Value in CCl_4: 4.5 × 10^9 M^{-1} s^{-1}. [i] Assuming the same triplet lifetime in benzene and cyclohexane. [j] Determined by the energy transfer method using triplet 1-methylnaphthalene (λ_{max} = 416 nm; E_T = 61 kcal/mol) as indicator for triplet formation and benzophenone as reference (Φ_T = 1.00); the selected quencher concentration (70 mM) ensured total quenching (>99%) of **1** and benzophenone (k_q *ca.* 10^{10} and 10^9 M^{-1} s^{-1}). [k] Reference 13. [l] Values refer to oxygen-saturated solutions. [m] Fraction of quenched excited states, *cf.* eq 7.

The possible interactions of molecular triplet oxygen with sensitizers are generally discussed in terms of processes 1−5. For azoalkane **1** the energy transfer process 1 does not have to be considered due to the singlet−triplet energy gap, ΔE_{ST}, which is significantly smaller than for oxygen (16 *versus* 22.5 kcal mol^{-1}); all singlet oxygen must arise from ^{3}**1** through process 4. Singlet oxygen formation from azoalkane **2** may originate from both processes 1 and 4, but whether process 1 is at all feasible cannot be decided since the energy gap is not accurately known (ΔE_{ST} = 20−23 kcal/mol).[12]

$$^1\mathrm{Sens}^* + O_2 \rightarrow {}^3\mathrm{Sens}^* + O_2(^1\Delta_g) \tag{1}$$

$$^1\mathrm{Sens}^* + O_2 \rightarrow {}^3\mathrm{Sens} + O_2 \tag{2}$$

$$^1\mathrm{Sens}^* + O_2 \rightarrow \mathrm{Sens} + O_2 \tag{3}$$

$$^3\mathrm{Sens}^* + O_2 \rightarrow \mathrm{Sens} + O_2(^1\Delta_g) \tag{4}$$

$$^3\mathrm{Sens}^* + O_2 \rightarrow \mathrm{Sens} + O_2 \tag{5}$$

Singlet oxygen quantum yields (Φ_Δ) were determined by detection of its phosphorescence at 1270 nm upon laser excitation of oxygen-saturated solutions, relative to phenazine in benzene ($\phi_\delta^{\mathrm{ref}} = 0.83$)[3] and phenalenone in CCl_4 ($\phi_\delta^{\mathrm{ref}} = 0.97$).[9] For azoalkane **1**, three independent measurements in benzene afforded $\Phi_\Delta = 0.40 \pm 0.03$ and two determinations in CCl_4 gave $\Phi_\Delta = 0.51 \pm 0.03$. The actual singlet oxygen efficiencies for **1** (S_Δ) are calculated as $S_\Delta = \Phi_\Delta/(f_t\phi_t^{ox})$, where F_T and ϕ_t^{ox}

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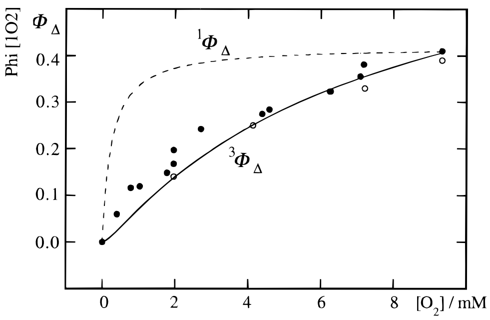

Figure 1. Singlet oxygen quantum yields for the direct (●) and triplet-sensitized (○) irradiation of azoalkane **2** in benzene as a function of oxygen concentration. The fitting with the experimental data ($r = 0.98$) assumes exclusive singlet oxygen production from the triplet state with $^1k_q\tau_S = 4 \times 10^3$ M^{-1}, $^3k_q\tau_T = 150$ M^{-1}, and $S_\Delta = 0.72$ (eq 7). The dashed line refers to the expected behavior for exclusive singlet oxygen production from the singlet-excited state with $^1k_q\tau_S = 4 \times 10^3$ M^{-1} and $\alpha^S = 0.42$ (eq 6).

are the fraction of quenched triplets and the triplet quantum yield in the presence of oxygen.[3,5] The value S_Δ is the fraction of singlet oxygen molecules formed per triplets quenched. Since the values for F_T and ϕ_t^{ox} can be experimentally determined (Table 1),[13] the singlet oxygen efficiency S_Δ for azoalkane **1** is found to be *ca.* 0.95 for both solvents, which constitutes, within a rather large error of at least 15%, a singlet oxygen efficiency close to unity! The larger error is characteristic for sensitizers with modest ISC and inefficient oxygen quenching, since in addition to the experimental error and the inaccuracy of the reference, ϕ_δ^{ref}, one needs to consider the individual errors in the quenching rate constant and triplet quantum yield. It is reassuring, however, that two quite different solvent/reference systems agree well, since all relevant values vary with solvent (Table 1) and have been independently determined.

The low singlet oxygen quantum yield from benzophenone ($\phi_\delta^{ref} = 0.35$)[3] serves as a well-established value for the low efficiencies of n,π* triplet states, since its S_Δ and Φ_Δ values coincide due to quantitative ISC and quenching.[1−8] The singlet oxygen quantum yield of **1** in oxygenated benzene was found to be *ca.* 15% higher than for benzophenone. Consequently, since the triplet yield of **1** is significantly less than unity and since oxygen can intercept only about two-thirds of the azoalkane **1** triplets due to the low quenching rate constant (Table 1), the n,π* triplet azoalkane **1** exhibits a much higher S_Δ value than assumed to be characteristic for this electronic configuration (0.3−0.4); indeed, it falls into the 0.9 ± 0.1 range applicable for most π,π* chromophores.

Azoalkane **2** is another interesting singlet oxygen sensitizer, and in oxygenated benzene $\Phi_\Delta = 0.41 \pm 0.03$ was determined relative to phenazine. Phenomenologically, this measurement constitutes the first example for singlet oxygen production from a *singlet-excited* n,π* state;[1,7b] mechanistically, as we will demonstrate in the following, all singlet oxygen is formed from the short-lived triplet state ^{3}**2** after oxygen-catalyzed ISC.[1,7b]

The relative contributions of processes 1 and 4, which may both contribute to singlet oxygen production from azoalkane **2**, can be determined by measuring Φ_Δ as a function of oxygen concentration (Figure 1). If only singlet quenching is responsible for singlet oxygen formation, the expected quantum yield ($^1\Phi_\Delta$) is given by eq 6. If only triplet quenching produces singlet oxygen, the expected quantum yield ($^3\Phi_\Delta$) should follow eq 7, which takes the efficiency of process 2 as 100% as confirmed by other measurements (see below). The terms are additive if both mechanisms apply ($\Phi_\Delta = {}^1\Phi_\Delta + {}^3\Phi_\Delta$). F_S and F_T are the fractions of quenched singlets and triplets, ^1k_q and ^3k_q are the oxygen quenching rate constant for the excited singlet and triplet states, and α^S is the efficiency for process 1.[7a]

$$\Phi_\Delta = \alpha^S F_S \quad \text{with} \quad F_S = {}^1k_q\tau_S[O_2]/(1 + {}^1k_q\tau_S[O_2]) \qquad (6)$$

$$\Phi_\Delta = S_\Delta F_S F_T \quad \text{with} \quad F_T = {}^3k_q\tau_T[O_2]/(1 + {}^3k_q\tau_T[O_2]) \qquad (7)$$

The upper function in Figure 1 was calculated from eq 6 by using the known Stern−Volmer quenching constant $^1k_q\tau_S$ (Table 1); scaling to achieve the experimental quantum yield in oxygen-saturated benzene required $\alpha^S = 0.42$, but clearly no correlation with the experimental data is found. Satisfactory fitting ($r = 0.98$) to the experimental data was obtained with eq 7 by employing $S_\Delta = 0.72 \pm 0.10$ and $^3k_q\tau_T = 150 \pm 40$ M^{-1}. This suggests that essentially all of the singlet oxygen is formed by quenching of the triplet state and that quenching of the singlet state contributes only through population of the triplet state (process 2). Process 1 does not have to be invoked to explain the experimental data.

When the triplet state ^{3}**2** was independently generated by triplet sensitization in oxygen-saturated benzene,[14] the observed singlet oxygen quantum yield was the same (0.39 *versus* benzophenone), within experimental error, as the value observed for direct excitation. Thus, since triplet energy transfer from benzophenone to azoalkanes is expected to be quantitative, singlet quenching by oxygen must occur with unit efficiency through oxygen-assisted ISC (process 2). Otherwise, if processes 1 and 3 were important, the singlet oxygen quantum yields upon triplet sensitization would have to be different from the values found upon direct irradiation. The triplet-sensitized quantum yield for singlet oxygen formation followed the same dependence on oxygen concentration as in the direct irradiation mode; the data from the triplet-sensitized photolysis are shown in Figure 1 for comparison. Fitting of the data points according to eq 7 (taking $F_S = 1$ to mimic the triplet-sensitized situation) provides $S_\Delta = 0.73 \pm 0.05$ and $^3k_q\tau_T = 122 \pm 15$ M^{-1} ($r = 0.99$; $n = 5$), in good agreement with the data obtained from the fitting of the quantum yields measured for the direct irradiation of **2** (see above).

The Stern−Volmer quenching constants ($^3k_q\tau_T$ *ca.* 120−150 M^{-1}) and the known triplet lifetime of **2** ($\tau_T = 25$ ns) provide a quenching rate constant of *ca.* 5−6 × 10^9 M^{-1} s^{-1}. It is not clear why the quenching rate constant for the triplet-excited azoalkane **1** is much lower than that for **2**. More importantly, the S_Δ value of *ca.* 0.7 for **2** corroborates that the n,π* triplet azoalkanes display high singlet oxygen efficiencies. Therefore, the criterion that low S_Δ values are characteristic for n,π* configurations cannot be generalized. Moreover, since several examples of π,π* states with relatively low singlet oxygen efficiencies are also known,[1,5b] a universal correlation between singlet oxygen efficiency and electronic configuration must be questioned.

The lower singlet oxygen efficiencies of n,π*-excited ketones have been attributed to their higher polarizability,[3] to larger Frank−Condon factors,[2a] to the localization of excitation,[2c] and to their relatively high triplet energies,[8] but even a cursory examination reveals that the higher S_Δ values of azoalkanes relative to ketones cannot be readily accounted for by any of the suggested explanations.

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[13] The triplet quantum yield under oxygen (ϕ_t^{ox}) is a composite of spontaneous (Φ_T, Table 1) and oxygen-enhanced ISC. The latter was found to occur with unit efficiency for **2** (see below) and was thus taken to be the same as the fraction of fluorescence quenching under oxygen (F_S, Table 1). This yields the relationship $\phi_t^{ox} = F_S + (1 - F_S)\Phi_T$, which provides ϕ_t^{ox} for **1** under oxygen as 0.10 + 0.90 × 0.77 = 0.79 in CCl_4 and 0.18 + 0.82 × 0.59 = 0.66 in benzene.

[14] This experiment was performed with a sample containing benzophenone (OD = 0.6 at 308 nm) and azoalkane **2** (70 mM) by measuring the singlet oxygen quantum yields upon 308 nm excitation relative to a sample containing only benzophenone. Under these conditions, 95% of the 308 nm light is absorbed by benzophenone, and more than 96% of the triplet energy is transferred from triplet benzophenone to **2** (k_q *ca.* 8 × 10^9 M^{-1} s^{-1}, this work), while direct quenching of triplet benzophenone by oxygen (k_q *ca.* 2 × 10^9 M^{-1} s^{-1})[3,8b] accounts for less than 4%, even under oxygen-saturated conditions (9.3 mM).