CHEMISTRY LETTERS, pp. 1339-1340, 1989.

Photochemistry in the Adsorbed State. Energy Transfer from Electronically Excited SO_2 to 1,6-Diphenyl-1,3,5-hexatriene

Masakazu ANPO,* Yasushi YAMAMOTO, and Satoshi SUZUKI+
Department of Applied Chemistry, College of Engineering,
University of Osaka Prefecture, Sakai, Osaka 591
+Department of Industrial Chemistry, Faculty of Engineering
Shinshu University, Wakasato, Nagano 380

Photoluminescence spectrum of 1,6-diphenyl-1,3,5-hexatriene adsorbed on porous Vycor glass has been studied in the absence and presence of SO_2, O_2, N_2, or N_2O. The yields of the phosphorescence increase with increasing the amount of added SO_2, but not with added O_2, N_2, or N_2O, indicating that an intermolecular energy transfer occurs from the electronically excited SO_2 to 1,6-diphenyl-1,3,5-hexatriene in the adsorbed layer.

The photochemistry and photophysics on solid surfaces and/or in the adsorbed layer have recently been given considerable attention in connection with the most important and promising subject of functionalizing solid surfaces.1) However, there seems to be few reports concerning the intermolecular energy transfer in the adsorbed state, except for the energy transfer between the excited molecules and oxygen which leads to the efficient quenching of the emission.2)

Although it is well known that the electronically excited SO_2 sensitizes the isomerization of the olefins in the gas phase3-5) and in the adsorbed layer,6) there is no report about direct evidence for the energy transfer in the sensitized photoluminescence system. In the present work, we have investigated the photoluminescence of 1,6-diphenyl-1,3,5-hexatriene (DPH) adsorbed on porous Vycor glass in the presence of SO_2, O_2, N_2, or N_2O molecules and observed direct evidence for the intermolecular energy transfer between the electronically excited SO_2 and DPH.

Porous Vycor glass (PVG) (Corning, code No. 7930, major composition: SiO_2, BET surface area: 150 m^2/g) was used as an adsorbent. Prior to the adsorption of DPH, PVG was degassed (dehydrated) at 473 K for 10 h. The adsorption of DPH was done from methanol solution of DPH. The surface coverage of adsorbed DPH was to be 0.01. Each gas of SO_2, O_2, N_2, and N_2O was introduced onto the samples at 298 K.

Figure 1 shows the photoluminescence spectra at 77 K of DPH adsorbed on PVG in the absence (spectrum; 1) and the presence of added SO_2 (spectra; 2-4), N_2 (spectrum; 1), N_2O (spectrum; 1), and O_2 (spectra; 5-7). The emissions show the peak at around 435 nm, being assigned to the phosphorescence of DPH on the basis of a large temperature dependence in the yield and its peak position.7) O_2 leads to a decrease in intensity of the phosphorescence, i. e., efficient quenching of the phosphorescence, its extent depending on the amount of added O_2. On the evacuation of the system at 295 K, the decreased intensity recovered completely to the initial level. Quenching of DPH by O_2 might be contributed to the formation of $^1O_2^*$.7) The phosphorescence scarcely changes by the addition of N_2 and N_2O, even with the excessive amounts of N_2O or N_2.

On the other hand, the intensity of the phosphorescence of DPH is drastically enhanced by added SO_2 (spectra; 2, 3). The intensity of the phosphorescence increased with the amounts of added SO_2. On the evacuation of the system at 295 K after the enhancement of the emission, the enhanced phosphorescence decreased in intensity. However, the recovery in the intensity was not complete (spectrum; 4), the intensity being still higher than that of the original one, suggesting that the interaction of SO_2 with the surface is quite strong. It is known that SO_2 has a weak absorption at around 260-320 nm, which overlaps with the excitation wavelength for the emission, and a lowest excited triplet state at around 3.2 eV (at around 380 nm).8)

From these results, it is clear that the enhancement of the phosphorescence of DPH adsorbed on PVG by added SO_2 is not a physical phenomenon such as light scattering but a chemical one, suggesting that the energy transfer occurs from the excited SO_2 to DPH in the adsorbed layer. In fact, Morikawa and Otsuka6) have found that the isomerization of 2-butene is induced by the electronically excited SO_2 on PVG.

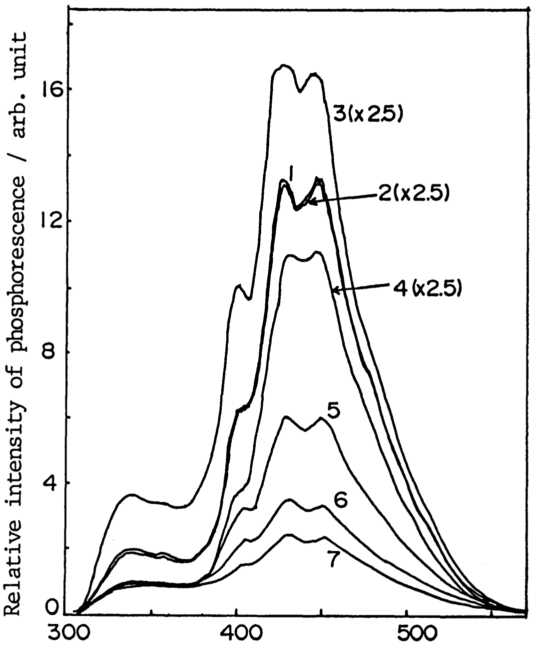

Fig. 1. Phosphorescence spectra of DPH adsorbed on PVG in the absence (1) and presence of SO_2 (2-4), N_2 (1), N_2O (1), and O_2 (5-7). (excitation; 300 nm, temperature; 77 K, amounts of added molecules (in 10^{-6} mol/g); SO_2, 2; 9.9, 3: 129, 4: after evacuation at 298 K for 20 m of (3); O_2, 5: 69, 6: 198, 7: 320, N_2, 1: excess; N_2O, 1: excess)

Thus, the results obtained in the present work first show a direct evidence for the intermolecular energy transfer from the excited SO_2 to DPH in the adsorbed layer. It is likely that the characteristic strong coadsorption of DPH and SO_2 plays a significant role in the occurrence of the intermolecular energy transfer in the adsorbed state.

References

1) M. Anpo, Chem. Lett., 1987, 1221; their earlier series.
2) M. Anpo, "Photochemistry on Solid Surfaces," Elsevier, Amsterdam, p. 120 (1989).
3) R. B. Cundall and T. F. Palmer, Trans. Faraday Soc., 56, 1211 (1960).
4) R. D. Penzhorn and H. Gusten, Z. Naturforsh., A, 27, 1401 (1972).
5) K. L. Demerjian and J. G. Calvert, Int. J. Chem. Kinet., 7, 45 (1975).
6) K. Otsuka, M. Fukaya, and A. Morikawa, Bull. Chem. Soc. Jpn., 51, 367 (1978).
7) S. K. Chattopadhhyay, C. V. Kumar, and P. K. Das, J. Phys. Chem., 89, 670 (1985); S. K. Chattopadhyay, P. K. Das, and G. L. Hug, J. Am. Chem. Soc., 104, 4507 (1982).
8) S. Wolfgang and H. D. Gafney, J. Phys. Chem., 87, 5395 (1983).

(Received April 14, 1989)