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The Interaction of Oxygen with Organic Molecules. II.[1] Oxygen Quenching of the Excited States of Adsorbed Aromatic Hydrocarbons

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Quenching of phosphorescence and fluorescence of aromatic hydrocarbons adsorbed on powdered porous glass or silica gel have been examined as a function of oxygen pressure. It has been found that the phosphorescence quenching at low temperature can be explained mostly by assuming that only those aromatic molecules having an oxygen molecule or molecules within an effective interaction radius are nonphosphorescent (static quenching model). The fluorescence quenching occurs only at much higher oxygen pressures and it has been proposed that contact pairs between aromatic and oxygen molecules, which have shorter intermolecular distances compared to the distances effective for the phosphorescence quenching and give rise to the charge-transfer absorption bands, are relevant. It has been observed that the excimer fluorescence of naphthalene appearing at a higher sample concentration is more strongly affected by oxygen than the monomer fluorescence. The emission spectra from naphthalene-porous glass adsorbate immersed in liquid oxygen and nitrogen have also been examined. The formation of the singlet oxygen ($^1\Delta_g$ or $^1\Sigma_g^+$) through the interaction of oxygen with triplet molecules has been confirmed by use of the peroxidation reaction of adsorbed anthracene.

The interaction of oxygen with electronically excited organic molecules is associated with a number of interesting phenomena.[2] For example, it is well known that molecular oxygen quenches both the excited singlet and triplet states of organic molecules. Theoretical investigation of the quenching of organic triplet states by oxygen indicated that singlet-state oxygen are formed by the intermolecular energy transfer.[3] This mechanism has now been supported by the results of recent experiments.[4-6] The oxygen quenching has been studied mainly in fluid media where the bimolecular quenching is controlled by the diffusion of oxygen and organic

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2) P. Pringsheim, "Phosphorescence and Fluorescence," Interscience Publisher, Inc., New York (1965).

3) K. Kawaoka, A. U. Khan and D. R. Kearns, *J. Chem. Phys.*, **47**, 1842 (1967); **48**, 3272 (1968).

4) D. R. Snelling, *Chem. Phys. Lett.*, **2**, 346 (1968).

5) D. R. Kearns, A. U. Khan, C. K. Duncan and A. H. Maki, *J. Amer. Chem. Soc.*, **91**, 1039 (1969).

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molecules.[7-10] It has not been possible to estimate intrinsic quenching efficiencies from such diffusion-controlled reactions. Siegel and Judeikis have recently determined the relative interaction radius for the oxygen quenching of naphthalene triplet-state in rigid matrices where material diffusion is minimized.[11] Oxygen quenching of phosphorescence of aromatic molecules has been used to measure the diffusion rates of oxygen in polymer matrices.[12,13]

It is well known that molecules adsorbed on solid surface have relatively long lifetimes in their triplet states even at room temperature. The luminescent properties of adsorbed molecules have been extensively investigated in the presence of oxygen.[14-17] Previous investigations of oxygen quenching have almost extensively dealt with dye molecules adsorbed on silica gel. In the preceding paper, we have reported the extra charge-transfer absorption spectra caused by the interaction between adsorbed oxygen and organic molecules.[1] The present paper is mainly concerned with the effective quenching interaction between oxygen and electronically excited aromatic hydrocarbons adsorbed on porous glass or silica gel.

Experimental

Materials. Oxygen and naphthalene were purified in the same way as described in the preceding paper. Commercially available α-chloronaphthalene was distilled under reduced pressure. Anthracene and biphenyl were purified by recrystallization from benzene and ethanol, respectively, and by sublimation in vacuum. The particle sizes of silica gel and powdered porous glass[1] used here were 30—42 mesh, and were treated in the same way as described in the preceding paper. It was confirmed that no luminescence was detectable from porous glass itself by excitation in the near ultraviolet region even at liquid nitrogen temperature (77°K). The phosphorescence of silica gel itself at 77°K was negligible in comparison with that of adsorbed molecules.

Procedure. Naphthalene, α-chloronaphthalene and biphenyl were adsorbed from the vapor phase in the same way as described before.[1] Anthracene was adsorbed from the chloroform solution and the adsorbate was dried and thoroughly evacuated at 100—150°C. Sample concentrations ranged from 1×10^{-7}—5×10^{-6} mol/g of the adsorbent for the study of the fluorescence and phosphorescence quenching by oxygen. In this range we detected no luminescence characteristic of the aggregates or microcrystals of adsorbed molecules. However, when sample concentrations were increased (above 5×10^{-5} mol/g), a new band ascribable to excimer fluorescence was detected besides monomer fluorescence in the case of naphthalene or α-chloronaphthalene.

After adsorption, the sample in the ampoule was distributed into several cylindrical quartz cells, 4 mm in diameter, previously attached to the ampoule. Then oxygen was introduced into the vacuum system at room temperature and the quartz cells were sealed off carefully from the ampoule at desired oxygen pressure. Pressures below 5 Torr were read with a McLeod gauge. An ordinary mercury manometer was used for reading higher pressures.

The emission spectra were measured with an Aminco-Bowmann Spectrophotofluorometer. The lifetimes of the phosphorescence were determined from the decay curves traced on an osciloscope. Fluorescence decay curves were measured by exciting the samples with a device for producing nanosecond flash light.[18] The absorption spectra of adsorbed molecules was measured by the reflection method with a Shimadzu MPS-50L Recording Spectrometer as described in the preceding paper.

Results

Phosphorescence and Fluorescence of Adsorbed Aromatic Hydrocarbons. Phosphorescence spectra of the adsorbed molecules at 77°K were found to be nearly in agreement with those

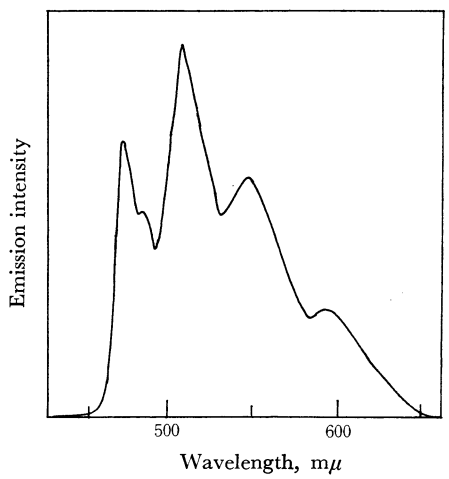

Fig. 1. Phosphorescence spectrum of naphthalene adsorbed on porous glass at 77°K.
Sample concentration: 1×10^{-6} mol per gram of porous glass.

7) W. R. Ware, *J. Phys. Chem.*, **66**, 455 (1962).
8) B. Stevens and B. E. Algar, *ibid.*, **72**, 2582 (1968).
9) A. D. Osborne and G. Porter, *Proc. Roy. Soc.*, **A284**, 9 (1965).
10) C. S. Parmenter and J. D. Rau, *J. Chem. Phys.*, **51**, 2242 (1969).
11) S. Siegel and H. S. Judeikis, *ibid.*, **48**, 1613 (1968).
12) G. Shaw, *Trans. Faraday Soc.*, **63**, 2181 (1967).
13) B. A. Baldwin and H. W. Offen, *J. Chem. Phys.*, **49**, 2933 (1968).
14) H. Kautsky, *Trans. Faraday Soc.*, **35**, 216 (1939).
15) S. Kato, This Bulletin, **30**, 34 (1957).
16) R. F. Weiner and H. H. Seliger, *Photochem. Photobiol.*, **4**, 1207 (1965).
17) J. L. Rosenberg and F. S. Humphries, *J. Phys. Chem.*, **71**, 330 (1967).
18) N. Mataga, M. Tomura and H. Nishimura, *Mol. Phys.*, **9**, 367 (1965).

measured for the same molecules dissolved in rigid matrices, although the spectra showed slight broadening of their vibrational structures in the adsorbed state. As an example, phosphorescence spectrum of naphthalene adsorbed on porous glass is shown in Fig. 1. The similar broadening was found also for fluorescence spectra. This broadening can be interpreted to be due to the wide energy distribution of the adsorbed molecules in the variety of the field of the polar adsorbent.

No difference in the luminescent properties of aromatic molecules have been found between silica gel and porous glass adsorbates. The phosphorescence lifetimes (τ_p) of adsorbed biphenyl, naphthalene and α-chloronaphthalene at 77°K were 4.0, 2.3 and 0.2 sec, respectively, at negligible oxygen pressures. These values also agree very closely with those in rigid matrices at 77°K.[19]

The band maxima of fluorescence show a slight blue shift when cooled down to 77°K. The fluorescence lifetime of naphthalene adsorbed on porous glass was 100 ns at room temperature, in good agreement with the values in the solutions.[18] Increase of the concentrations of naphthalene and α-chloronaphthalene resulted in the appearance of new broad bands almost identical with the corresponding excimer fluorescence in solutions.[20] The intensity ratio of this new band to the monomer fluorescence band depends on the wavelength of the exciting light as shown in Fig. 2 for the case of naphthalene. This ratio increases with increasing the sample concentration. The lifetimes of the new fluorescence band of naphthalene were found to

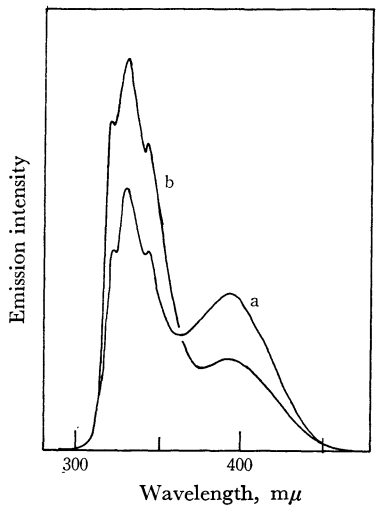

Fig. 2. Fluorescence spectra of naphthalene adsorbed on porous glass at 77°K.
Sample concentration: 5×10^{-5} mol per gram of porous glass; excitation wavelength: (a) 275 mμ and (b) 300 mμ.

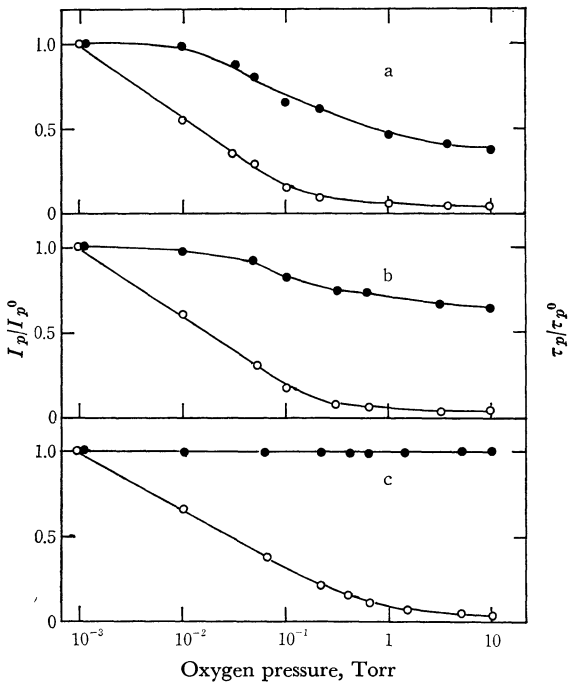

Fig. 3. The relative phosphorescence intensities I_p/I_p° (○) and lifetimes τ_p/π_p° (●) of aromatic-porous glass adsorbates as a function of oxygen pressure at 77°K. (a), for biphenyl; (b), for naphthalene; (c), for α-chloronaphthalene. I_p° and τ_p° are, respectively, the phosphorescence intensity and lifetime at negligible oxygen pressures. The value of I_p/I_p° was normalized to be 1 at 10^{-3} Torr oxygen pressure. τ_p° at 77°K is 4.0 sec for biphenyl, 2.3 sec for naphthalene and 0.2 sec for α-chloronaphthalene.

be 65 and 100 ns at 300°K and 77°K, respectively, in good agreement with the long lifetimes characteristic of excimer fluorescence.[21] It is therefore concluded that, with increasing the sample concentration, adsorbed naphthalene molecules are forced to form loosely bound dimers on the surface and when this dimer is excited as well as monomer, the dimer is led to the configuration favorable to excimer formation.[22] The effect of oxygen on excimer fluorescence as well as monomer fluorescence is of considerable interest.

Quenching of Phosphorescence by Oxygen. The phosphorescence of the samples prepared in the way described in the experimental section was too weak at room temperature to examine the effect of oxygen quantitatively. Therefore, most of the studies were made at low temperature. The quenching effect of oxygen at 77°K is shown by the curves in Fig. 3, in which the values of the

19) D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).
20) C. A. Parker, *Spectrochemica Acta*, **19**, 989 (1963).
21) N. Mataga, Y. Torihashi and Y. Ota, *Chem. Phys. Lett.*, **1**, 385 (1967).
22) E. A. Chandross, J. Ferguson and E. G. McRae, *J. Chem. Phys.*, **45**, 3546 (1966); **45**, 3554 (1966).

relative phosphorescence intensities I_p/I_p^0 and the relative phosphorescence lifetimes τ_p/τ_p^0 are plotted as a function of oxygen pressure. I_p^0 and τ_p^0 are, respectively, the phsophorescence intensity and lifetime of the sample containing negligible amounts of oxygen. The phosphorescence decays at various oxygen pressures were found to obey the first order kinetics. The dependence of the phosphorescence lifetime on oxygen pressure was also examined at 203°K (−70°C) in the case of biphenyl. The temperature was obtained by dropping liquid nitrogen into the Dewar containing 99% ethanol. This curve, being different from that at 77°K, showed a rapid decrease in the lifetime with increasing the oxygen pressure. Although the absolute amount of adsorbed oxygen at each oxygen pressure is unknown, qualitative discussion on the interaction of oxygen with excited molecules can be made from these quenching curves.

Although oxygen pressure above 10 Torr is sufficient to quench phosphorescence totally, weak emission was detected from the naphthalene-porous glass adsorbate immersed in liquid oxygen at 77°K. This emission was observed to lie in almost the same region as the phosphorescence of naphthalene and could not be detected using a sector presumably because of the extremely short lifetime ($<10^{-3}$ sec). The phosphorescence of naphthalene from the naphthalene-porous glass adsorbate immersed in liquid nitrogen was strong and the lifetime was 1.4 sec. This short lifetime in liquid nitrogen compared to the original value (τ_p^0, 2.3 sec) may be due to impurities, such as oxygen, possibly contained in liquid nitrogen.

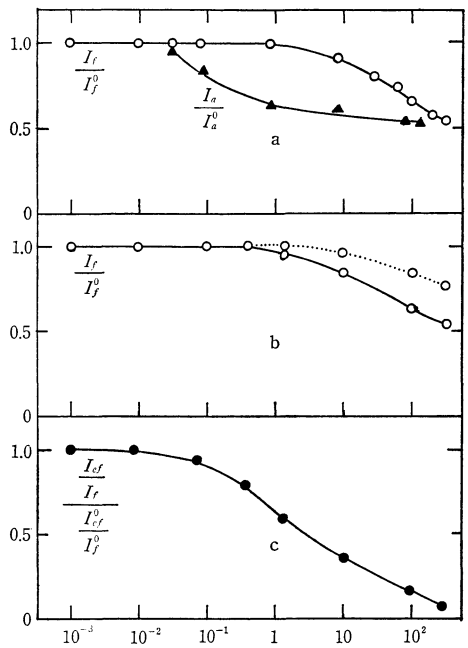

Fig. 4. The relative fluorescence intensities I_p/I_p° (○) and the relative ratios of the intensity of excimer fluorescence versus monomer fluorescence $(I_{ef}/I_f)/(I_{ef}^\circ/I_f^\circ)$ (●) of aromatic-porous glass adsorbates as a function of oxygen pressure at room temperature (———) and 77°K (- - - - -). (a), for anthracene; (b) and (c), for naphthalene. I_f° and I_{ef}° are, respectively, the fluorescence intensities of monomer and excimer at negligible oxygen pressures. The relative absorption intensities I_a/I_a° (▲) of adsorbed anthracene are shown in (a) as a function of oxygen pressure, when the sample containing a known pressure of oxygen is irradiated. I_a° is the absorption intensity of adsorbed anthracene before irradiation.

Quenching of Fluorescence by Oxygen. The quenching effect of oxygen was examined mainly at room temperature. The quenching effect of oxygen on monomer fluorescence is shown in Fig. 4 (a) and (b) in cases of naphthalene and anthracene. The values of the relative fluorescence intensities I_f/I_f^0 are plotted as a function of oxygen pressure. It is found from the curves in Fig. 4 that the quenching curve of naphthalene is almost the same as that of anthracene in spite of the large difference between the fluorescence lifetimes (4.2 ns for anthracene[23] and 100 ns for naphthalene), and the quenching by oxygen is less effective at 77°K than at room temperature. No fluorescence quenching is found at oxygen pressures below 1 Torr where phosphorescence is quenched to some extent. Fluorescence quenching occurs gradually at oxygen pressures above 1 Torr where phosphorescence is quenched to a great extent. No difference was found between the quenching curves of anthracene for both porous glass and silica gel adsorbates.

The quenching effect of oxygen on excimer fluorescence is shown in Fig. 4 (c) in the case of naphthalene (5×10^{-5} mol naphthalene per gram of porous glass). The wavelength of the excitation was fixed at 275 mμ. The relative ratio of the intensity of excimer fluorescence versus monomer fluorescence is plotted as a function of oxygen pressure. It is found from this curve that excimer fluorescence is more strongly affected by oxygen than monomer fluorescence, though the lifetime of excimer fluorescence (65 ns) is rather short compared to monomer fluorescence (100 ns). The flourescence of monomer and excimer was little quenched by nitrogen gas admitted to the sample instead of oxygen.

Liquid oxygen also showed a remarkable effect on the fluorescence of naphthalene. The fluorescence intensity of the naphthalene-porous glass adsorbate immersed in liquid oxygen condensed at 77°K was roughly 1/7 of the original intensity (I_p^0). Liquid nitrogen showed no effect on the fluorescence of adsorbed naphthalene.

23) W. R. Ware and B. A. Baldwin, *ibid.*, **40**, 1703 (1946).

Discussion

Quenching of Phosphorescence by Oxygen. As shown in Fig. 3 the dependence of I_p/I_p^0 on oxygen pressure is obviously different from that of τ_p/τ_p^0 and the curves of I_p/I_p^0 for the three compounds show almost common behavior. I_p/I_p^0 decreases rapidly with increasing the oxygen pressure and approaches to zero at oxygen pressures above 10 Torr. The lifetimes of biphenyl and naphthalene are affected a little by oxygen, but do not decrease indefinitely with increasing the oxygen pressure in such a way as the intensities do, and the values approach approximately to 1.6 and 1.4 sec, respectively, so far as we could detect the phosphorescence. On the other hand, the lifetime of α-chloronaphthalene, naturally having a short lifetime (0.2 sec), is almost constant irrespective of oxygen presure.

In the case where the quenching of phosphorescence of adsorbed organic molecules is assumed to take place by the collision of these organic molecules with oxygen (dynamic quenching model), the lifetime of phosphorescence should be shortened in the presence of oxygen. Under such a condition, the curve of the relative phosphorescence intensity, I_p/I_p^0, should be almost in accord with that of the relative phosphorescence lifetime, τ_p/τ_p^0. On the other hand, in the absence of such collisional processes, the lifetime of the observed phosphorescence should be independent of oxygen pressure. In that case, it should be assumed that only those molecules that have oxygen molecules within an effective interaction radius before excitation are nonphosphorescent (static quenching model). Our results indicate that in the case of α-chloronaphthalene, the phosphorescence quenching is due to static quenching alone and in the cases of naphthalene and biphenyl, having naturally longer lifetimes compared to the former, there exists a slight contribution from the dynamic quenching as well as the static quenching. From these results, it is suggested that the dynamic quenching process is considerably slow at 77°K in the adsorbed state, although the quantitative interpretation of the curves of τ_p/τ_p^0 is impossible because of the inhomogeneity of the surface condition. As the dynamic process is controlled by the diffusion of oxygen, the observed behaviors of τ_p/τ_p^0 should be explained by the slow surface diffusion of oxygen at 77°K. This conclusion is supported by the result of the lifetimes of biphenyl phosphorescence measured at 230°K where the diffusion of oxygen must be faster than at 77°K.

As described in the preceding paper, we have found the existence of the contact pairs between the adsorbed oxygen and organic molecules at high oxygen pressures, which give rise to the charge-transfer absorption spectra. From the absence of any observed effect of oxygen on the absorption spectra at low oxygen pressures where phosphorescence quenching occurs to a large extent, it should be concluded that no contact pairs are formed at such oxygen pressures. It may be worthwhile to add that the effect of oxygen on the phosphorescence quenching is easily removed by evacuation. As it is reported that the binding energy between oxygen and aromatics is negligible in the ground state,[3,24] it is expected that oxygen is physically adsorbed at random on the aromatic-porous glass adsorbate at low oxygen pressures and the aromatic molecules form pairs with some of the adsorbed oxygen which can have an effective interaction for the phosphorescence quenching. The amount of these pairs is considered to increase with increasing the oxygen pressure, in agreement with the observed monotonous decrease of I_p/I_p^0 at low oxygen pressures. The relative situations between the adsorbed aromatic and oxygen molecules are illustrated schematically in Fig. 5.

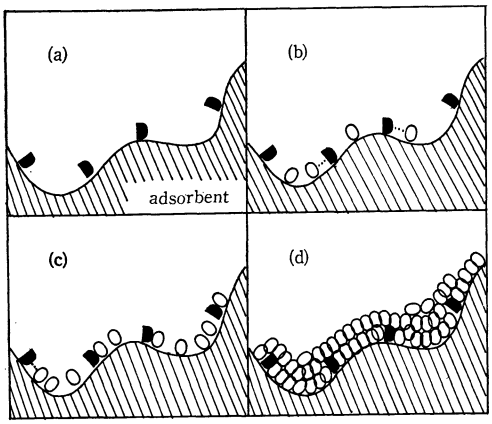

Fig. 5. Schematic illustrations indicating the relative situation between aromatic (◗) and oxygen (O) molecules in the adsorbed state. (a), before admitting oxygen; (b), at low oxygen pressures where phosphorescence quenching occurs; (c), at high oxygen pressures where contact pairs responsible for fluorescence quenching are formed between them; (d), when immersed in liquid oxygen.

Figure 6 shows the schematic potential curves for the states caused between aromatic and oxygen molecules versus the distance between them. Kearns *et al.*,[3] have suggested theoretically that a significant binding energy is expected through the interaction of triplet-state organic molecules with oxygen (curve b in Fig. 6). At a low oxygen pressure where effective phosphorescence quenching, but not the fluorescence quenching, occurs, we assume that most of the oxygen molecules are at distance r_2, or

24) H. Tsubomura and R. S. Mulliken, *J. Amer. Chem. Soc.*, **82**, 5966 (1960).

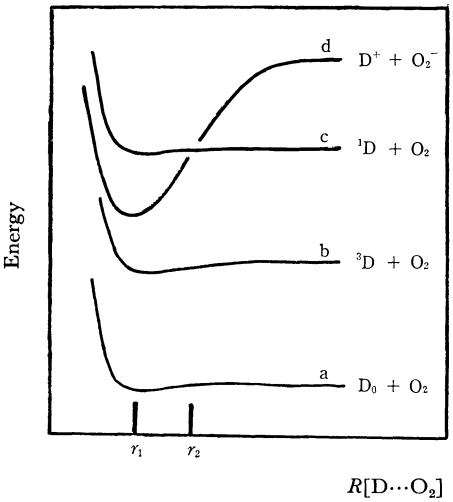

Fig. 6. Schematic potential curves for the states caused between aromatic (D) and oxygen (O_2) molecules versus the distance (R) between D and O_2. D_0 indicates the ground state of aromatic molecule. ^1D and ^3D indicate, respectively, the excited singlet and triplet states. In the adsorbed state, the intermolecular distance R is throught to decrease with increasing oxygen pressure.

larger, from the aromatic molecule D_0. When the aromatic molecule is excited to a ^3D level at such a distance, the interaction between ^3D and oxygen at that distance is thought to be sufficiently strong to cause a radiationless decay process which competes with the slow natural radiative decay process of the phosphorescent state, leading to the quenching of the phosphorescence.

Rosenberg and Humphries[17] have studied the phosphorescence quenching of acriflavine adsorbed on silica gel and suggested the existence of relatively nonphosphorescent complex between the dye and oxygen. Recently, Siegel and Judeikis[11] have investigated the oxygen quenching of naphthalene triplet state in 3-methylpentane glass at 77°K and found a slight contribution from the dynamic quenching process in addition to the static quenching process. They have also determined the effective interaction distance for the quenching to be 10.5 Å. These results seem to be consistent with our conclusion.

We have reported in the preceding paper that the S→T absorption spectrum of naphthalene is enhanced to a great extent when the naphthalene-porous glass adsorbate is immersed in liquid oxygen. The weak emission observed under such an environment may be assigned to the phosphorescence of naphthalene having a shortened lifetime, one possible explanation for this being that the T→S radiative decay process as well as the radiationless decay process is enhanced remarkably by the strong perturbation due to liquid oxygen (see Fig. 5d). The natural radiative lifetime of naphthalene triplet state, which can be calculated in the same way as described by McGlynn and Azumi[25] using the observed S→T absorption, was 9×10^{-4} sec. This value is very short compared to the unperturbed one, 11 sec,[26] in agreement with the observed shortlived emission.

Quenching of Fluorescence by Oxygen. Our results of fluorescence quenching show no difference in the characteristics between the two curves for naphthalene and anthracene despite of the large difference in their fluorescence lifetimes. This indicates that the decreases in I_f/I_f^0 are due to the static quenching alone at room temperature (21°C), and seems to indicate the surface diffusion of oxygen to be much slow compared to the decay of fluorescence. As described in the preceding paper, the extra charge-transfer absorption spectra caused through the interaction between adsorbed oxygen and organic molecules have been detected at high oxygen pressures where fluorescence quenching is observable. It can therefore be concluded that the fluorescence quenching occurs between oxygen and organic molecules in such a close contact as giving rise to the charge-transfer absorption bands, because of the fast decay of fluorescence (for example, at a distance r_1 in Fig. 6). The amount of contact pairs formed on the surface is thought to increase with increasing the oxygen pressure as Fig. 5 shows. From the results obtained for naphthalene fluorescence in liquid oxygen and at 77°K, it seems to be reasonable to assume that the radiationless decay process in contact pair becomes slow when cooled down to the low temperature and becomes comparable to the decay processes of fluorescence.

We have also found that the excimer fluorescence of naphthalene is affected more strongly by oxygen than the monomer fluorescence. This result is consistent with the earlier qualitative report on oxygen quenching of aromatic-hydrocarbon excimers in liquid solutions.[27] Chandross and Ferguson[28] found a very marked heavy-atom effect on the excimer fluorescence which can be explained by the increase in the intersystem crossing to the nearby triplet state of the excimer. Recently, the excimer phosphorescence of naphthalene has been observed in liquid solutions at low temperature.[29,30]

25) S. P. McGlynn and T. Azumi, *J. Chem. Phys.*, **40**, 507 (1964).
26) E. H. Gilmore, G. E. Gibson and D. S. McClure, *J. Chem. Phys.*, **23**, 399 (1955).
27) N. S. Bazilevskaya and A. S. Cherkason, *Opt. Spectry.*, **18**, 77 (1965).
28) E. A. Chandross and J. Ferguson, *J. Chem. Phys.*, **45**, 397 (1966).
29) J. Langelaar, R. P. H. Rettschnick, A. M. F. Lambooy and G. J. Hoytink, *Chem. Phys. Lett.*, **1**, 609 (1968).
30) G. Briegleb, H. Shuster and W. Here, *ibid.*, **4**, 53 (1969).

One possible explanation for the remarkable quenching of excimer fluorescence by oxygen is to take account of the smaller energy difference of excimer between the lowest singlet and triplet states compared to that of monomer.

The Relationship between the Oxygen Quenching and Peroxidation Reaction of Adsorbed Anthracene. Here we present the evidence for the formation of singlet oxygen ($^1\Delta_g$ or $^1\Sigma_g^+$) during the course of oxygen quenching by use of the well-established peroxidation reaction of anthracene with the singlet oxygen.[31] Anthracene adsorbed on silica gel was exposed to a known pressure of oxygen and irradiated with a 250 W high pressure Hg-lamp for five minutes at the wavelength of the first absorption band. The decrease in the first absorption band of anthracene due to the formation of anthracene peroxide was measured by use of the reflection method[1] as a function of oxygen pressure. The result is shown in Fig. 4 (a). The decrease of the anthracene absorption is seen to occur at low oxygen pressures where no fluorescence quenching is observed, although no decrease was observed by the irradiation of the sample without oxygen. This result has thus provided a rigorous experimental proof for the formation of singlet oxygen through the interaction between oxygen and triplet-state anthracene. The rate of peroxidation reaction showed a tendency to become independent of oxygen pressure in the region of high oxygen pressures where the fluorescence quenching begins to be observed and, no characteristic relationship was obtained between the rate of the peroxidation and the fluorescence quenching by oxygen. This seems to indicate that the singlet oxygen is not formed through the interaction with anthracene in the singlet excited state. However, further detailed experimental and theoretical investigations are necessary in order to establish the mechanism of fluorescence quenching by oxygen.

The authors are indebted to Professor N. Mataga and Mr. H. Ohari for the measurement of fluorescence lifetimes by use of a nanosecond flash apparatus.

31) B. Stevens and B. E. Algar, *J. Phys. Chem.*, **72**, 3468 (1968).