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RADIATIONLESS TRANSITIONS IN THE EXCITED AROMATICS–OXYGEN SYSTEMS ADSORBED ON POROUS GLASS AT LOW TEMPERATURE

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SUMMARY

The efficiency of fluorescence quenching by oxygen has been extensively studied for a number of aromatic hydrocarbons adsorbed on porous Vycor glass plates immersed in liquid oxygen at 77 K. Quite unexpected is the fact that the fluorescences of most aromatic hydrocarbons were detectably strong even in the presence of liquid oxygen. It has been found that the intrinsic rate constants for the oxygen-enhanced radiationless transitions in the excited aromatics–oxygen pairs are reasonably explained by taking account of the Franck–Condon factors, the location of the second triplet states, and the symmetries of the related electronic states. It has been concluded that in some aromatics, the radiationless transition from the excited singlet state to the second triplet state ($S_1 \rightarrow T_2$) is possible, leading to high intrinsic quenching rate constants by large Franck–Condon factors. In other aromatics, the major process is $S_1 \rightarrow T_1$ and the rate constants in these cases depend on the symmetry of the S_1 and T_1 electronic wave functions. A relatively strong phosphorescence of benzophenone has also been observed in the presence of liquid oxygen. The results of the phosphorescence quenching efficiencies for benzophenone and naphthalene by oxygen are also discussed.

INTRODUCTION

It is well known that oxygen quenches the excited singlet and triplet states of aromatic molecules almost at a diffusion-controlled rate in the solutions[1–3]. Recent theoretical[4] and experimental[5,6] results of the oxygen quenching of triplet-state molecules have established that the quenching is due dominantly to the energy transfer to singlet excited oxygen. Ottolenghi and coworkers[7] recently showed by use of a pulsed nitrogen laser that the conversion of the aromatic

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singlet excited state to the triplet state is the major path for the fluorescence quenching of aromatic hydrocarbons by oxygen (*i.e.*, enhanced intersystem crossing processes)[7].

As can be seen from the experimentally observed diffusion-controlled quenching by oxygen in the solutions, the absolute rate of quenching must be higher than 10^{10} s^{-1}, the reciprocal of the possible lifetime of a collision complex between an excited aromatic molecule and oxygen in the solutions[4,7]. Kearns *et al.*[4] theoretically predicted an absolute quenching rate of $10^{11} \sim 10^{12}$ s^{-1} for the oxygen quenching of the excited triplet state. Because of the reason mentioned above, it has been impossible to derive any reliable intrinsic rates of quenching experimentally for a D* ... O_2 pair, where D* denotes an excited aromatic molecule. The purpose of the present work is to obtain these intrinsic rate constants for several aromatic molecules, which are considered to be of great importance for understanding the mechanism and nature of the enhanced intermolecular radiationless transitions as well as the effective quenching interaction.

In a previous paper[8], we investigated the oxygen quenching of the fluorescence and phosphorescence of adsorbed aromatic hydrocarbons, and reported an interesting phenomenon that the fluorescence and short-lived phosphorescence are observed even from naphthalene adsorbed on porous glass immersed in liquid oxygen at 77 K. Under such a condition where the adsorbed aromatic hydrocarbon molecules are surrounded by oxygen molecules, it is possible to examine the intrinsic quenching rate for the D*...O_2 pair. In the present work, we have extensively studied the fluorescence quenching efficiencies for several aromatic hydrocarbons adsorbed on porous Vycor glass plates immersed in liquid oxygen at 77 K.

EXPERIMENTAL

Materials

Oxygen, naphthalene and anthracene were purified in the same way as described in previous papers[8,9]. Thiophene-free benzene was dried with phosphorus pentoxide and repeatedly distilled. Pyrene, perylene and chrysene were chromatographed on activated alumina and silica gel, and recrystallized from benzene, followed by sublimation under vacuum. Tetracene and 2-methylanthracene were recrystallized from benzene and sublimed under vacuum. 9,10-Diphenylanthracene from Nakarai Chemicals Co. was used without further purification. Benzophenone was purified by recrystallization from ethanol and sublimation under vacuum. Small pieces of the porous Vycor glass (PVG) plates of Corning Glass Works, 749303-7930, about 1 mm in thickness, were washed with ethanol and water, treated with 46% hydrofluoric acid for 30 s, and left in water for several days. After drying, the plates were heated in air at 400° C for two days. In this way, almost transparent colourless glass plates were obtained.

Procedure

Benzene and naphthalene were adsorbed on the PVG plates (40 × 10 × 0.8 mm) from the vapour phase in a thin (1.5 mm) quartz cell[8,9]. Other aromatic hydrocarbons were adsorbed from the n-hexane solutions and the adsorbate was dried in the quartz cell by evacuation at 100°C for 5 ~ 10 h. First, the fluorescence spectrum and decay time of the aromatic–PVG adsorbate were recorded at 77 K in the absence of liquid oxygen, and then purified oxygen gas was condensed into the quartz cell containing the PVG cooled down to 77 K. The fluorescence spectrum of the aromatic–PVG adsorbate immersed in liquid oxygen was recorded under the same conditions at 77 K. In the case of benzophenone, the phosphorescence spectra and decay times were examined in the same way.

A Shimadzu–Bausch & Lomb Monochromator with a dispersion of 7.4 nm/mm was used to obtain the monochromatic exciting light from a 500 W high pressure mercury lamp. A Nalumi 1 m Grating Spectrograph RM-23-I equipped with an RCA lp-28 photomultiplier was used for recording the fluorescence spectra. The fluorescence decay times of adsorbed aromatic hydrocarbons were measured using the exciting light pulse of a coaxial u.v.–N_2 laser (337 nm)[10]. A Q-switched Ruby laser was used for the measurement of the phosphorescence decay times of benzophenone without and with the presence of liquid oxygen[10]. Absorption spectra were measured with a Shimadzu Multi-Purpose Spectrophotometer, Model 50L.

RESULTS AND DISCUSSION

Absorption and fluorescence spectra of adsorbed aromatic hydrocarbons

The concentrations of adsorbed aromatic hydrocarbons were set in the range from 1×10^{-7} to 1×10^{-6} mol/g of PVG, where no luminescence and absorption bands characteristic of the aggregates or microcrystals of aromatic hydrocarbons could be detected. At higher sample concentrations, new bands ascribable to excimer fluorescence were observed besides monomer fluorescence for several aromatic hydrocarbons as described in a previous paper[8]. As an example, the absorption and fluorescence spectra of adsorbed anthracene at two sample concentrations are shown in Fig. 1. At the lower concentration, the absorption and fluorescence spectra are in good agreement with those in solution, while the observed excimer fluorescence of anthracene is nearly in agreement with that observed in the photolytic dissociation of dianthracene in a low-temperature matrix[11], where the sandwich dimer of anthracene giving rise to the excimer fluorescence is formed by the photolysis. The intensity ratio of the excimer band to the monomer band increases with the concentration and depends on the exciting wavelength. From these results, the absorption spectrum at the higher concentration (b in Fig. 1) is reasonably interpreted as the superposition of the absorption bands of the monomer and sandwich dimer formed at the higher concentration possibly due to the attrac-

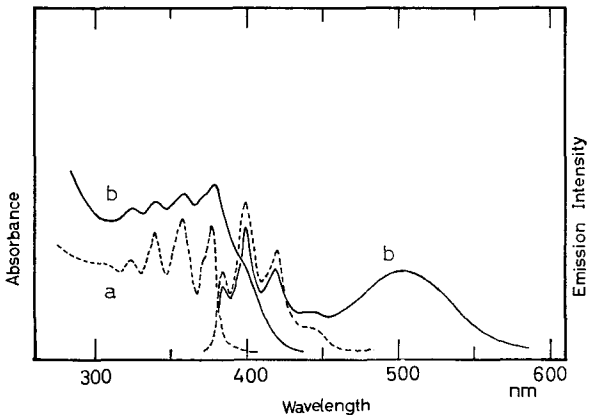

Fig. 1. Absorption and fluorescence spectra of anthracene adsorbed on porous Vycor glass (PVG) plates at 77 K: (a) 2×10^{-7} mol/g; (b) 5×10^{-6} mol/g. Excitation wavelength: 340 nm.

tive interaction of adsorbed aromatic hydrocarbon with the surface of PVG. For the present purpose, the samples with lower concentrations are used as described above.

The absorption spectrum of aromatic hydrocarbon–PVG adsorbate does not appreciably change in intensity, but only shows a slight red shift by the contact with liquid oxygen as shown in Fig. 2 for the case of anthracene. The charge-transfer bands arising from the interaction between the aromatic hydrocarbons and oxygen were negligible in the present work because of the low sample concentrations and the weakness of the charge-transfer bands[12]. The energies of the first excited singlet states (S_1) were determined for several aromatic hydrocarbons

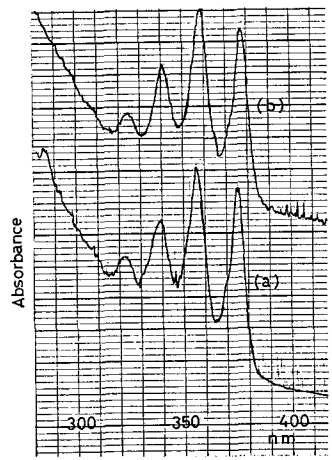

Fig. 2. Absorption spectra of anthracene adsorbed on PVG plate: (a) without and (b) with the presence of liquid oxygen at 77 K.

TABLE 1

FLUORESCENCE QUENCHING EFFICIENCIES OF AROMATIC HYDROCARBONS BY OXYGEN

Aromatic	$I_f(O_2)/I_f$	$\Delta k_n(O_2)$ (s^{-1})	S_1[a] (cm^{-1})	$T_1[L_a]$[b] (cm^{-1})	$\Delta E(S_1-T_1)$ (cm^{-1})	$\Delta E(S_1-T_2)$ (cm^{-1})	I_p[c] (eV)	τ_f[d] (ns)	E_{CT_1}[e] (cm^{-1})
Benzene	$\leqslant 0.0001$	$\geqslant 3.4 \times 10^{11}$	38,100[L_b]	29,400	8700	1000[e,f]	9.245	29	36,000
Naphthalene	0.15	5.2×10^{7}	31,800[L_b]	21,300	10,500	0[e,g,h]	8.12	110	28,500
Anthracene	0.046	1.6×10^{9}	26,400[L_a]	14,850	11,550	280[g,i]	7.38	13	22,500
2-Methyl-anthracene	0.023	3.9×10^{9}	26,100[L_a]	14,560	11,540	340[g,i]		11	
9,10-Diphenyl-anthracene	0.028	2.2×10^{9}	24,500[L_a]	14,290	10,210	<0[i]		16	
Tetracene	0.14	3.0×10^{8}	21,100[L_a]	10,300	10,800	400[g]	6.88	21	
Chrysene	0.49	2.3×10^{7}	27,000[L_b]	19,800	7200	$\leqslant$0[j]	7.80	44	
Pyrene	$\leqslant 0.001$	$\geqslant 3.6 \times 10^{10}$	26,600[L_b]	16,800	9800	(>0[k])	7.55	280	
Perylene	0.0011	8.3×10^{10}	22,900[L_a]	12,600	10,300		7.03	12	

[a] Data from the absorption spectra of adsorbed aromatic hydrocarbons in the presence of oxygen at 77 K. The electronic states are represented by Platt's notation in brackets (see ref. 28).
[b] Data from ref. 3; also, P. S. Engel and B. M. Monroe, in W. A. Noyes, G. S. Hammond and J. N. Pitts, (eds.), *Advances in Photochemistry*, Vol. 8, Wiley–Interscience, New York, 1971, p. 297.
[c] Ref. 31.
[d] Data measured for the present systems in the absence of oxygen at 77 K except benzene (ref. b).
[e] Ref. 12.
[f] Ref. 17.
[g] Ref. 19.
[h] Ref. 18.
[i] Refs. 20 and 21.
[j] Refs. 22 and 23.
[k] Refs. 24 and 25.

from the absorption spectra observed in the presence of liquid oxygen as summarized in Table 1, which are also in good agreement with those obtained in the solutions. As described previously, the $T_1 \leftarrow S_0$ absorption spectra of aromatic hydrocarbons (T_1 being the lowest triplet state and S_0 the ground state) and the charge-transfer absorption bands are observed clearly at much higher concentrations in the presence of excess oxygen or liquid oxygen at 77 K[9,12]. The energies of the lowest triplet states (T_1) for benzene and naphthalene were determined from the observed $T_1 \leftarrow S_0$ absorption bands, which are in good agreement with those in solution. Therefore, the T_1 energies for other compounds were taken from the literature as summarized in Table 1. The onset energies of the observed first charge-transfer bands, E_{CT}, are also listed together with the ionization potentials (I_p) of aromatic hydrocarbons. The values of the fluorescence lifetimes measured in the absence of oxygen at 77 K are also summarized in Table 1.

Fluorescence quenching efficiencies

The fluorescence spectra were essentially unchanged in shape but weakened by the presence of liquid oxygen as shown in Fig. 3 for perylene. From the results of the absorption spectra in liquid oxygen, we can expect that the rate constants for radiative transitions (k_f) from the excited singlet-states of the aromatic hydrocarbons are unchanged by oxygen.

If we assume that the effective quenching interaction occurs not in the higher or non-relaxed excited singlet state but only in the relaxed lowest fluorescent state, S_1, the following equation can be obtained for the oxygen quenching:

$$I_f(O_2)/I_f = \tau_f(O_2)/\tau_f = 1/[1 + \tau_f \Delta k_n(O_2)] \tag{1}$$

$$\tau_f = 1/(k_f + k_n),\ \tau_f(O_2) = 1/[k_f + k_n + \Delta k_n(O_2)]$$

where $I_f(O_2)$ and I_f are the fluorescence intensities at the peaks with and without

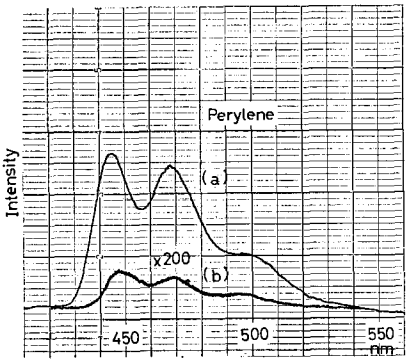

Fig. 3. Fluorescence spectra of perylene adsorbed on a PVG plate: (a) without and (b) with the presence of liquid oxygen at 77 K.

the presence of liquid oxygen, respectively, $\tau_f(O_2)$ and τ_f are the corresponding fluorescence lifetimes, k_n is the rate constant for the radiationless transition from S_1 with the absence of oxygen and $\Delta k_n(O_2)$ is its increment by the interaction of oxygen. The fluorescence decay curve was measured for chrysene as an example in the presence of liquid oxygen at 77 K and was found to be completely exponential, with the lifetime, $\tau_f(O_2)$, of 22 ns. It is seen from Table 1 that $I_f(O_2)/I_f$ value of 0.49 is in good agreement with $\tau_f(O_2)/\tau_f$ value of 0.50 in the case of chrysene. These results indicate the validity of the postulate that all the adsorbed aromatic molecules are interacting with oxygen in the excited fluorescent state, S_1, in the presence of liquid oxygen.

We calculated $\Delta k_n(O_2)$ values from eqn. (1) based on the measured τ_f and $I_f(O_2)/I_f$ values for nine aromatic hydrocarbons as summarized in Table 1. The $\Delta k_n(O_2)$ values for these molecules vary from 10^7 to 10^{11} s^{-1}. These values can be regarded as the intrinsic quenching rate constants in the $D(S_1)...O_2$ pairs at the low temperature and, therefore, may reflect the nature of the electronic states inherent to each of the aromatic hydrocarbons. On the other hand, the fluorescence quenchings by oxygen as studied previously in solutions are most reasonably ascribed to be diffusion-controlled processes ($\sim 10^{10}$ M^{-1} s^{-1})[3,14].

Mechanism and classification of the oxygen-enhanced radiationless transitions from singlet excited aromatic hydrocarbons

The energy levels of the low-lying excited singlet and triplet states, and the ionization potentials of aromatics as well as the $\Delta k_n(O_2)$ values are diagramatically

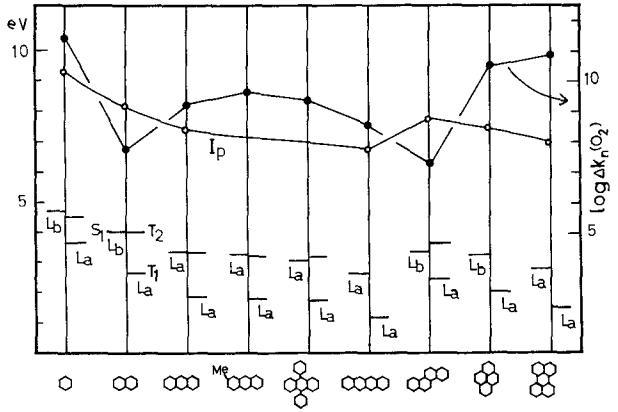

Fig. 4. A schematic representation of the energy levels, the ionization potentials of aromatic hydrocarbons, I_p, and the rate constants of the oxygen-enhanced radiationless transitions $\Delta k_n(O_2)$. For each molecule, the energy levels of the excited triplet states are marked on the right side and those of the excited singlet states on the left side of the vertical line as indicated for the case of naphthalene.

shown in Fig. 4. The first charge-transfer states for some aromatic hydrocarbons and oxygen lie between their S_1 and T_1 levels as shown in Table 1. So, the first charge-transfer states for other hydrocarbons are also expected to lie between their S_1 and T_1 levels. As the experimental results show no correlation between the $\Delta k_n(O_2)$ values and the position of the charge-transfer state or the donor ionization potentials, the radiationless transition to the charge-transfer state:

$$D(S_1)...O_2 \rightarrow CT(D^+O_2^- \qquad (a)$$

does not seem to be the dominant quenching process. The insensitivity of the $\Delta k_n(O_2)$ values to the location of S_1 also indicates that the oxygen-induced internal conversion process:

$$D(S_1)...O_2 \rightarrow D(S_0)...O_2 \qquad (b)$$

is not the main path for the oxygen-enhanced quenching process. The process (b) is expected to depend mainly on the Franck–Condon factors[4,15,16]. Therefore, if this is the major process, the $\Delta k_n(O_2)$ values should increase with decreasing S_1 energy because of the increasing Franck–Condon factor.

We can also exclude the energy transfer process

$$D(S_1)...O_2 \rightarrow D(T_1)...O_2^*(^1\Delta_g \text{ or } ^1\Sigma^+_g) \qquad (c)$$

from the experimental observation that the $\Delta k_n(O_2)$ value of naphthalene with the S_1-T_1 energy gap of 10,500 cm^{-1} is nearly comparable to that for chrysene with the S_1-T_1 energy gap smaller than 7900 cm^{-1}, the energy required to promote oxygen to the $^1\Delta_g$ state. Though Parmenter and Rau[3] have already excluded the quenching process (c) from the diffusion controlled quenching rate constants for several aromatic hydrocarbons in the solutions, our results provide more reliable experimental evidence for the same conclusion.

Taking into account the relative location of the second triplet states T_2 compared to S_1 and the symmetries of S_1 and T_1 along with the general theory of radiationless transitions[16] as will be shown below, we conclude that the oxygen-enhanced intersystem crossing process:

$$D(S_1)...O_2 \rightarrow D(T_1 \text{ or } T_2)...O_2 \qquad (d)$$

appears to be the main path in the oxygen-enhanced quenching process of $D(S_1)...O_2$.

Reliable data on the energies of the second triplet states T_2 of aromatic hydrocarbons are not sufficient at the present stage as seen from Table 1. T_2 of benzene was confirmed from the $T_2 \leftarrow S_0$ absorption band enhanced by oxygen[12], which is in good agreement with that determined by Colson and Bernstein[17] from the oxygen-perturbed solid benzene at 4.2 K. In the case of naphthalene, Hanson and Robinson[18] reported a weak $T \leftarrow S_0$ absorption band for crystals at 4.2 K, just below S_1, which was recently confirmed to be the second triplet state by Meyer

et al.[19]. Therefore, the second triplet state of naphthalene seems to lie at about the same energy as S_1. The second triplet states of anthracene and 2-methylanthracene were determined by the $T_2 \leftarrow T_1$ absorption spectra by Kellogg[20], by Bennet and McCartin[21], and by Meyer *et al.*[19]. The second triplet state of tetracene was also found to lie under S_1[19]. The second triplet state of 9,10-diphenylanthracene is said to lie above S_1 from the very high fluorescence quantum yield even at room temperature[21], since the intersystem crossing to T_2 is considered to be precluded by the large activation energy. In the case of chrysene having the lowest S_1-T_1 energy gap, the second triplet state is expected nearly at the same energy as S_1 or above S_1 from the result of $T_n \leftarrow T_1$ absorption[22] and the theoretical calculation by Pariser[23]. Ham and Ruedenberg[24] have theoretically predicted the T_2 energy level of pyrene to be below S_1 (by 2600 cm^{-1}). This result seems to be consistent with the results of the temperature dependence of the fluorescence quantum yield of pyrene in solutions[22,25].

From the general theory of radiationless transitions, the rate constant for process (d) can be expressed as follows[4,16]:

$$\Delta k_n(O_2) = (2\pi/\hbar)\varrho\beta^2 F_{if} \tag{2}$$

where β is the electronic matrix element between the initial and final states, ϱ is the density of the final state quasi-degenerate with the initial state, and F_{if} is the Franck–Condon factor for the transition, *i.e.* the overlap integral between the vibrational wave functions of the initial and final states. This Franck–Condon factor is generally thought to be the larger, the smaller the energy difference between the lowest vibrational levels of the initial and final states for the transition. Therefore, if other factors remain the same, the rate constant for the radiationless transition (enhanced by oxygen) is governed by this Franck–Condon factor.

According to the notation of Platt[26], the lowest triplet states T_1 of the nine aromatic hydrocarbons are all represented by ^3L_a. The S_1 states are ^1L_b for benzene, naphthalene, chrysene and pyrene, and ^1L_a for others. The second triplet states T_2 are believed to be ^3B_b[19,23,24]. L_a corresponds to the B_{2u} electronic state of the aromatic hydrocarbons belonging to the D_{2h} point group, and both L_b and B_b to B_{1u}[26,27]. The possible symmetry correlation diagram of the excited states in the D...O_2 pair with C_{2v} or C_s symmetry is shown below:

C_s		C_{2v}		D_{2h}
A′	———	B_1	———	$B_{1u}(L_b, B_b)$
A″	———	B_2	———	$B_{2u}(L_a)$
	D...O_2			D

The various cases of process (d) may be classified into the following three types for the aromatic hydrocarbons examined.

Case I: S_1 is L_b or L_a and T_2 lies appreciably below S_1.

Case II: S_1 is L_a and T_2 lies at nearly the same energy as S_1 or above S_1.

Case III: S_1 is L_b and T_2 lies at nearly the same energy as S_1 or above S_1.

Benzene and pyrene belong to case I, where the radiationless process from S_1 to T_2 is possible, which is thought to be very fast because the S_1-T_2 energy gaps are much smaller than those between S_1 and T_1[15,16]. From the large $\Delta k_n(O_2)$ value comparable to those of benzene and pyrene, perylene seems to belong to case I. Anthracene, its derivatives, and tetracene belong to case II, where the radiationless process to T_2, which is nearly at the same energy as S_1 or above S_1, is thought to be precluded by the presence of a fairly large activation energy[21,25]. In this case, therefore, the oxygen-enhanced intersystem crossing process from $S_1(L_a)$ to $T_1(L_a)$ is dominant. Because the symmetry of S_1 is the same as that of T_1 in case II, the electronic matrix elements β should be larger than those for case III, where the symmetry of $S_1(L_b)$ is different from that of $T_1(L_a)$. Naphthalene and chrysene belong to case III. It seems reasonable to assume that there is no appreciable difference in the F_{if} values between case II and case III because of the comparable S_1-T_1 energy gaps associated with the oxygen-enhanced radiationless process. So, the small $\Delta k_n(O_2)$ values in case III compared to case II can be explained by the difference in β.

Phosphorescence quenching efficiencies of naphthalene and benzophenone in liquid oxygen

In a previous paper[8], we detected weak phosphorescence of naphthalene with an extremely short lifetime ($<10^{-3}$ s) from naphthalene–porous glass adsorbate immersed in liquid oxygen at 77 K. The natural radiative lifetime of oxygen-perturbed triplet-state naphthalene was calculated to be 9×10^{-4} s from the observed $T_1 \leftarrow S_0$ absorption spectrum under the same conditions[8,9] which is much shorter than the unperturbed value, 11 s[28]. The increment of the rate constant for the radiationless transition from the triplet state by the interaction of oxygen $\Delta k_{pn}(O_2)$ can be estimated to be $\sim 10^5$ s^{-1} from the relative phosphorescence intensities without and with the presence of liquid oxygen, the obtained $\Delta k_n(O_2)$ value, and the perturbed radiative rate constant $k_p(O_2)$ in the presence of liquid oxygen, although the phosphorescence lifetime in liquid oxygen could not be measured.

The effect of oxygen on the phosphorescence of benzophenone is rather small compared to that of naphthalene. The phosphorescence decay curves with and without oxygen were exponential with the lifetimes, $\tau_p(O_2)$ and τ_p, of 2.8 and 9.8 ms, respectively. The shape and position of the phosphorescence spectrum are virtually unchanged with oxygen and the ratio of the phosphorescence intensity $I_p(O_2)/I_p$ is calculated to be 0.22 from the observed data. This value agrees with the $\tau_p(O_2)/\tau_p$ value of 0.28 calculated from the decay curves to within experimental error. Since it is well known that the quantum yield of intersystem crossing in benzophenone is nearly one even without the presence of oxygen[29], the following equation can hold:

$$I_p(O_2)/I_p = k_p(O_2)\tau_p(O_2)/k_p\tau_p \quad (5)$$

where k_p and $k_p(O_2)$ indicate the rate constants of the radiative transitions from the unperturbed and perturbed benzophenone, respectively. From the experimental fact that $I_p(O_2)/I_p$ approximately equals $\tau_p(O_2)/\tau_p$, it can be concluded that the radiative transition is little affected by the presence of oxygen, that is, $k_p \approx k_p(O_2)$. Our conclusion is also consistent with the result by Kanda *et al.*[30], who showed that the presence of oxygen has no apparent effect on the $T_1 \leftarrow S_0$ absorption of benzophenone in solution. Consequently, $k_{pn}(O_2)$ in this case can be obtained by the following equation:

$$I_p(O_2)/I_p = 1/[1 + \tau_p \Delta k_{pn}(O_2)] \quad (6)$$

The calculated $\Delta k_{pn}(O_2)$ value, 3.8×10^2 s^{-1}, is very small compared to that of naphthalene.

The above mentioned weak oxygen effect on the triplet-state benzophenone may be regarded as further evidence for the important role of the charge-transfer interaction in the oxygen quenching. The charge-transfer state between benzophenone and oxygen must lie at a higher energy than those of aromatic hydrocarbons due to the former's large ionization potential (9.45 eV[31]). Consequently, the mixing between the excited phosphorescent n–π^* triplet state and the charge-transfer state will be small. Recently, it has also been suggested by Brewer[32], based on his experimental results of the oxygen quenching for the fluorescence of benzene derivatives, that the lack of observed oxygen quenching for the excited singlet state of many ketones may be due to their high ionization potentials.

Further comments on the oxygen quenching of the excited states of aromatics

In our present system, liquid oxygen seems to act as a kind of non-polar solvent on adsorbed $D^*...O_2$, which seems to be unfavourable for enhancing the internal conversion to the charge-transfer state. In addition, the rigid intermolecular configurations between adsorbed aromatics and oxygen at 77 K might suppress the degree of freedom neccesary for the radiationless relaxation processes of $D^* \ldots O_2$[33]. The presence of these unfavourable factors for enhancing the radiationless processes might be the reason why the fluorescence of adsorbed aromatics is observable even under conditions where they are surrounded by oxygen molecules. The $\Delta k_n(O_2)$ values are expected to be at least a few orders of magnitude larger at room temperature than those in the present system. This is consistent with the experimental observation that fluorescence quenching by oxygen in solution is a diffusion-controlled processes.

Recently, Porter *et al.*[14] and Thomas *et al.*[34] revealed by using laser photolysis techniques that the oxygen quenching of triplet-state aromatics in solution is a factor of $\sim$ 10 slower than the diffusion-controlled quenching of the fluorescence

by oxygen. This observation corresponds to our result that the $k_{pn}(O_2)$ values of naphthalene and benzophenone are very much smaller than the $k_n(O_2)$ values.

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