New Exciplex Emission of Pyrene and O_2 Co-deposited in Argon Matrices

Martin Kalb and Murthy S. Gudipati*

Institut für Physikalische Chemie, Universtiät zu Köln, Luxemburger Strasse 116, D-50939 Köln, Germany

Received: September 5, 1997; In Final Form: October 28, 1997

A new emission, broad and structureless, centered at 260 nm is observed by exciting Ar matrices containing 1% O_2 and ~0.2% pyrene at 183 nm ($5^1B_{2u} \leftarrow 1^1A_g$ transition in pyrene). The excitation spectrum measured by monitoring the emission at 260 nm is identical with the excitation spectrum measured by monitoring the fluorescence of pyrene itself at 366.8 nm ($1^1B_{2u} \rightarrow 1^1A_g$ transition in pyrene). We assign this new emission at 260 nm as being due to an exciplex of charge-transfer nature between pyrene and O_2.

Introduction

Photophysical, photochemical, and chemical interactions involving molecular oxygen (O_2) span all branches of chemistry,[1] physics,[2] and biology.[3] Ever since the observations by Evans,[4] by Tsubomura and Mulliken,[5] and by Lim and Kowalski,[6] the charge-transfer (CT) nature of exciplexes formed between organic molecules and O_2 is well-established.[7] Most recently Frei and co-workers[8] achieved stabilization of the CT states of complexes between O_2 and aliphatic hydrocarbons on the order of 2−3 eV by incorporating them in zeolites. Despite the growing interest in the CT nature of the interactions between O_2 and organic molecules,[7,8] the amount of literature that deals with quenching of the excited singlet and triplet states of aromatic molecules by O_2 outnumbers the former.[9]

CT states of organic molecule−O_2 (here on M•O_2) complexes have so far been studied in two extreme conditions. These are: (a) using an excess of O_2 as in the case of well-studied benzene•O_2 in the gas phase,[10] or benzene derivatives[11] and naphthalene[11b] in O_2 matrices, where the maximum of the CT absorption occurs at higher energies, but in O_2 matrices[11b] the onset of this absorption occurs at lower energies than the absorption due to the first excited singlet state of M; (b) using an excess of M as in the case of pure liquids of M saturated with O_2,[12] where the CT absorption is measured at much lower energies than the absorption due to the first excited singlet state of M. To study the nature of M•O_2 complexes it is necessary to generate isolated M•O_2, which, as noted by Grover et al.,[13] is difficult to realize. However, by using the matrix-isolation technique, it is possible to increase the probability of generating isolated M•O_2 by co-depositing M and O_2 diluted with rare gases. Due to the statistical nature of the formation of such M•O_2 complexes, it is expected that the spectral features due to M•O_2 would be much weaker than those due to M or O_2. It has been our aim to investigate these weak spectral features caused by the interactions between M and O_2 in rare-gas matrices.[14] In this paper we report first observation of exciplex emission from the CT state of a pyrene•O_2 contact complex in Ar matrices.

Experimental Section

All the experiments were carried out at the synchrotron radiation facility BESSY at Berlin, using a 3-m normal incidence monochromator (3m-NIM-1). The experimental setup has been described in an earlier publication in detail.[15] Premixed O_2:Ar (1:100) was passed through the sample chamber where pyrene was heat-sublimed through an aperture of the sample holder. The vapor−gas mixture was deposited on a LiF window at 20 K. The matrices produced by this procedure were optically clear and transparent. The ratio of pyrene and Ar was approximately 1:500, which we estimate from the residual pressure in the matrix chamber before and after heating the sample holder. Ar (99 999%), O_2 (99 995%), from Linde, and pyrene (99+%) (Gold Label) from Aldrich were used in these experiments. Polarized excitation and emission spectra were measured using a Glan UV polarizer (B. Halle, PGL-10) as described earlier.[16]

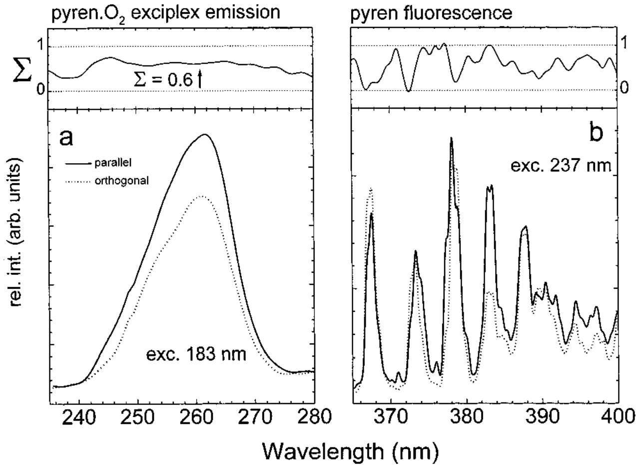

Figure 1. Polarized emission spectra and the corresponding Σ curves of 0.2% pyrene and 1% O_2 in Ar matrices. Matrices were irradiated (a) at 183 nm corresponding to the $5^1B_{2u} \leftarrow 1^1A_g$ transition of pyrene and (b) at 237 nm corresponding to the $2^1B_{1u} \leftarrow 1^1A_g$ transition of pyrene.

Results and Discussion

Emission spectra measured by irradiating an Ar matrix containing 1% O_2 and 0.2% pyrene are shown in Figure 1. The excitation spectra, which were recorded by monitoring the emission at 260 nm and the fluorescence of pyrene at 366.8 nm ($1^1B_{2u} \rightarrow 1^1A_g$ transition), are collected in Figure 2. The Σ curves shown in Figures 1 and 2 contain the information on the excitation transition moment directions with respect to the

---

* Corresponding author. E-mail: murthy@hartree.pc.uni-koeln.de. Fax: +49-221-470-5144.

S1089-5639(97)02912-5 CCC: $15.00

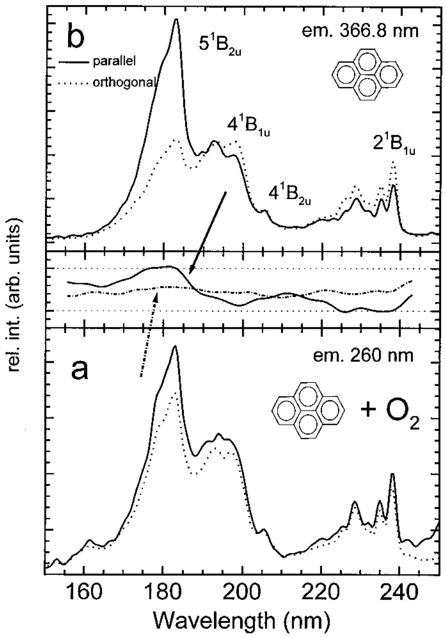

Figure 2. Polarized excitation spectra and the corresponding Σ curves of 0.2% pyrene and 1% O_2 in Ar matrices: (a) monitoring the CT emission and (b) monitoring the 0−0 band of pyrene fluorescence ($1^1B_{2u} \rightarrow 1^1A_g$ transition).

emission transition moment direction in the molecular coordinate system[16] and hence the information on the symmetry of the excited states. If a_x, a_y, and a_z are the direction cosines of the transition moment of excitation into S_n (*n*th singlet state) from S_0 and e_x, e_y, and e_z are the direction cosines of the emission transition moment ($S_1 \rightarrow S_0$), then $\Sigma = \cos^2(\phi) = (a_xe_x + a_ye_y + a_ze_z)^2$. S_n, S_1, and S_0 are here synonyms for any excited state, the emitting state, and the ground state, respectively. The limiting cases are $\Sigma = 1$ and 0, signifying parallel and orthogonal ($\phi = 0$ and 90) transition moment directions of excitation and emission, respectively.[16]

Both fluorescence (Figure 1b) and excitation (Figure 2b) spectra and their respective Σ curves of pyrene are in good agreement with our previous spectra.[16a] A comparison between parts a and b of Figure 2 clearly indicates that the emission at 260 nm (Figure 1a) results from excitation of pyrene molecules. In the absence of O_2, with only pyrene isolated in Ar matrices, we did not observe the emission at 260 nm when excited at 183 or 237 nm. The intensity of the band at 260 nm is approximately 300 times weaker than the fluorescence band at 366.8 nm. On the basis of these observations, we interpret the emission at 260 nm as being due to a contact CT complex between pyrene and O_2. Such an emission of a complex between an aromatic molecule and O_2 has not yet been reported in the literature.

Assuming that the ionization energies and electron affinities of molecules do not change significantly (see below) between the gas phase and in Ar matrices, we have used the well-known procedure to get the distance between centers of pyrene$^+$ and O_2^-. Using the equation $E_{CT} = I_D - A_A - (\Delta E_E - \Delta E_N)$, where I_D is the ionization energy of the donor, here pyrene (7.55 eV),[17] A_A, electron affinity of the acceptor, here O_2 (0.44 eV),[18] ΔE_N, energy of formation of unexcited complex (taken to be the same as in benzene·O_2, 0.045 eV[7b]), E_{CT}, the energy of the CT transition, here the emission observed at 260 nm, 4.77 eV, and the stabilization energy of the CT complex, ΔE_E, is calculated to be 2.385 eV. By substituting this value in the following equation

$$\Delta E_E = \frac{e^2}{R} = \frac{14.41}{R}\ (\text{eV})$$

where *R* is the electrical length of the dipole in Å, we obtain a distance of 6.04 Å between the centers of pyrene$^+$ and O_2^-. Keeping in mind that the data used above, except for E_{CT}, is pertinent only to the gas phase and that in rare-gas matrices the ionization energies may be higher (Rydberg states of some small molecules in rare-gas matrices are observed to be shifted by ~0.5 eV above the gas-phase values[19]), the *R* value derived here should not be overinterpreted. If, for example, we raise the ionization energy of pyrene by 0.3 eV to 7.85 eV, then we obtain $R = 5.37$ Å. Important to note here is that these *R* values lie close to that derived for benzene·O_2 at 5.0 ± 0.4 Å.[20]

We have used the polarized excitation and emission spectra and the Σ curves derived from these spectra to understand the nature of the CT complex in Ar matrices. Both the excitation and emission spectra that are pertinent to pyrene·O_2 show constant polarization effect, which is reflected in the Σ curves (Figures 1a and 2a). As the polarized spectra of isolated pyrene in the same matrix (by monitoring the fluorescence of pyrene, Figures 1b and 2b) and the corresponding Σ curves behave as expected,[16a] the Σ curves derived from the other set of spectra are real, not artifacts. The Σ curve derived from the polarized excitation spectra by monitoring the CT emission at 260 nm oscillates between 0.4 and 0.6. Hence, the transition moment direction of CT emission, which should be along the line joining the centers of pyrene$^+$ and O_2^-, makes an angle in the range between 40° and 50° with the transition moment directions of both the long-axis as well as short-axis polarized in-plane transitions of pyrene. It is important to note here that for any given transition, the Σ value derived is only an average of a spread of transition moment directions in an ensemble of molecules (or complexes) and does not give us the information on how wide this spread could be.[21] Rare-gas matrices are not amorphous solids but microcrystals with a face-centered cubic (fcc) lattice if the impurities are below 5%.[15] Pyrene, with molecular dimensions of 9.15 Å along the long axis and 6.72 Å along the short axis, respectively, is expected to orient itself in the (111) plane occupying a lattice position. The lattice constant of Ar crystal is 5.311 Å,[22] and a deformation of the lattice around pyrene is expected. Due to the deformation of the cavity around pyrene, irrespective of the ground-state orientation of the contact complex, the CT complex between pyrene and O_2 may reorient itself before the emission takes place. Thus the geometrical orientation derived from the polarized spectra may correspond to the minimum on the potential energy hypersurface of the CT state, at least to the extent permitted by the cavity in the Ar lattice.

We have extensively scrutinized all the other possibilities that may involve transfer of excitation energy from the high-lying 2^1B_{1u} state of pyrene to O_2, its dimer or impurity gases such as N_2, CO_2, CO, or H_2O. A broad and structureless emission centered at 260 nm is not observed in the spectroscopic studies of these species. The only other possibility is that the emission might be due to pyrene excimer, from a high-lying excimer state to the ground state. However, we did not observe the well-known excimer emission of pyrene from the lowest excimer state, which should have its maximum at 460 nm.[23] All these considerations leave us no other choice than to interpret the emission as being due to exciplex emission involving the CT state of a pyrene·O_2 contact complex.

Very recently the first attempt to get spectroscopic data of benzene·O_2 complex using ab initio theory has been carried out by Minaev et al.[24] Several CT states have also been computed by these authors. At 5.22 Å, close to the experimental distance between benzene and O_2, the predicted oscillator strengths of excitations from the ground state to the CT states are very weak, and at shorter distances (3.6 Å), though they become more significant, they are at least 10 times weaker than the oscillator strengths of locally excited (LE) states in benzene. Thus, observing only the LE states of pyrene in the excitation spectrum (lower part of Figure 2) is not surprising. Weak transition into the CT state may be buried under the LE transitions of pyrene. The onset of the CT emission at 240 nm indicates that this CT state should lie very close to the 2^1B_{1u} state of pyrene (onset at 240 nm, Figure 2). During the internal conversion process after excitation of pyrene, due to near degeneracy of these two states, an efficient internal conversion can occur from the 2^1B_{1u} state of pyrene (total spin multiplicity of the complex = 3) to the CT state, which should also be a triplet. The CT state can relax radiatively emitting a photon or relax to LE states of pyrene and O_2. The latter of these two processes is known in the literature.[25] Investigations are in progress to understand the nature of the contact complexes between aromatic molecules and O_2 in Ar, Kr matrices as well as in low-temperature organic glasses. Time-resolved measurements that are aimed at the lifetime of the CT state as well as the transient absorption of the CT complex are warranted to understand further the nature of the CT states of isolated complexes between O_2 and organic molecules.

Conclusions

A new emission at 260 nm has been observed from Ar matrices containing pyrene and O_2. The corresponding excitation spectrum is due to pyrene. We assigned this emission to a radiative transition from a CT state (pyrene$^+$·O_2^-) to the ground state of the contact complex. It has been found that the transition moment direction of the CT emission makes an angle in the range of 40°−50° with both long-axis and short-axis polarized in-plane transitions in pyrene. The same geometrical orientation has been interpreted as the minimum of the potential energy hypersurface of the CT state in the cavity of Ar lattice.

Acknowledgment. M.S.G. gratefully acknowledges the financial support and Habilitandenstipendium from Deutsche Forschungsgemeinschaft (Grant No. GU 413/2).

References and Notes

(1) Li, X.; Ramamurthy, V. *J. Am. Chem. Soc.* **1996**, *118*, 10666.

(2) Salloum, A.; Dubost, H. *Chem. Phys.* **1994**, *189*, 179.

(3) Freyer, W.; Leupold, D. *J. Photochem. Photobiol. B* **1995**, *30*, 77.

(4) Evans, D. F. *J. Chem. Soc.* **1953**, 345; **1957**, 1351, 3885; **1959**, 2753.

(5) Tsubomura, H.; Mulliken, R. S. *J. Am. Chem. Soc.* **1960**, *82*, 5966.

(6) Lim, E. C.; Kowalski, V. L. *J. Chem. Phys.* **1962**, *36*, 1729.

(7) (a) Gooding, E. A.; Serak, K. R.; Ogilby, P. R. *J. Phys. Chem.* **1991**, *95*, 7868. (b) Casero, J. J.; Joens, J. A. *J. Phys. Chem. A* **1997**, *101*, 2607.

(8) (a) Blatter, F.; Sun, H.; Frei, H. *Chem. Eur. J.* **1996**, *2*, 385. (b) Blatter, F.; Frei, H. *J. Am. Chem. Soc.* **1994**, *116*, 1812.

(9) (a) Wilkinson, F.; Abdel-Shafi, A. A. *J. Phys. Chem. A* **1997**, *101*, 5509. (b) Wirp, C.; Bendig, J.; Brauer, H.-D. *Ber. Bunsen-Ges. Phys. Chem.* **1997**, *101*, 961. (c) Bodesheim, M.; Schmidt, R. *J. Phys. Chem. A* **1997**, *101*, 5672. (d) Fu, Y.; Krasnovsky, A. A., Jr.; Foote, C. S. *J. Phys. Chem. A* **1997**, *101*, 2552. (e) Sato, C.; Kikuchi, K.; Okamura, K.; Takahashi, Y.; Miyashi, T. *J. Phys. Chem.* **1995**, *99*, 16925.

(10) Birks, J. B.; Pantos, E.; Hamilton, T. D. S. *Chem. Phys. Lett.* **1973**, *20*, 544.

(11) (a) Rest, A. J.; Salisbury, K.; Sodeau, J. R. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 265, 1396. (b) Hashimoto, S.; Akimoto, H. *J. Phys. Chem.* **1989**, *93*, 571.

(12) Scurlock, R. D.; Ogilby, P. R. *J. Phys. Chem.* **1989**, *93*, 5493.

(13) Robb Grover, J.; Hagenow, G.; Walters, E. A. *J. Chem. Phys.* **1992**, *97*, 638.

(14) Gudipati, M. S.; Kalb, M. *Chem. Phys. Lett.* **1997**, *268*, 169.

(15) Gudipati, M. S. *Chem. Phys.* **1995**, *201*, 451.

(16) (a) Gudipati, M. S.; Daverkausen, J.; Hohlneicher, G. *Chem. Phys.* **1993**, *173*, 143. (b) Gudipati, M. S.; Maus, M.; Daverkausen, J.; Hohlneicher, G. *Chem. Phys.* **1995**, *192*, 37.

(17) Lesclaux, R.; Joussot-Dubien, J. In *Organic Molecular Photochemistry*; Birks, J. B., Ed.; John Wiley: London, 1973; Vol. 1, p 462.

(18) Drzaic, P. S.; Marks, J.; Brauman, J. I. in *Gasphase Ion Chemistry;* Bowers, M. T., Ed.; Academic Press: Orlando, FL, 1984; Vol. 3, p 167.

(19) Chergui, M.; Schwentner, N. *Chem. Phys. Lett.* **1994**, *219*, 237.

(20) Birks, J. B. In *Organic Molecular Photochemistry*; Birks, J. B., Ed.; John Wiley: London, 1973; Vol. 2, p 520.

(21) Michl, J.; Thulstrup, E. W. *Spectroscopy with Polarized Light*; VCH: New York, 1986.

(22) Jodl, H. J. In *Chemistry and Physics of Matrix-Isolated Species*; Andrews, L., Moskovits, M., Eds.; North-Holland: Amsterdam, 1989; p 343.

(23) Förster, T.; Kasper, K. *Z. Elektrochem.* **1955**, *59*, 976.

(24) Minaev, B. F.; Mikkelsen, K. V.; Ågren, H. *Chem. Phys.* **1997**, *220*, 79.

(25) Kristiansen, M.; Scurlock, R. D.; Iu, K.-K.; Ogilby, P. R. *J. Phys. Chem.* **1991**, *95*, 5190.