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Fraction of excited-state oxygen formed as b $^1\Sigma_g{}^+$ in solution-phase-photosensitized reactions
II. Effects of sensitizer substituent

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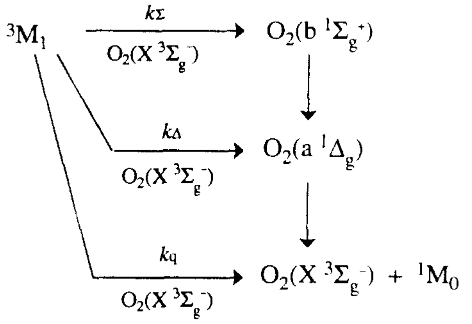
Abstract

The fraction F_Σ of excited-state oxygen formed as b $^1\Sigma_g{}^+$ was determined for a series of triplet-state photosensitizers in CCl_4 solutions. F_Σ was determined by monitoring the intensities of (a) O_2(b $^1\Sigma_g{}^+$) fluorescence at 1926 nm (O_2(b $^1\Sigma_g{}^+$) $\rightarrow$ O_2(a $^1\Delta_g$)) and (b) O_2(a $^1\Delta_g$) phosphorescence at 1270 nm (O_2(a $^1\Delta_g$) $\rightarrow$ O_2(X$^3\Sigma_g{}^-$)). Oxygen excited states were formed by energy transfer from substituted benzophenones and acetophenones. The data indicate that F_Σ depends on several variables including the orbital configuration of the lowest triplet state and the triplet-state energy. The available data indicate that the sensitizer–oxygen charge transfer (CT) state is not likely to influence F_Σ strongly by CT-mediated mixing of various sensitizer–oxygen states.

Keywords: Solution-phase singlet sigma oxygen; Energy transfer; Triplet state orbital configuration

1. Introduction

The deactivation of organic molecule triplet states ($^3M_1$) by ground-state molecular oxygen [O_2(X $^3\Sigma_g{}^-$)] in the solution phase is a well-studied process that has received a great deal of recent attention [1–9]. Of particular interest is the efficiency of energy transfer from $^3M_1$ to form an excited electronic state of molecular oxygen. Until recently, such studies have only been able to address the extent to which the lowest excited state of oxygen (O_2(a $^1\Delta_g$)) is formed. The latter, which lies 94.3 kJ mol^{-1} above O_2(X $^3\Sigma_g{}^-$), is routinely detected by its phosphorescence at about 1270 nm. It is now possible, however, also to spectroscopically detect the second excited state of oxygen (O_2(b $^1\Sigma_g{}^+$)) in the solution phase. This state is 62.7 kJ mol^{-1} more energetic than the O_2(a $^1\Delta_g$) state and can be monitored either by its fluorescence at about 1925 nm (O_2(b $^1\Sigma_g{}^+$) $\rightarrow$ O_2(a $^1\Delta_g$)) [10–12] or by its phosphorescence at about 762 nm (O_2(b $^1\Sigma_g{}^+$) $\rightarrow$ O_2(X $^3\Sigma_g{}^-$)) [13–15]. In the past year, O_2(b $^1\Sigma_g{}^+$) and O_2(a $^1\Delta_g$) have been spectroscopically monitored both by ourselves [12] as well as by Schmidt and coworkers [14,15] in attempts to understand better the partitioning of electronic energy when O_2(X $^3\Sigma_g{}^-$) induces $^3M_1$ deactivation.



Scheme 1.

It has now been amply documented for solution-phase systems that, when a photosensitizer whose triplet state energy exceeds about 160 kJ mol^{-1} 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 formed [10–15]. Furthermore, the formation of O_2(a $^1\Delta_g$) can proceed via the intermediacy of O_2(b $^1\Sigma_g{}^+$). Indeed, essentially all the O_2(b $^1\Sigma_g{}^+$) formed decays to yield O_2(a $^1\Delta_g$) [14]. These events are illustrated in Scheme 1.

In our previous study, we indicated that by measuring the intensities of O_2(b $^1\Sigma_g{}^+$) fluorescence and O_2(a $^1\Delta_g$) phosphorescence, it is possible to quantify the fraction F_Σ of excited-state oxygen formed as O_2(b $^1\Sigma_g{}^+$) [12]. A limitation of our technique is that, for a given sensitizer M,

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this fraction can only be obtained relative to that for a sensitizer arbitrarily chosen as a standard:

$$F_{\Sigma}^{\mathrm{rel}}=\frac{[k_{\Sigma}/(k_{\Sigma}+k_{\Delta})]_{\mathrm{M}}}{[k_{\Sigma}/(k_{\Sigma}+k_{\Delta})]_{\mathrm{std}}} \quad (1)$$

Nevertheless, for a series of sensitizers M selected to test a specific phenomenon, values of $F_{\Sigma}^{\mathrm{rel}}$ can provide useful insight into events that control the partitioning of electronic excitation energy. With additional information, values of $F_{\Sigma}^{\mathrm{rel}}$ can be normalized to yield absolute F_{Σ} values. Bodesheim et al. [15] have recently reported a technique by which values of k_{Σ}, k_{Δ} and k_q can be determined. Thus, for the sensitizer chosen as the standard, the quantity $F_{\Sigma}^{\mathrm{std}}=k_{\Sigma}/(k_{\Sigma}+k_{\Delta})$ can be independently obtained. On the basis of eq. (1), therefore, the product $F_{\Sigma}^{\mathrm{rel}}F_{\Sigma}^{\mathrm{std}}$ yields the absolute fraction F_{Σ} of excited-state oxygen formed as $O_2(b\ ^1\Sigma_g^+)$ for the sensitizer M.

In our earlier study on a series of aromatic ketone sensitizers, we determined that $F_{\Sigma}^{\mathrm{rel}}$ was much smaller for sensitizers that had a comparatively high triplet-state energy E_T. These data were not consistent with the theoretical predictions of Kearns and coworkers [16–18]. In an attempt to interpret our results, we focused on the rather large body of compelling evidence that indicates the importance of the sensitizer–oxygen charge transfer (CT) state in the production of $O_2(a\ ^1\Delta_g)$ [1–3,9,19–22]. The CT state is usually represented in terms of the organic molecule radical cation and the oxygen radical anion ($^{1,3}(M^{\cdot+}O_2^{\cdot-})$). For ketones, the CT state is expected to be higher in energy than other states of the M–O_2 complex and thus will participate only through state mixing. We suggested that, for sensitizers with a high E_T, CT-mediated indirect coupling between the $^{1,3}(^3M_1\cdots O_2(X\ ^3\Sigma_g^-))$ and both the $^1(^1M_0\cdots O_2(a\ ^1\Delta_g))$ and $^3(^1M_0\cdots O_2(X\ ^3\Sigma_g^-))$ states of the M–O_2 complex would decrease the relative yield of $O_2(b\ ^1\Sigma_g^+)$. In an independent experiment, Bodesheim et al. [15] determined values of k_{Σ} and k_{Δ} for some of the ketones examined in our study. Although our values of $F_{\Sigma}^{\mathrm{rel}}$ were consistent with those calculated from the data of Bodesheim et al., absolute values of k_{Δ} reported by Bodesheim et al. were not consistent with our interpretation. Rather, the results of Bodesheim et al. indicated that F_{Σ}, and more specifically k_{Δ} and k_{Σ}, depended principally on the energy differences (E_T-E_{Σ} and E_T-E_{Δ}) between the $^3M_1$ and the $O_2(b\ ^1\Sigma_g^+)$ and $O_2(a\ ^1\Delta_g)$ states respectively.

The data of Bodesheim et al. [15] were obtained using a series of different sensitizers (i.e. ketones, aromatic hydrocarbons and aromatic heterocycles) and as such are significant. Nevertheless, we felt that it would be important to reduce the number of variables in this photosystem and to focus on the effect that a simple change in sensitizer substituent would have on F_{Σ}. Thus we set out to determine F_{Σ} for a series of substituted benzophenones and acetophenones where changes in E_T are not pronounced. We were specifically interested in working with systems in which values of F_{Σ} might reflect the potentially subtle effects of the sensitizer orbital configuration and/or the energy of the sensitizer–oxygen CT state.

2. Experimental section

Details of the instrumentation and approach that we use to monitor $O_2(b\ ^1\Sigma_g^+)$ and $O_2(a\ ^1\Delta_g)$ have been published previously [3,11,12,23,24]. The experiments were performed in CCl_4. The sensitizers were irradiated with a pulsed laser at 309 nm (first anti-Stokes line obtained by stimulated Raman scattering of a 355 nm pump wavelength in H_2 gas). The laser energy at 309 nm was 0.4 mJ pulse^{-1}. The sensitizer concentrations used were in the range $(1–2)\times10^{-3}$ M. Solutions were saturated with air.

All chemicals were obtained from Aldrich except 4-cyanobenzophenone, which was obtained from Apin Chemicals Ltd. Acetophenone, 4-fluoroacetophenone and 4-methylacetophenone were purified by distillation. The remaining acetophenones were recrystallized twice from ethanol. The benzophenones were recrystallized twice from benzene–methanol. CCl_4 was used as received.

3. Results and discussion

Values of $F_{\Sigma}^{\mathrm{rel}}$ were obtained for a series of substituted benzophenones and acetophenones by the methods described in our earlier report [12]. Benzophenone and acetophenone respectively were chosen as the standards for these two series. The data, which are an average of at least four independent measurements, are listed in Tables 1 and 2. Errors in $F_{\Sigma}^{\mathrm{rel}}$ are ±10%. Values of k_{Δ} and k_{Σ} reported by Bodesheim et al. [15] for benzophenone and acetophenone were used to calculate $F_{\Sigma}^{\mathrm{std}}(\text{benzophenone})=0.28\pm0.06$ and $F_{\Sigma}^{\mathrm{std}}(\text{acetophenone})=0.25\pm0.10$. Multiplication of our experimentally obtained $F_{\Sigma}^{\mathrm{rel}}$ values by these respective $F_{\Sigma}^{\mathrm{std}}$ values yield the F_{Σ} values listed in Tables 1 and 2. Also listed in Tables 1 and 2 are the orbital configuration of $^3M_1$ and average values of the sensitizer ionization potential (IP) and E_T which have been compiled from various sources [25–37].

3.1. The benzophenones

For the eight compounds listed in Table 1, differences in E_T are very slight. Although the error bars for these E_T values probably exceed some of the differences shown, we have nevertheless listed these sensitizers in approximate order of decreasing E_T. As a consequence, a correlation between E_T and F_{Σ} becomes apparent; as E_T decreases, F_{Σ} increases. This observation is consistent with data presented in our previous report. The sensitizers that yielded the largest F_{Σ} values, the 4-trifluoromethyl and 4-cyano-substituted compounds, have triplet energies that are about 5 kJ mol^{-1} and 10 kJ mol^{-1} respectively smaller than the E_T of benzophenone.

Table 1
Effect of substituents on F_Σ, the triplet state energy and the ionization potential of benzophenones

Molecule	$E_T(n-\pi^*)$ (kJ mol^{-1})	IP (kJ mol^{-1})	F_Σ^{rel} [a]	F_Σ
Benzophenone	290	909	1.00	0.28 [b]
4-Methylbenzophenone	289	879	1.00	0.28
4-Bromobenzophenone	289	901	1.05	0.29
4-Chlorobenzophenone	287	926	1.05	0.29
3,4-Dimethylbenzophenone	287		1.10	0.31
4,4'-Dichlorobenzophenone	286		1.20	0.34
4-Trifluoromethylbenzophenone	285		1.50	0.42
4-Cyanobenzophenone	279	947	1.80	0.50

[a] Errors in F_Σ^{rel} are ±10%.

[b] Using the k_Δ and k_Σ data reported by Bodesheim et al. [15], the absolute value of F_Σ for benzophenone is calculated to be 0.28 ± 0.06. Our relative data were scaled accordingly. Propagation of errors yields an uncertainty of approximately ±30% in the absolute values of F_Σ reported.

Table 2
Effect of substituents on F_Σ, the triplet state energy and the ionization potential of acetophenones [a]

Molecule	$E_T(n-\pi^*)$ (kJ mol^{-1})	$E_T(\pi-\pi^*)$ (kJ mol^{-1})	IP (kJ mol^{-1})	F_Σ^{rel} [b]	F_Σ
Acetophenone	**310**	322	897	1.00	0.25 [c]
4-Fluoroacetophenone	[d]			1.10	0.28
4-Trifluoromethylacetophenone	**301**	312		1.15	0.29
4-Methylacetophenone	319	**304**	876	1.50	0.38
4-Bromoacetophenone	315	**302**	868	1.80	0.45
4-Methoxyacetophenone	326	**299**	811	2.20	0.55
4-Cyanoacetophenone		**290**	960	2.60	0.65
4-Acetylacetophenone		**281**		3.20	0.80

[a] In the acetophenones, where the energy difference between the n–π^* and π–π^* states is comparatively small, the lowest energy state is listed in bold type.

[b] Errors in F_Σ^{rel} are ±10%.

[c] Using the k_Δ and k_Σ data reported by Bodesheim et al. [15], the absolute value of F_Σ for acetophenone is calculated to be 0.25 ± 0.10. Our relative data were scaled accordingly. Propagation of errors yields an uncertainty of approximately ±50% in the absolute values of F_Σ reported.

[d] We were unable to find a value of E_T for this compound. However, data for other aromatic ketones indicate that the substitution of fluorine for hydrogen does not change the energy and orbital configuration of the triplet state [27].

Although the differences in E_T for the substituted benzophenones are slight, the data shown in Table 1 may nevertheless reflect the phenomenon observed by Bodesheim et al. [15]; as E_T, or rather $E_T - E_\Sigma$, becomes smaller, k_Σ increases. This increase in k_Σ may, in turn, be reflected as an increase in F_Σ. If it is assumed that the magnitude of the change in k_Σ reported by Bodesheim et al. can be applied to the series of benzophenones shown in Table 1, the change in $E_T - E_\Sigma$ from about 133 kJ mol^{-1} (benzophenone) to about 122 kJ mol^{-1} (4-cyanobenzophenone) is expected to result in only about 40% increase in k_Σ. The 80% increase in F_Σ seen in Table 1 thus may reflect a corresponding decrease in k_Δ as E_T decreases. Although such a decrease in k_Δ may derive from a change in the extent to which $^3(n-\pi^*)$ and $^3(\pi-\pi^*)$ states are mixed in the benzophenones as described below in our discussion of the acetophenone data, we suspect that the $^3(\pi-\pi^*)$ state in the benzophenones is sufficiently higher in energy than the $^3(n-\pi^*)$ state that the effects of such mixing are not likely to be pronounced.

Our data may also reflect a substituent-dependent change in the extent to which the sensitizer–oxygen CT state plays a role in the deactivation of the $^{1,3}(^3M_1\cdots O_2(X\ ^3\Sigma_g^-))$ state. Although we were unable to obtain IPs for all the sensitizers used, it nevertheless appears that an electron-withdrawing substituent indeed increases the IP of the compound relative to that of benzophenone. The difference $E_{CT} - E_T$ is thus expected to be larger for the cyano- and trifluoromethyl-substituted benzophenones than for benzophenone itself.[1] In turn, this increase in $E_{CT} - E_T$ may reduce the extent to which an indirect CT-mediated interaction could couple the $^{1,3}(^3M_1\cdots O_2(X\ ^3\Sigma_g^-))$ state with the lower-lying $^1(^1M_0\cdots O_2(a\ ^1\Delta_g))$ and $^3(^1M_0\cdots O_2(X\ ^3\Sigma_g^-))$ states. This decrease in CT-mediated indirect coupling, which may be accompanied by an increase in the direct interaction between the $^{1,3}(^3M_1\cdots O_2(X\ ^3\Sigma_g^-))$ and $^1(M_0\cdots O_2(b\ ^1\Sigma_g^+))$ states due to the smaller $E_T - E_\Sigma$, could thus contribute to an increase in F_Σ for the cyano- and trifluoromethyl-substituted benzophenones. As discussed in the next section,

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[1] In making this statement, we assume that the sensitizer IP reflects the ease with which M^{+} is formed in solution. A compound with a high IP will thus have a comparatively large E_{CT}.

however, this model of CT-mediated mixing is not supported by the acetophenone data.

3.2. The acetophenones

Although differences in E_T for the eight compounds listed in Table 2 are larger than those for the benzophenones, these differences are nevertheless still slight. In the benzophenones, the ^{3}(n–π^*) state is sufficiently low in energy compared with the ^{3}(π–π^*) state that substituents do not change the orbital configuration of the state ultimately quenched by oxygen [27,32,38,39]. In the acetophenones, however, the energy difference between the ^{3}(n–π^*) and ^{3}(π–π^*) states is comparatively small and a change in the substituent can result in a change in the orbital configuration of the lowest energy triplet state. In Table 2, we list the energies of both the ^{3}(n–π^*) and the ^{3}(π–π^*) states, with the lowest energy state indicated by bold type. It should be recognized, however, that, for compounds where the energy difference between the ^{3}(n–π^*) and ^{3}(π–π^*) states is small, vibronic coupling will probably mix these states.

Once again, we have listed the sensitizers in Table 2 in approximate order of decreasing E_T, grouping the compounds with an n–π^* configuration at the top of the list. As found previously, a correlation between E_T and F_Σ again appears; F_Σ increases with decreasing E_T.

Although the acetophenone data probably reflect the previously described energy level arguments of Bodesheim et al. [15], it is also apparent that the orbital configuration of the triplet state influences F_Σ. Specifically, the trifluoromethyl-, methyl-, bromo- and methoxy-substituted acetophenones all have a similar E_T (about 300 kJ mol^{-1}). Nevertheless, each of these sensitizers sequentially yields a larger value of F_Σ. The trifluoromethyl-substituted compound has an n–π^* triplet state. The methyl-, bromo- and methoxy-substituted compounds have π–π^* triplet states. Furthermore, when these latter compounds are considered in this sequence, the extent of n–π^* character in the lowest triplet probably decreases owing to an increase in the energy gap between the ^{3}(n–π^*) and ^{3}(π–π^*) states. Thus the data indicate that π–π^* character in the triplet state gives rise to a larger F_Σ and that an n–π^* triplet yields a smaller F_Σ. Data in our previous report are also consistent with this conclusion [12].

In their study, Bodesheim et al. [15] examined two sensitizers with an n–π^* triplet state orbital configuration (benzophenone and acetophenone). These sensitizers gave rise to a value of k_Δ that was larger than that obtained from sensitizers with a ^{3}(π–π^*) state of comparable energy. Thus it is possible that the sequential increase in F_Σ for the entries in Table 2 reflects a decrease in k_Δ as the sensitizer triplet state acquires π–π^* character. Bodesheim et al. suggested that the larger value of k_Δ associated with a triplet state of n–π^* character may reflect phenomena related to changes in orbital angular momentum. It was proposed that the change in orbital angular momentum associated with the $O_2(X\,^3\Sigma_g^-) \rightarrow O_2(a\,^1\Delta_g)$ transition ($\Lambda = 0 \rightarrow 2$) may be more facile with a concomitant orbital angular momentum change in the sensitizer that occurs as a result of the $\pi^* \rightarrow$ n transition.

Although the rate of $O_2(a\,^1\Delta_g)$ formation (i.e. k_Δ) may be larger for sensitizers with an n–π^* orbital configuration, independent reports indicate that the yield of $O_2(a\,^1\Delta_g)$ formation is larger for ^{3}(π–π^*) sensitizers than for sensitizers with a ^{3}(n–π^*) configuration [6,40]. The latter observation is not inconsistent with the data in Table 2 when it is recognized that $O_2(b\,^1\Sigma_g^+)$ is a precursor to $O_2(a\,^1\Delta_g)$.

For compounds with $E_T \approx 300$ kJ mol^{-1}, the acetophenone data do not support the model discussed above of CT-mediated mixing between states of the M–O_2 complex. For the methyl-, bromo- and methoxy-substituted sensitizers, the ionization potential sequentially decreases but F_Σ increases. If the CT-mixing model were correct, F_Σ should decrease and not increase for this series of sensitizers. Thus, even if the amount of CT character in the $^{1,3}[^3M_1 \cdots O_2(X\,^3\Sigma_g^-)]$ state increases owing to a decrease in $E_{CT} - E_T$ for the substituent series methyl, bromo and methoxy, it does not appear that such mixing influences F_Σ.

4. Conclusions

The fraction F_Σ of excited-state oxygen formed as $O_2(b\,^1\Sigma_g^+)$ in a solution-phase-photosensitized reaction depends on both the energy and the orbital configuration of the sensitizer state quenched by $O_2(X\,^3\Sigma_g^-)$. Comparatively large values of F_Σ were obtained for sensitizers with a low E_T. This phenomenon probably derives from an increase in the rate constant k_Σ with a decrease in the energy difference between the $^3M_1$ and $O_2(b\,^1\Sigma_g^+)$ states, as described by Bodesheim et al. [15]. Our data indicate that F_Σ also depends on the orbital configuration of the sensitizer triplet state; F_Σ values obtained for a π–π^* sensitizer were larger than those obtained for an n–π^* sensitizer of similar triplet energy. Finally, it appears that, for these substituted ketones, CT-mediated mixing of sensitizer–oxygen states does not strongly influence F_Σ.

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