

Surface Photochemistry: Translational Motion of Organic Molecules Adsorbed on Silica Gel and Its Consequences¹

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Abstract: The occurrence of inter- and intragranular motion of aromatic hydrocarbons on dry silica gel has been demonstrated. Evidence presented includes (a) the observation of dimerization of acenaphthylene in static and agitated systems to give cis and trans isomers; (b) the quenching and sensitization of the dimerization of acenaphthylene; (c) the dimerization of 9-cyanophenanthrene; (d) the quenching of pyrene emission by 2-halonaphthalenes, with a linear plot of $\tau_0/\bar{\tau}$ vs. halonaphthalene concentration; (e) the equilibration of adsorbed pyrene as regards preferred sites, from a study of the emission decay characteristics, as well as those of anthracene and 9-cyanophenanthrene; (f) the direct (static) observation of pyrene diffusion by observation of translational movement using its emission; (g) a direct, kinetic demonstration of intergranular movement of adsorbed acenaphthylene and pyrene between grains of silica gel of different sizes; and (h) the demonstration, by the fluorescence quenching of pyrene, of the intergranular motion of 2-bromonaphthalene. These studies provide the first qualitative data for diffusion rates on silica gel, that from (b) and (d) being in agreement, and reveal the possibilities for photochemical and photophysical studies in the adsorbed state.

Introduction

The study of photochemistry of organic molecules adsorbed on surfaces is in its infancy. Indeed, there is little recorded about the general physical behavior of other than small molecules in their ground states when adsorbed on an inorganic surface, such as silica gel, alumina, porous Vycor, etc.; photochemical studies of any kind are sparse⁴⁻⁷ and reveal little, as yet, about the restrictions on motion, rotational and translational, imposed by the surface, although the nature of the binding forces has been studied extensively.⁸ In the particular case of silica gel, in general it is assumed that there are two kinds of surface functions: the silanol and siloxane groups. In addition, it is recognized that the silanol functions may be isolated, vicinal or geminal. Klein has included the hydrated silanol function in which water acts as a bridge in binding.^{8b} According to Kisilev⁹ and Snyder^{8c} the principal sites responsible for the adsorption of organic molecules on silica gel

consist of surface silanol groups and the forces responsible for the adsorption have been assumed to be electrostatic interactions,^{8c} hydrogen bonding,^{8c,9} and dispersion forces.^{4a} The siloxane functions may contribute. The nature and degree of the interactions must depend on the organic molecule as well as the activation treatment of the silica gel.^{7c} Highly polar materials can be considered anchored; i.e., they have a high activation energy for breaking binding forces. Aromatic hydrocarbons are more loosely held and benzene, for instance, has been claimed to show high mobility.^{10,11}

The mobility of radicals has been studied using EPR.¹²⁻¹⁴ From the line width and shape of the resonance signal it was concluded that there was both rotational and translational movement. The silica gel surface, however, is not homogenous, and the effect of this inhomogeneity has not been determined; the conclusions reached may be oversimplified. Recently, chemical evidence for translational movement in monocyclic aromatic radical pairs generated on silica gel has been adduced,¹⁵⁻¹⁷ but radicals cannot be taken as models for closed-shell systems. The basic questions remain: Do medium-sized molecules migrate on dry silica gel? In the lifetime of a photochemically excited species can translational movement of it, or its closed-shell ground state, occur? And, if so, is all movement intragranular, or can intergranular migration take place also? It is the purpose of this report to provide photochemical and photophysical evidence to answer these questions conclusively for certain polycyclic aromatic systems.¹⁸ Since many types of evidence will be provided, the results and discussion will be presented in sections.

Results and Discussion

Irradiation of Acenaphthylene. The irradiation of acenaphthylene (1) in solution gives the cis (2) and trans (3) dimers.¹⁹ The

(1) Publication No. 281 from the Photochemistry Unit, University of Western Ontario.

(2) On sabbatical from N. Copernicus University, Torun (Poland).

(3) On leave from Adam Mickiewicz University, Poznan (Poland).

(4) On silica gel slurries in cyclohexane: (a) Nicholls, C. H.; Leermakers, P. A. *Adv. Photochem.* **1971**, *8*, 315. (b) Donati, M.; Fiorenza, M.; Sarti-Fantoni, P. *J. Heterocycl. Chem.* **1979**, *16*, 253. (c) Kiefer, E. F.; Carlson, D. A. *Tetrahedron Lett.* **1967**, 1617. (d) Griffiths, J.; Hart, H. *J. Am. Chem. Soc.* **1968**, *90*, 5296. (e) Fassler, D.; Gade, R.; Guenther, W. *J. Photochem.* **1980**, *13*, 44. (f) Fassler, D.; Gade, R.; Guenther, W. *Z. Chem.* **1980**, *20*, 229, and papers there cited. (g) Kortum, G.; Braun, K. *Justus Liebig's Ann. Chem.* **1960**, 632, 104.

(5) On dry silica gel: (a) Werbin, H.; Stron, E. T. *J. Am. Chem. Soc.* **1968**, *90*, 7296. (b) Balny, C.; Douzou, P. *C. R. Acad. Sci., Ser. C* **1967**, *264*, 477. (c) Balny, C.; Djaparidze, K.; Douzou, P. *Ibid.* **1967**, *265*, 1148.

(6) On porous Vycor: (a) Otsuka, K.; Fukaya, M.; Morikawa, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 367. (b) Otsuka, K.; Morikawa, A. *Ibid.* **1974**, *47*, 2335. (c) Anpo, M.; Wada, T.; Kubokawa, Y. *Ibid.*, **1977**, *50*, 31, and earlier papers in this series.

(7) On alumina: (a) Moesta, H. *Discuss. Faraday Soc.* **1974**, *58*, 244. (b) Eden, C.; Shaked, Z. *Isr. J. Chem.* **1975**, *13*, 1. (c) Hecht, H. G.; Crackel, R. L. *J. Photochem.* **1981**, *15*, 263. (d) Hecht, H. G.; Jensen, J. L. *Ibid.* **1978**, *9*, 33. (e) Oelkrug, D.; Radjaipour, M.; Erbse, H. Z. *Phys. Chem. (Frankfurt Am Main)* **1974**, *88*, 23. (f) Oelkrug, D.; Erbse, H.; Plauschinat, M. *Ibid.* **1975**, *96*, 283. (g) Oelkrug, D.; Schrem, G.; Andra, L. *Ibid.* **1977**, *106*, 197. (h) Oelkrug, D.; Plauschinat, M.; Kessler, R. W. *J. Lumin.* **1979**, *18/19*, 434. (i) Oelkrug, D.; Radjaipour, M. Z. *Phys. Chem. (Frankfurt Am Main)* **1980**, *123*, 163. (j) Kessler, R. W.; Wilkinson, F. J. *Chem. Soc. Faraday Trans. 1* **1981**, *77*, 309. (k) Ishida, H.; Takahashi, H.; Tsubomura, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3130.

(8) See, for example: (a) Klemm, L. H.; Antoniadis, E. P.; Capp, G.; Chiang, E.; Mak, E. Y. K. *J. Chromatogr.* **1961**, *6*, 420. (b) Klein, P. D. *Anal. Chem.* **1962**, *34*, 733. (c) Snyder, L. R. *J. Phys. Chem.* **1963**, *67*, 2622. (d) Kondo, S.; Tomoi, K.; Pak, C. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2046. (e) Boehm, H. P., *Adv. Catal.* **1966**, *16*, 179.

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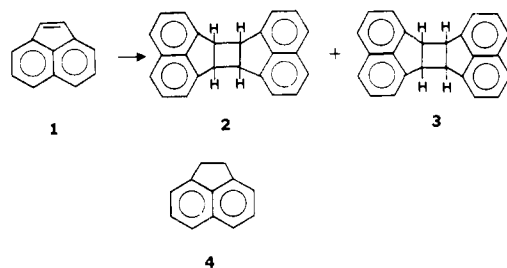
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(18) A small part of this material from the subject of a preliminary communication: Mayo, P. de; Okada, K.; Rafalska, M.; Weedon, A. C.; Wong, S. K. *J. Chem. Soc., Chem. Commun.*, **1981**, 820.

(19) For a review, see: Cowan, D. O.; Drisko, R. L. "Elements of Organic Photochemistry"; Plenum Press: New York, 1976; pp 435-443.



singlet has been shown to give **2** while the triplet gives both **2** and **3** in comparable amounts. Increasing the concentration of acenaphthylene increases the encounter probability of singlet and ground-state species before intersystem crossing to the triplet can occur, resulting in higher cis/trans ratios.

When dried silica gel coated with **1** was irradiated, the powder being tumbled during irradiation, the dimers **2** and **3** were formed. In principle, dimerization could occur via (a) a kinetic bimolecular encounter process, (b) reaction of nearest neighbors, even at low coverage because of possible nonhomogeneous distribution of the acenaphthylene, and (c) molecular intergranular encounters caused by tumbling. In the first case as in solution, the ratio of **2**:**3** should vary linearly with increasing coverage, until such a point that either (i) the surface, as experienced by the migrating molecule, is changed significantly (steric interference could be one such case) or (ii) all excited acenaphthylene molecules formed have then an adjacent ground-state molecule with which to react. In the former situation, the consequences are not easy to predict; in the latter, depending on the relative rate constants for reaction as compared with intersystem crossing to the triplet and its deactivation, a plateau should be reached. If the second case (b) obtains, then the ratio should not change with coverage. The system c will be discussed later.

The observed results are shown in Figure 1. The ratio does vary with coverage, approximately linearly up to 15%²⁰ ($r = 0.995$; conversion, 1–9%). At above 40% the curve flattens to an asymptote of about 21 for **2**:**3**. This might be interpreted as being indicative of a proportion of **3** formed from the singlet (in this case ~5%), but triplet quenching studies, to be described, predict a ratio of >39 (>2.5% **3**), and from the ratio of **2**:**3** obtained from the pure triplet (0.59) it follows that, at the plateau, the reaction is derived 95–97% from the singlet and 3–5% from the triplet. Above 40% coverage only the number of “nearest-neighbor” reactive molecules increases (case b). During the lifetime of the singlet (~1 ns²¹) rotation of the excited member of the juxtaposed pairs prior to dimerization or eximer formation¹⁹ allows for leakage to the triplet in at least some of the pairs. It seems improbable that the singlet can react in other than essentially already juxtaposed pairs, which suggests that at low coverage these already may exist in greater amount than statistical, i.e., that the distribution is nonhomogeneous.

Coadsorption of the structurally similar acenaphthene **4** with **1** should change the relative molecular distribution, and reduce the number of nearest-neighbor **1** molecules. The cis/trans dimer ratio, as a function of surface coverage of **1** in the presence of **4**, is shown in Figure 1, the total amount of **1** + **4** being ~1.46 mmol/g of silica gel (60% coverage). In fact, the cis/trans dimer ratio is *smaller* in the relevant low **1** coverage region (<30%) in the presence than in the absence of **4**, strongly suggesting that there is, indeed, a reduction of nearest-neighbor **1** pairs, and that dimerization is now taking place from the longer lived triplets. The straight-line plot below 15% coverage in the absence of **4** does not require that reaction of both singlet and triplet occur in a kinetic encounter (case a), but supports the view that because of inhomogeneous distribution, the short-lived singlet affords dimer by nearest-neighbor reaction (case b).

(20) Assuming homogeneous distribution 15% coverage is equivalent to about 0.4 M in three dimensions, with an average molecular separation of ca. 16 Å.

(21) Assuming the lifetime be the same as in solution: Castellan, A.; Dumartin, G.; Bouas-Laurent, H. *Tetrahedron* **1980**, *36*, 97.

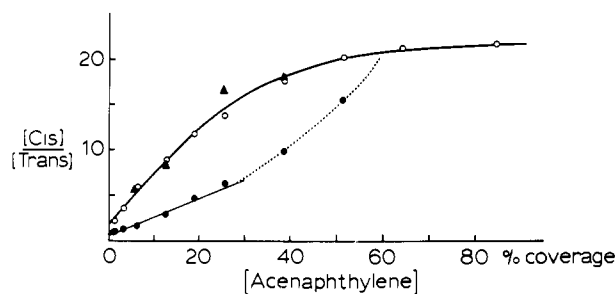


Figure 1. Plot of isomer ratio against acenaphthylene coverage: (O) with tumbling, (▲) without tumbling, (●) with tumbling in the presence of acenaphthene (total coverage: 1.46 mmol/g of silica gel).

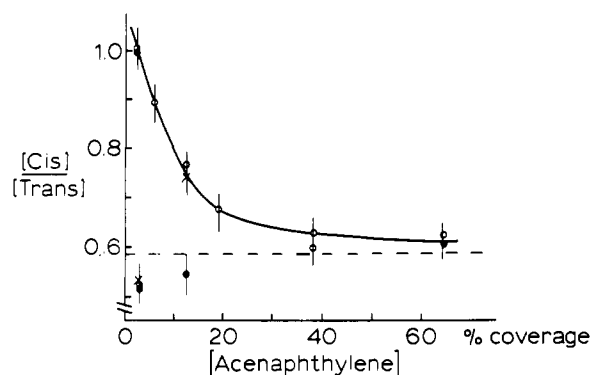


Figure 2. Plot of isomer ratio derived from sensitization against acenaphthylene coverage (—) in the absence of acenaphthene (- - -) in the presence of acenaphthene using (●) Rose Bengal, (○) Eosin Y, (X) Acridine Orange as sensitizer.

As in solution,¹⁹ the dimerization could be sensitized. Using Rose Bengal ($E_T = 44.6$ kcal/mol), Eosin Y ($E_T = 46.8$ kcal/mol), or Acridine Orange ($E_T = 49.2$ kcal/mol)²² (see Figure 2) at low coverages (~0.1%) with acenaphthylene 64.5% coverage (1.5×10^{-3} mole/g silica gel), as in solution,¹⁹ a mixture of **2** and **3** was produced. Even at 10% conversion one molecule of Rose Bengal (~114 Å²;²³ 1.38×10^{-6} mol/g of silica gel) sensitized >57 molecules of acenaphthylene (~53 Å²²³) (see also, “static” conditions, below). Such an efficiency cannot be attained with the closest packing possible. Assuming energy transfer is effective at 5 Å, less than 20% of the observed dimerization could occur, and the efficiency found is most probably not the maximum obtainable. In any event, such close packing could not be induced by the mere presence of the sensitizer, and the results of the direct irradiation require a substantial number of separated molecules. These results, therefore, also require that translational movement of monomer and dimer on the time scale of the triplet lifetime occur.

Although, as will be shown, intergranular transfer (case c above) occurs under “tumbling” conditions, it must play a minor role in the kinetic phenomena observed. This is shown by the fact that irradiation of adsorbed acenaphthylene on silica gel in a stationary thin layer gave the points in Figure 1; they fall on the same curve as that obtained by tumbling. Further, the sensitized dimerization could also be induced under the same “static” conditions: 368 acenaphthylene molecules could be excited by one Rose Bengal molecule (64.5% conversion at 64.5% coverage). Finally, the cis–trans ratio of dimers obtained at high conversion (71–74%) by tumbling²⁴ and static were essentially the same [2.9–3.2 (direct irradiation) and ca. 0.6 (sensitized)].

In Figure 2 is shown the change of **2**:**3** ratio of the sensitized reaction with coverage: the ratio decreases from 1.0 to 0.6 (at about 30% coverage). Since only the triplet is reacting, this change

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(23) Calculated from the projected area of a space model.

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Table I. Quenching of 2 and 3 Formation by Ferrocene^a

ferrocene concn ^b	$\frac{C}{T}$	$\frac{[\text{cis}]_0}{[\text{cis}]_q}$	$\frac{[\text{trans}]_0}{[\text{trans}]_q}$
0	9.12	1.00	1.00
0.57	14.9	1.03	1.53
1.14	14.5	1.67	2.51
1.72	23.8	1.36	3.35
2.29	28.2	1.25	3.66
2.86	39.2	1.36	5.61

^a The acenaphthylene concentration was 5.64×10^{-9} mol (dm)⁻² equivalent to 48.0 mg/g of silica gel (12.9% coverage). ^b The ferrocene concentration is expressed in 10^{-10} mol (dm)⁻². The concentrations corresponds to 0, 0.596, 1.19, 1.79, 2.38, and 2.98 mg/g of silica gel, respectively.

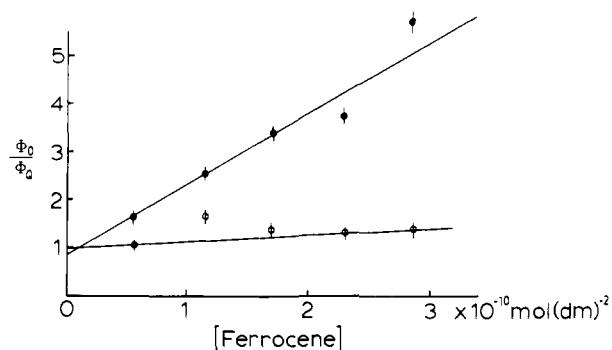


Figure 3. Stern-Volmer plot of the quenching of acenaphthylene in cis (O) and trans (●) dimer formation by ferrocene.

cannot be attributed to the previously discussed inhomogeneous distribution. A clue is provided by the fact that it has been recorded²⁵ that the triplet dimerization is solvent-polarity dependent, a higher value of 2:3 being obtained with polar solvents. If the surface of silica gel itself is considered polar, then higher coverage may reduce the polarity for the acenaphthylene itself.²⁶ If this is the case, the addition of 4, similar in polarity to acenaphthylene, should decrease the ratio of 2:3 to that found at higher acenaphthylene coverages. This proved to be the case: varying the proportion of 1 to 4, maintaining a total 60% coverage, gave an essentially constant ratio of 2:3 (Figure 2) of ~0.55–0.63. The direct irradiation in the presence of 4 (Figure 1) gave a straight-line plot up to ca. 25% coverage ($r = 0.995$) and an intercept of 0.44 ± 0.13 . This intercept at "infinite dilution" should arise from triplet reaction (in the presence of 4) and the agreement found with the sensitized reaction in the presence of acenaphthene is good.

In solution, oxygen has been reported to quench acenaphthylene triplet^{19,21,27} and essentially suppresses the formation of 3: the same observation has been made on silica gel. In aerated 0.4 M methanol solution $\phi = (3.75 \pm 0.14) \times 10^{-2}$. Determined in apparatus described elsewhere,²⁸ with 3, 14, and 27% coverage,²⁰ the values of ϕ found were (1.1 ± 0.15) , (4.3 ± 0.6) , and $(7.9 \pm 1.2) \times 10^{-2}$, respectively, the increased quantum yield reflecting an increased "nearest neighbor" concentration.

The dimerization of acenaphthylene ($E_T = \text{ca. } 46 \text{ kcal/mol}^{29}$) could be quenched by the triplet quencher ferrocene ($E_G < 43 \text{ kcal/mol}$). The results are given in Table I. The Stern-Volmer

(25) Hartmann, I. M.; Hartmann, W.; Schenck, G. O. *Chem. Ber.* **1967**, *100*, 3146.

(26) Leffler¹⁶ has observed that the rate constant for loss of nitrogen from azocumene depends on surface coverage. This assumes importance at about 30% coverage with a "hydroxylated" silica gel, but not with a dehydrate gel. This phenomenon may also be attributed to a surface polarity change with coverage; Leffler prefers an "active site" rationalization.

(27) Livingston, R.; Wei, K. S. *J. Phys. Chem.* **1967**, *71*, 541. Wei, K. S. Thesis, University of Minnesota, 1966.

(28) Lazare, S.; Mayo, P. de; Ware, W. R. *Photochem. Photobiol.* **1981**, *34*, 187.

(29) Cowan, D. A.; Koziar, J. C. *J. Am. Chem. Soc.* **1975**, *97*, 249.

Scheme I

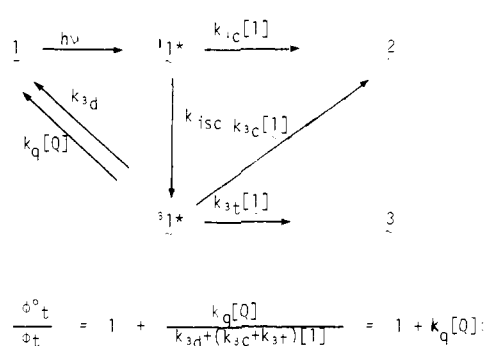


Table II. Percentage Conversion on Irradiation of Adsorbed 5

coverage (%)	temp (°C)	conditions	conversion (%)
24	10	undegassed	<1
	10	degassed	2
50	65	undegassed	<1
	68	degassed	12
	10	undegassed	<1
65	10	degassed	5
	65	undegassed	18
	68	degassed	18

Table III. Effect of Temperature on the Quantum Yield of Dimerization of 5^{a,b}

solvent	temperature (°C)			
	10	18	48	75
propanol	0.054 ± 0.002	0.055 ± 0.004	0.081 ± 0.006	0.091 ± 0.004
	(2.85 cP)	(2.30 cP)	(1.17 cP)	(0.76 cP)
methanol	0.088 ± 0.002		0.127 ± 0.003	
	(0.68 cP)		(0.40 cP)	

^a Concentration $4.0 \pm 0.2 \times 10^{-3}$ M. ^b Viscosity in centipoises in parentheses.

plots for the quenching of 2 and 3 are shown in Figure 3 (see Scheme I and ref 19). The slope for the trans isomer 3 is an indication of the value of $k_q\tau$ provided that the singlet excited state leads essentially to the isomer 2. This assumption is reasonable since a ratio of 39 (97% selectivity) is obtained experimentally at the maximum ferrocene concentration (2.86×10^{10} mol (dm)⁻²) at a concentration of acenaphthylene of 5.64×10^{-9} mol (dm)⁻², or 13% coverage. The lifetime in solution of triplet acenaphthylene (2.15×10^{-6} s) is abnormally short (three or more orders of magnitude shorter than naphthalene), which is determined in part by impurity quenching and bespeaks the existence of an especially rapid unimolecular radiationless decay mechanism. Such is unlikely to be greatly affected by adsorption of the molecule on silica gel. Using the value from solution, we obtain a value of k_q of 7.02×10^{15} (dm)² mol⁻¹ s⁻¹. Quenching is probable on every encounter, since diffusional apart will be slow, and so this value represents the diffusional rate constant for a molecule of ferrocene and acenaphthylene toward each other. Obviously, the value of the diffusion rate depends on the substances, but it is gratifying that the value found is of the order reported (see Table IV) for the quenching of singlet pyrene by iodo- and bromonaphthalene. Such a rate constant suggests that, at the concentration used, acenaphthylene, as already surmised, may move ~2 Å during the singlet lifetime, or as the singlet, whereas as the triplet or in the triplet lifetime, it may move ~300 Å.

Dimerization of 9-Cyanophenanthrene. The dimerization of 9-cyanophenanthrene (5) in ethanolic solution has been reported.³⁰ The reaction proceeds via the singlet state³¹ and is inhibited by

(30) Sargen, M. V.; Timmons, C. J. *J. Chem. Soc.* **1964**, 5544.

(31) Castellan, A. Thesis, University of Bordeaux, 1974.

oxygen. Adsorbed on silica gel at 24 and 50%³² coverage, the dimerization was initiated by irradiation ($\lambda > 350$ nm) at 10^9 both degassed and nondegassed under standard conditions. No product could be detected in the nondegassed samples (Table II), whereas 2 and 5% dimerization was found at 24 and 50% coverage, respectively, from the degassed samples. With raised temperature (65–68 °C) there was again no reaction in the undegassed samples, whereas the conversion in the degassed samples had risen to 12 and 18%. The effect of heat could be interpreted in two ways: either as an activation energy for reaction or an activation energy for motion. Were it the former, the same should be observed in solution. The dimerization in methanol and in propanol was accordingly examined (Table III). It was found that in *n*-propanol the quantum yield almost doubled over the range 10–75 °C. However, the viscosity dropped also. An increase in quantum yield dimerization was also observed over the range 10–48 °C for methanol. However, the quantum yields in propanol at 75 °C and in methanol at 10 °C, where the viscosities are similar, were also close. We conclude that in solution the activation energy is that for diffusional motion, and that the same is true for the adsorbed molecules. The possibility of movement in the case of **5** exists because, although more strongly adsorbed than **1**, it has a lifetime one order of magnitude longer.

1,1'-Binaphthyl. The emission spectrum of 1,1'-binaphthyl (**6**) adsorbed on silica gel (8×10^{-7} mol/g) has the same shape and is in the same region (λ_{\max} 360 nm) as that of a solution in cyclohexane. The same is true for the excitation spectrum. When the silica gel sample was cooled to 77 K, the emission shifted <5 nm to shorter wavelength.

The UV absorption spectrum of **6** and the emission spectrum in glassy matrix at liquid nitrogen temperature are similar to those of naphthalene. The emission spectrum, however, at room temperature is broad and structureless and is shifted more than 50 nm to longer wavelength than that of the corresponding naphthalene emission.³³ This peculiar characteristic is attributed to the rotation of the two naphthalene moieties in **6** to a more coplanar conformation in the excited state at room temperature. The emission characteristics of **6** adsorbed on silica gel indicate that rotation into the plane is still occurring. The rate of this rotation was not reduced significantly by lowering the temperature since the emission spectra on silica gel was not much affected by cooling to 77 K; that is, molecules adsorbed on silica gel can still undergo rotational motion.

Quenching of Pyrene Emission by Halonaphthalenes. As reported earlier,³⁴ and discussed below, the emission decay of pyrene adsorbed on silica gel was not a single exponential. Usually the decay in the presence of various amounts of quencher could be described well by the rate law: $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$. The values of A_1 , A_2 , τ_1 , and τ_2 varied from one measurement to another, but it was found that the mean lifetime, $\bar{\tau}$, given by eq 1, was constant to within $\pm 0.5\%$ throughout the

$$\bar{\tau} = P_1\tau_1 + P_2\tau_2 = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2) \quad (1)$$

measurement. In eq 1, P_i refers to the fraction of the emission having lifetime τ_i . Emission measurements were made one day after sample preparation. Typically, $\tau_0 = 250$ ns for samples which had been shaken for 5 h (see below) and $\tau_0 = 290$ ns for undisturbed samples. If the lifetime measurement was taken about 2 weeks after sample preparation, τ_0 was ~ 250 ns for the undisturbed sample also. This decrease may be, in part, attributed to the slow degassing of adsorbed oxygen on the silica gel.

The emission spectrum of pyrene on silica gel was slightly affected by the presence of the coadsorbed quencher. Figure 4 shows the effect of 2-chloronaphthalene on the emission of pyrene.

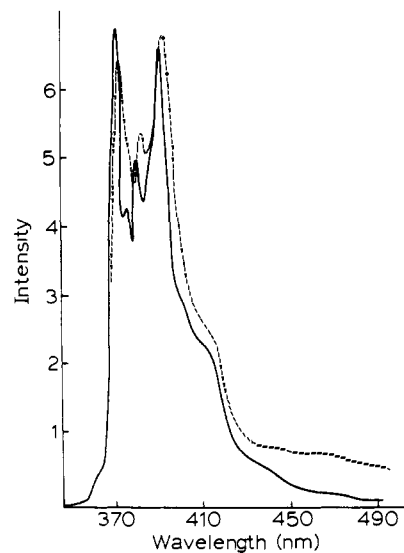


Figure 4. Emission spectra of adsorbed pyrene (5.0×10^{-6} mol/g of silica gel, 1% coverage) in the absence (—) or in the presence (---) of 2-chloronaphthalene (1.7×10^{-4} mol/g of silica gel).

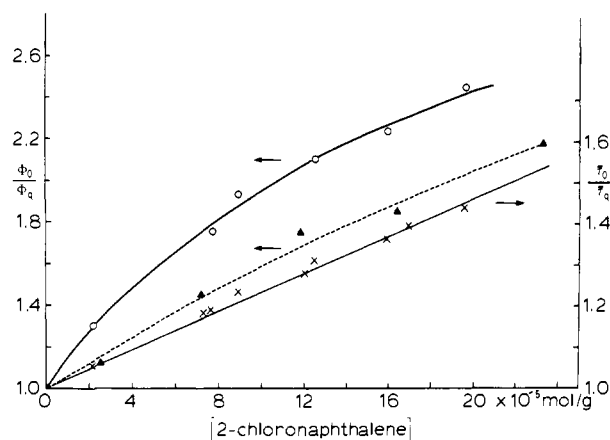


Figure 5. Stern-Volmer plot of quenching of pyrene fluorescence intensity (O, ▲, without tumbling, after tumbling for 5 h, respectively) and lifetime (X) by 2-chloronaphthalene.

The vibrational structure in the pyrene monomer region (370–400 nm) became more diffuse and was slightly red-shifted. Furthermore, the intensity of emission in the excimer region (450–500 nm) was increased. Both the emission yield ϕ in the pyrene monomer region and the $\bar{\tau}$ value were decreased by the presence of coadsorbed quenchers, 2-chloro-, 2-bromo-, 2-iodonaphthalene. Figure 5 shows the effect of the concentration of the coadsorbed 2-chloronaphthalene on ϕ and $\bar{\tau}$ at λ 390 nm. Tumbling of the samples for 5 h had relatively little effect on τ_0/τ_q as compared with the ϕ_0/ϕ_q plot. A reasonable straight line ($r > 0.98$) was obtained for the plot of $\tau_0/\bar{\tau}$ vs. $[Q]$. The concentration of adsorbed pyrene in the quenching experiments was typically about 5×10^{-7} mol/g (0.1% coverage). At this coverage pyrene excimer formation was negligible.

The increase of pyrene emission in the excimer region (at higher pyrene concentrations) by coadsorbed quencher is an interesting observation. Measurements of the time decay characteristics in this wavelength region show that this emission has true excimer characteristics; i.e., is formed by a subsequent diffusion process between an excited pyrene in a ground-state pyrene molecule as indicated by a "growing in" of excimer intensity. In the absence of quencher this was not observed because, as will be shown, ground-state association is responsible for the "excimer-like" emission.^{34,38} The effect of large amounts of coadsorbed molecules on the emission of pyrene on silica gel will be reported in greater detail elsewhere, but it should be noted this "growing in" of the

(32) 9-Cyanophenanthrene is very efficiently adsorbed on silica gel; 100% surface coverage, from adsorption isotherms, was ca. 152×10^{-3} g/g of SiO_2 (mean intermolecular distance 13 Å, mean occupied area 124 Å²). Since the molecular area is ca. 74 Å², this suggests that at least some molecules may be oriented perpendicularly to the surface at high coverages.

(33) Hochstrasser, R. M. *Can. J. Chem.* **1961**, *39*, 459.

(34) Hara, K.; Mayo, P. de; Ware, W. R.; Weedon, A. C.; Wong, G. S. K.; Wu, K. C. *Chem. Phys. Lett.* **1980**, *69*, 105.

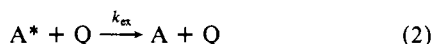
Table IV. Rate Constants for the Quenching of Pyrene Fluorescence by Halonaphthalenes on Silica Gel and in Cyclohexane Solution

quencher	k_{ex} , on silica gel [(dm) ³ mol ⁻¹ s ⁻¹]	k_{ex} in cyclohexane (L mol ⁻¹ s ⁻¹)
2-chloronaphthalene tumbled 5 h	4.5×10^{14} 5.6×10^{14}	2.6×10^6
2-bromonaphthalene tumbled 5 h	2.4×10^{15} 2.1×10^{15}	7.3×10^7
2-iodonaphthalene	2.3×10^{15}	9.7×10^8

excimer emission constitutes evidence for translational motion.

The quenching of excited states can be achieved either by resonance energy transfer, involving large molecular separations, or by contact quenching. There is no overlap between the emission of pyrene and the adsorption spectra of the quenchers, and, hence, the quenching observed for the pyrene emission on silica gel is not due to resonance energy transfer.³⁵ There are two types of contact quenching.³⁶ The first, static quenching, does not require any motion on the part of the excited state and the quencher, but involves an excited state which is produced within the "active sphere" of a quencher molecule, that is, in that volume around a quencher molecule wherein an excited state once formed is quenched instantaneously. The other type of contact quenching, dynamic quenching, requires diffusional motion between the excited state and a quencher molecule to a critical separation before quenching can take place. Both types of quenching will decrease the emission yield from the excited state, but only the dynamic quenching mechanism will decrease the observed emission lifetime of the excited state. In Figure 5, it is obvious from the dependence of $\bar{\tau}_q$ on [Q] and the differing slopes of ϕ_0/ϕ_q and $\bar{\tau}_0/\bar{\tau}_q$ plots that both static and dynamic quenching processes are operating on the silica gel surface.

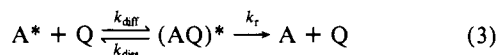
In cyclohexane solution pyrene emission is also quenched by the three quenchers studied here. If we write quenching process as



then the experimental rate of quenching k_{ex} is given by s/τ_0 where τ_0 is the lifetime of A^* in the absence of quenchers and s is the slope of τ_0/τ_q vs. [Q] plot. Table IV summarizes k_{ex} for the quenching of the pyrene emission by the 2-halonaphthalenes in cyclohexane solution and adsorbed on silica gel. For all three of the quenchers, k_{ex} is much smaller than the diffusion-controlled rate ($\sim 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) in cyclohexane. Hence, relative values of k_{ex} obtained are a good indication of the efficiency of quenching, with 2-iodonaphthalene being the most efficient and 2-chloronaphthalene the least efficient quencher. The quenching of pyrene emission by these three naphthalene derivatives is, from this ordering of efficiency of quenching, most probably by the external "heavy-atom" effect.

It should be noted from Table IV that tumbling of the samples does not affect k_{ex} very much. However, as noted in Figure 5, the value of ϕ_0/ϕ_q is strongly affected by tumbling. The difference between ϕ_0/ϕ_q and $\bar{\tau}_0/\bar{\tau}_q$, in the same sample, is to be attributed to static quenching which, as already mentioned, does not affect the $\bar{\tau}_q$ values. The process of tumbling, therefore, introduces a redistribution of pyrene and/or halonaphthalene molecules, that is, induces molecular displacement. This phenomenon will be discussed later in this paper.

The quenching process in eq 2 can be written as



where $(AQ)^*$ is a complex existing in the very short duration of

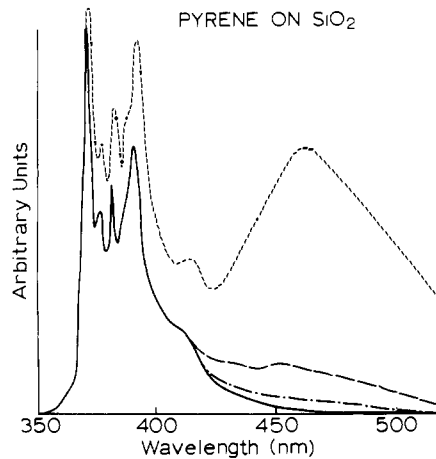


Figure 6. Emission spectra of adsorbed pyrene as a function of surface coverage: (---) at 3% (λ_{ex} 341 nm), (—) at 1% (λ_{ex} 341 nm), (-·-) at 0.2% (λ_{ex} 341 nm), (—) at 0.2% (λ_{ex} 331 nm).

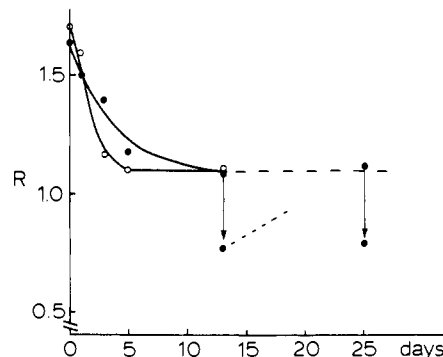


Figure 7. Intensity ratio (R) of "excimer-like" emission to monomer fluorescence of adsorbed pyrene, against time after preparation: (●) at 20 °C, (○) at 37 °C, and (→) changes introduced by shaking.

a molecular encounter. If k_{ex} is the overall quenching rate, it follows that eq 4 holds:³⁷

$$k_{ex} = k_r k_{diff} / (k_r + k_{diss}) \quad (4)$$

where k_{diff} and k_{diss} are the rate parameters for diffusion and dissociation of the reactants.

From Table IV, in cyclohexane solution, $0.08k_{ex}(2\text{-iodo}) \approx k_{ex}(2\text{-bromo}) \approx 28k_{ex}(2\text{-chloro})$, whereas for adsorbed molecules on silica gel $k_{ex}(2\text{-iodo}) \approx k_{ex}(2\text{-bromo}) \approx 4.5k_{ex}(2\text{-chloro})$. Here it is assumed that $\Delta(\bar{\tau}_0/\bar{\tau})/\Delta[Q] \approx \bar{\tau}_0 k_{ex}$. The most reasonable explanation for this observation is that in cyclohexane $k_{diss} \gg k_r$, whereas on silica gel $k_r \gtrsim k_{diss}$. In other words, in cyclohexane solution, the overall rate of quenching is determined by the efficiency of the quencher, whereas on silica gel the rate is approximately determined by how often an encounter complex is formed by diffusion, i.e., by a diffusion-controlled reaction. The inversion of rate k_r and k_{diss} in cyclohexane and on silica gel is not unexpected. For a given quencher, we expect $k_r(\text{cyclohexane}) \approx k_r(\text{silica gel})$, but, in contrast, $k_{diss}(\text{cyclohexane}) \gg k_{diss}(\text{silica gel})$ because it is relatively much more difficult for A^* and Q in $(AQ)^*$ to move apart.

Intergranular Motion of Adsorbed Pyrene. The emission spectrum of pyrene adsorbed on activated SiO_2 depends on surface coverage. For a surface coverage of 10^{-6} mol/g , essentially only monomer emission is seen and the shape of the spectrum is very similar to that observed for pyrene-alcohol solutions and even closer to that of pyrene in DMF. This means that the interaction of pyrene molecules with the SiO_2 used is weak. For higher coverages ($>10^{-5} \text{ mol/g}$) an additional band appears at 460 nm which is very similar to the excimer emission of pyrene in solution³⁴

(35) Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley-Interscience: New York, 1970, pp 567-569.

(36) Reference 35, pp 441-443.

(37) Alwattar, A. H.; Lumb, M. D.; Birks, J. B. In "Organic Molecular Photophysics"; Birks, J. B., Ed.; Wiley-Interscience: New York, 1973; p 416.

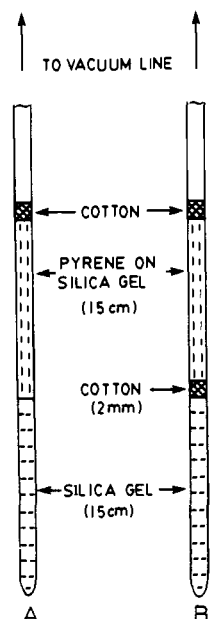


Figure 8. Apparatus used for measurement of boundary shift of adsorbed pyrene onto unadsorbed silica gel.

and, therefore, is called "excimer-like" emission band. For this band, however, a ground-state bimolecular arrangement is responsible, since one observes a red-shifted excitation spectrum.^{34,38} The ratio of this "excimer-like" to monomer fluorescence intensity ($R = I_{460}/I_{390}$) depends on coverage and excitation wavelength; it also varies from sample to sample.

Two equal samples of pyrene on SiO_2 were prepared, with surface coverage of 3% (1.44×10^{-5} mol/g). The emission spectra (Figure 6) of these samples were measured under similar experimental conditions as regards a function of the time after preparation (Figure 7). One of the samples was kept at $\sim 20^\circ\text{C}$; the other was stored at 37°C . Any shaking or other repositioning of SiO_2 granules was avoided. The excitation wavelength was 345 nm, which corresponds to the maximum in the excitation spectrum of the bimolecular ground-state arrangement of pyrene. As is seen from Figure 7, the ratio R decreases from 1.7 to an equilibrium value of 1.1 in about 5 days for higher storage temperature and in about 8 days for the sample kept at room temperature. After 13 days one sample was shaken about 1 h. Following this treatment the R value dropped further to 0.76. This situation, however, was not stable and R regained its equilibrium value of 1.1.

The dependence of R on time elapsed after sample preparation indicates that the sites occupied initially by pyrene molecules on the surface of SiO_2 during the solvent evaporation process do not represent the equilibrium situation. Pyrene molecules may, therefore, move from one adsorption site to another on the surface of one grain (intragranular motion). This diffusional motion depends on temperature, i.e., one can assume¹¹ a jump time $\tau = \tau_0 e^{E/kT}$, where τ_0 is a constant and E the activation energy for the breaking of adsorption bonds.

The abrupt change of the ratio R following shaking indicates fast intergranular motion, during which a site selection occurs which is not the most stable. This intergranular motion will be discussed in one of the following parts of this paper.

Intergranular motion was also demonstrated by another type of experiment. Two tubes were packed as shown in Figure 8 and were sealed off under (100 mmHg) nitrogen. The emission boundary was well defined. After 15 days the boundary in tube A had moved 3.5 mm with no change in tube B. After heating at 65°C for 4 days, the boundary in tube A had moved 1 mm further and was observable in B below the cotton plug about 4 mm. After a further 34 days, both A and B had moved about

(38) Bauer, R. K.; Wu, K. C., unpublished observations.

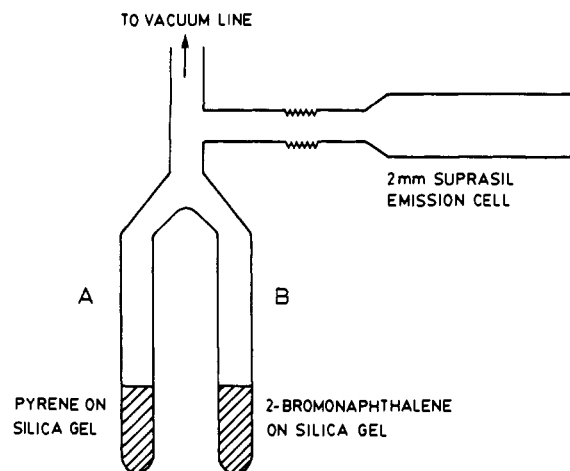


Figure 9. Apparatus for measurement of adsorbed pyrene lifetime before and after mixing with adsorbed 2-chloronaphthalene.

Table V. Intergranular Transfer of Adsorbed Acenaphthylene and Pyrene

adsorbed molecule on silica gel	time of shaking, (min)	observed % on silica gel
acenaphthylene on 50-70 mesh	5	82% on 35-50 mesh 18% on 50-70 mesh
acenaphthylene on 50-70 mesh	30	67% on 35-50 mesh 33% on 50-70 mesh
acenaphthylene on 35-50 mesh	5	32% on 35-50 mesh 68% on 50-70 mesh
acenaphthylene on 35-50 mesh	30	41% on 35-50 mesh 59% on 50-70 mesh
acenaphthylene on 35-70 mesh ^a	5	56% on 35-50 mesh 44% on 50-70 mesh
pyrene on 50-70 mesh	5	95% on 35-50 mesh 5% on 50-70 mesh
pyrene on 35-50 mesh	5	21% on 35-50 mesh 79% on 50-70 mesh

^a Acenaphthylene was adsorbed on equal amounts of mixture of 35-50 and 50-70 mesh silica gel at the same time.

3 mm further. In all cases there was no emission from the cotton plug in B.

The experiment demonstrates that, at room temperature, the movement of pyrene on silica gel is by intergranular and intragranular molecular motion and not via the vapor phase.⁴⁰

Intergranular Transfer of 2-Bromonaphthalene and Pyrene. In the apparatus shown in Figure 9, silica gel coated with pyrene (5×10^{-7} mol/g) and 2-bromonaphthalene (1.4×10^{-4} mol/g) were placed as indicated and evacuated for 2 h. After sealing, the pyrene adsorbed on silica was poured into the cell. The mean lifetime of this sample was 290 ns, decreasing to 280 ns a day later, a change observed in the absence of bromonaphthalene. The contents of the apparatus was mixed and shaken thoroughly for 5 minutes when $\bar{\tau}$ was found to be 142 ns. Further shaking (30 min) induced a change to 140 ns. A similar experiment carried out when 200 mmHg of nitrogen was introduced before sealing gave equivalent results.

As has been described, the quenching of pyrene by bromonaphthalene has been studied, and a value of $\bar{\tau}$ of 140 ns corre-

(39) Observed by viewing with a low-pressure lamp through Corning 7-51 filter.

(40) It is interesting that in the quenching of pyrene by 2-bromonaphthalene $\bar{\tau}_0/\bar{\tau} = 2$ when $[Q] = 1.2 \times 10^{-4}$ mol/g. Using a surface area of 560 m^2/g this corresponds to an average molecular separation of 32 Å. Assuming equal diffusion rates, the molecules move, therefore, ca. 16 Å in the lifetime of excited pyrene (300 ns). We observe a movement of 3.5 mm in 15 days. Assuming random walk theory applies,⁴¹ then $d \propto \sqrt{t}$, where d and t are the displacement and time of the motion. Then, when $d = 16$ Å, $t \approx 300$ ns, in remarkably good agreement.

(41) Moore, W. J. "Physical Chemistry", 4th ed.; Prentice-Hall: Englewood Cliffs, N.J.; 1972; pp 162-4.

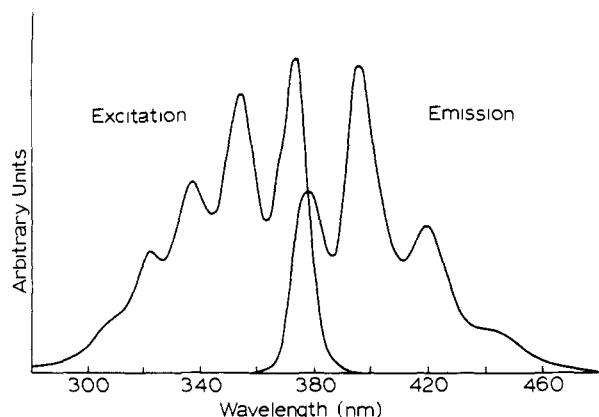


Figure 10. Emission and excitation spectra of adsorbed anthracene (1.0% coverage).

sponds to a quencher concentration of 7×10^{-5} mol/g. That is the value to be expected if the bromonaphthalene were distributed over *all* the silica gel in the apparatus. This distribution has therefore been essentially achieved in 5 minutes of shaking and must be by intergranular contact since it can also be carried out under 200 mmHg nitrogen.

Intergranular Transfer of Acenaphthylene and Pyrene: Direct Demonstration. Silica gel of 35–70 mesh was divided into coarse and fine portions using a 50-mesh sieve. Acenaphthylene was adsorbed onto one category of silica gel, an equal weight of the other added, and the mixture tumbled and shaken. The results are contained in Table V. Similar results were obtained with pyrene, but, on the other hand, no transfer at all was observed with Rose Bengal. The lack of transfer in the latter case was expected in view of the dye's great polarity and confirms that the transfer effected with hydrocarbons was not an experimental artifact. The speed of initial transfer is impressive.

Two extreme mechanisms can be envisioned for the transfer by this method. Either translationally mobile molecules use areas of contact as bridges, or contact is made by a grain in the area on another grain wherein lies already a hydrocarbon molecule; on separation of the grains, the molecule is transferred. The latter may be particularly effective at high coverages, when the exchange of the molecule of a weaker binding site for a stronger becomes more probable, but it is likely that both processes are operative simultaneously.

Site Equilibration with Anthracene and 9-Cyanophenanthrene by Intergranular Motion. Anthracene adsorbed on activated silica gel at low surface coverage interacts rather weakly with the surface and exhibits excitation and emission spectra similar to those obtained in solutions in polar solvents (Figure 10). The average decay time is similar to that obtained in deaerated solution (5.0 to 6.0 ns). The adsorption inhomogeneity causes, however, nonuniform luminescence centers with different deactivation rates of the excited state causing a nonexponential decay. The observed decay curves are deconvoluted assuming a two-exponential decay although actually the decay is multiexponential. Nevertheless, the ratio of amplitudes of the two decay components or their integrated intensities can be taken as a measure of uniformity of adsorption.

The nonuniform interaction causing the multiexponential decay should also cause a broadening of the adsorption and emission spectra, and one might expect that excitation and observation at different positions of the spectra could give rise to photoselection of certain adsorption sites and a decay curve approaching single exponential.

A sample of anthracene on SiO_2 with a surface coverage of 0.1% (1.8×10^{-7} mol/g) was prepared and the fluorescence decay measured shortly after sample preparation using different excitation and observation wavelengths. The results of these measurements are listed in Table VI. If the anthracene fluorescence is excited and observed at wavelengths corresponding to the maxima of these spectra, the decay is definitely nonexponential

Table VI. Lifetimes (τ_1, τ_2) and Coefficients A_1, A_2 of Anthracene on Silica Gel as a Function of Excitation and Emission Wavelength^a

$\lambda_{\text{ex}}, \lambda_{\text{em}}$ (nm)	A_1	τ_1 (ns)	A_2	τ_2 (ns)	$A_1\tau_1/A_2\tau_2$	$\bar{\tau}$ (ns)
320, 370	0.468	5.22	0.002	34.5	35.4	6.02
354, 397	0.639	5.49	0.228	3.81	4.03	5.16
377, 425	0.514	4.69	0.013	13.9	13.3	5.33

^a At 0.1% surface coverage.

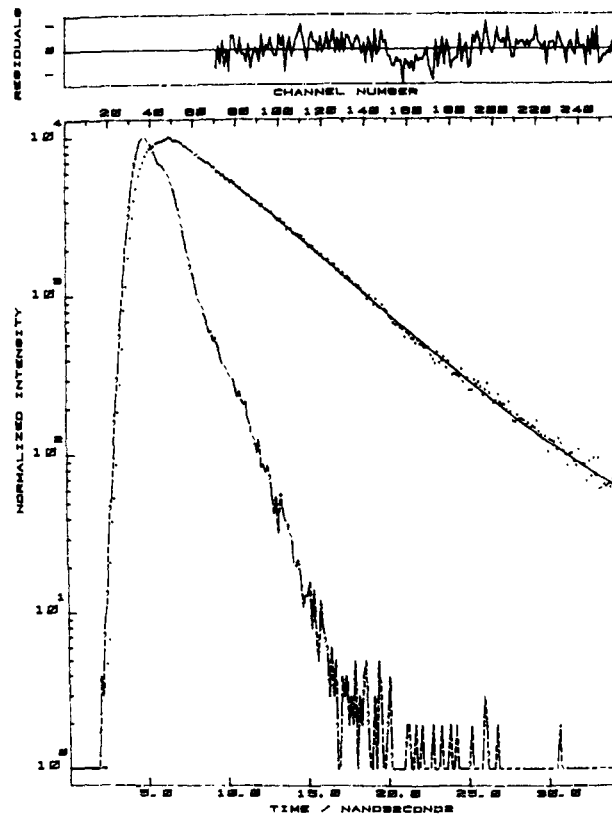


Figure 11. Decay curve of anthracene fluorescence on silica gel: surface coverage 0.1%, excitation wavelength 320 nm, emission viewed at 370 nm.

(amplitude ratio $A_1/A_2 = 2.8$, intensity ratio $A_1\tau_1/A_2\tau_2 = 4.03$) whereas excitation and observation at both red and blue edges of the spectra increases these ratios: a practically single-exponential decay (Figure 11) results if excitation and emission are at wavelengths 320 and 370 nm, respectively (amplitude ratio 234; intensity ratio = 35.4).

The decay curves were measured at varying temperatures with a decrease in mean lifetime from 5.3 ns at -10°C to 4.9 ns at 50°C : the decay for samples with 10, 1, and 0.1% surface coverage was still multiexponential. However, when decay measurements were made after shaking, practically single-exponential decay was found. In all cases there was still a very weak long-lived component; the decay curve for 1% surface coverage is shown in Figure 12.

To confirm these results they were repeated using different methods of sample preparation. It was found that spectral properties and decay curves were quite insensitive to the sample preparation method, although the most uniform adsorption is achieved if the evaporation of the solvent is very slow. The decay curves of anthracene on SiO_2 samples were measured as a function of time after sample preparation, temperature of storage, and time of heating at different temperatures. Although the decay of the anthracene emission did depend on storage time and heat treatment, single-exponential decay curves could not be obtained without shaking the silica gel grains. Thus, for a 0.1% surface coverage sample the decay component amplitude ratio rose from

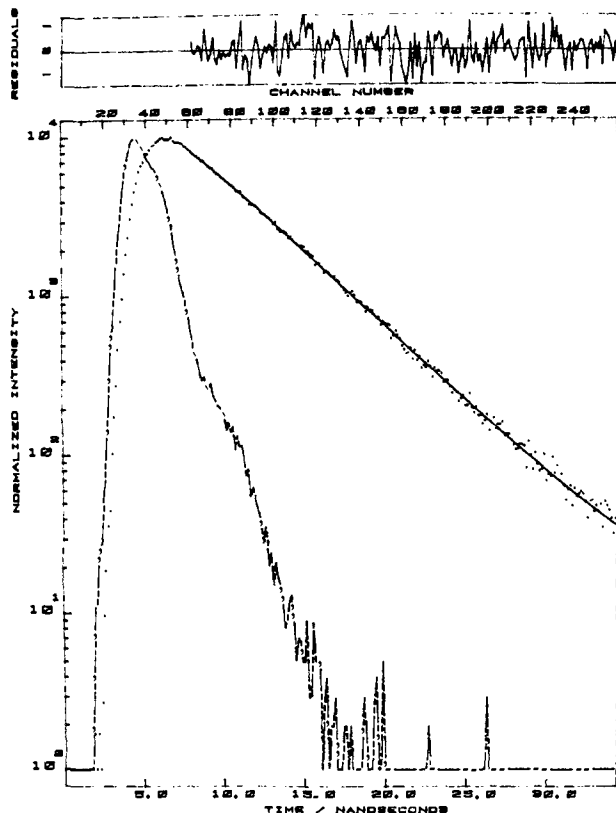


Figure 12. Decay curve of the fluorescence of adsorbed anthracene, after shaking, at surface coverage 0.1%: excitation wavelength 354 nm; emission viewed at 397 nm.

19.1 immediately after sample preparation to 31.5 after keeping the sample 4 weeks in darkness, and finally to 80.0 after shaking. It would appear that there is a slow molecular motion leading to a more energetically stable distribution of molecules on the surface, but there exists also an enforced faster intergranular molecular transfer by shaking.

The fluorescence spectrum of 9-cyanophenanthrene (**5**) provided, also indirectly, evidence for translational motion. The extinction coefficients of the two main vibronic bands of the first electronic transition of **5** dissolved in ethanol are about one and two orders of magnitude smaller than those for the second and third transitions. The emission spectrum has two broad bands at 362 and 379 nm. The excitation and emission spectra of **5** adsorbed on silica gel resemble those obtained from ethanolic solution rather than for cyclohexane, indicating the importance of hydrogen bonding. There is a strong overlap of the emission spectrum and the 356-nm band of the first electronic transition. This causes strong self-adsorption evident in the weakening of the 362-nm fluorescence band. Also observed is a relatively weak excitation band at 312 nm (second transition) and the disappearance of the 261-nm band; these phenomena can be reproduced in solution with rectangular illumination and concentration of the order of 10^{-4} M. They are not observed in the absorption spectrum. By careful comparison of the excitation spectra of solutions and silica gel samples with different concentrations and coverages of **5**, it was proven that the strong dependence of the excitation spectrum of **5** adsorbed on silica gel on coverage is an inner-filter effect caused by the significant difference of the extinction coefficient for the first, second, and third electronic transitions.

For high surface coverages³² the excitation light is absorbed before it reaches the area viewed by the detector. For a 2% surface coverage the mean intermolecular distance is ca. 88 Å, which corresponds, in solution, to a concentration of about 2.5×10^{-3} M. In Figure 13 the emission and excitation spectra of a 2.5×10^{-3} M solution of **5** are compared with those of **5** adsorbed on SiO₂ (2% coverage). One sees that the inner-filter effect is much stronger for the adsorbed material. A possible explanation is the

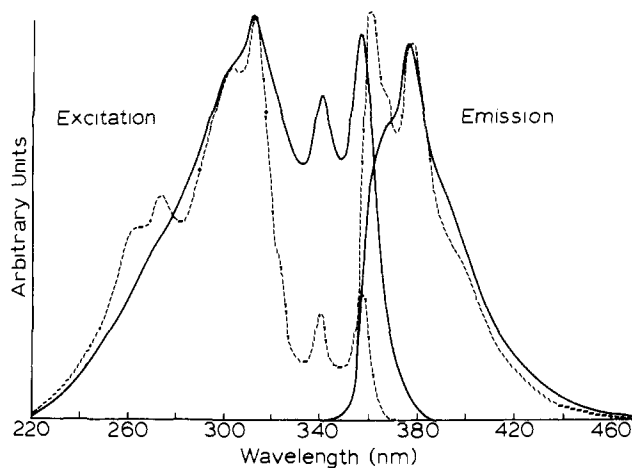


Figure 13. Excitation and emission spectra of 9-cyanophenanthrene (—) 2% coverage adsorbed on silica gel, (---) 2×10^{-3} M in ethanol.

formation of associations of molecules of **5**, reducing intermolecular distances and allowing strong absorption of the excitation light in the 210–310-nm region and reabsorption of fluorescence in the overlapping region of absorption and emission spectra.

The shape of the excitation spectrum of adsorbed **5** did not change on prolonged storage. However, when stored at 90 °C the ratio of the excitation bands at 312 and 341 nm increased gradually from 1.27 to 1.56 over 20 h and remained constant thereafter. This is attributed to an intragranular redistribution, similar to that leading to dimerization, which reduces the inner-filter reabsorption effect.

Further indication of translational movement of **5** at elevated temperatures derives from an examination of fluorescence decay. This decay at 0.2% coverage is not single exponential, but has a mean decay time of 19.8 ns, amplitude ratio = 5.5. The movement evoked by increased temperature led to a near-single exponential decay at $t > 65$ °C ($A_1/A_2 = 8.4$, intensity ratio 17.8).

Conclusions

The surface silica gel is not homogeneous. Except when dried under stringent conditions it contains ca. five silanol groups per 100 \AA^2 . With the dimensions of a medium-sized molecule (naphthalene, anthracene, pyrene) it is evident that, hydrogen bonding being the primary binding force, certain positions on the surface will permit more binding than others. These may constitute "preferred sites" and will exist regardless of inhomogeneities introduced by surface irregularities such as varying pore size. These "preferred sites" need not, however, all be identical. The energy well induced by the binding is not so deep, however, at these thermodynamically favored positions that molecules automatically fall into them. When molecules are allowed to equilibrate by standing, heating, or, better, shaking, these sites become filled. Having now more similar environments (at low coverage) than the arbitrary distribution after normal sample preparation, the emission decay processes approach more closely to single exponentials. Only with pyrene is there evidence for ground-state complex formation,³⁴ and the refusal to approach a single exponential is presumably associated with this.

However, it is not a simple matter to establish the extent to which a given system approaches true thermodynamic equilibrium. Shaking, for example, clearly changes the molecular distributions achieved upon sample preparation, but may in fact also cause an equilibrated system to depart from equilibrium. We lack reliable a priori criteria for sorting out the interplay between the tendency toward equilibrium and the kinetic barriers which impede this process.

That molecules may move in at least an intragranular fashion has been shown by several lines of evidence including (a) the changes in fluorescence decay characteristics on standing, (b) the changes in composition of acenaphthylene dimers by irradiation at different surface coverages and to different degrees of conversion, (c) the Stern–Volmer quenching of pyrene fluorescence

by halonaphthalene using $\bar{\tau}_0/\bar{\tau}$, and (d) the reversible changes in pyrene emission with shaking and standing.

Intergranular motion has been demonstrated directly between particle sizes of silica gel on shaking, and it is surprisingly rapid. A slower intergranular motion has been shown by pyrene migration over static silica gel, as indicated by a moving fluorescence band.

Inter- and/or intragranular molecular movement has been shown inter alia by (a) the sensitized dimerization of acenaphthylene, (b) the ferrocene quenching of acenaphthylene dimerization, and (c) the dimerization of cyanophenanthrene.

It thus appears that though molecules may prefer certain sites on the silica gel at room temperature, kT provides enough energy for them to move about. It should be noted that translational motion, unlike vaporization, does not require the simultaneous breaking of *all* bonding. If a silanol is present in the direction of molecular motion, bonding with it may occur as the original silanol bonding, or part of it, is disrupted. Only if the siloxane contribution is very weak will the molecule have to pay the full energetic price of bond disruption, and that when it leaves the silanol "oasis" and ventures into the siloxane "desert". However, on this energetically higher plateau translational movement should be more rapid and the discovery of a new silanol "oasis" comparatively fast. The most rapid translational motion must be expected, then, on this model when the amount of silanol bonding is unchanged or increases, or when there is none, the latter probably being the faster.

The association of adsorbed molecules is to be expected, even at low coverages, in nonequibrated systems. In equilibrated systems it will occur at low coverage if one adsorbed molecule is sufficiently perturbed electronically as to form a weak ground-state complex with another molecule, as in the case of pyrene.³⁴ The formation by weaker forces of hydrocarbon "pools" cannot be excluded, but these seem unlikely to survive equilibration.

We have shown that bimolecular processes are possible with molecular diffusion, on dry silica gel. These solvent-free optically "transparent" conditions may offer synthetic possibilities: it yet remains to be shown what effect the adsorption forces have on known inter- and intramolecular photochemical processes. Finally, we have shown that the techniques of molecular photochemistry and photophysics can reveal information about the nature of an adsorbing surface. The full potential of surface photochemistry remains to be explored.

Experimental Section

Materials. Silica gel (35–70 mesh, Merck) was activated by heating at 200 °C under vacuum (0.3 mmHg) for 5–7 h before use. Acenaphthylene (Aldrich) was purified by decomposition of the corresponding picrate followed by sublimation and recrystallization from ethanol (mp 94–95 °C). Ferrocene (Aldrich) was purified by sublimation (mp 175–176 °C). Pyrene was purified by passing through a silica gel column (mp 156 °C). 2-Chloro-, 2-bromo-, and 2-iodonaphthalene were recrystallized from ethanol. 1,1'-Binaphthyl was recrystallized several times and then purified by zone refining. 9-Cyanophenanthrene (Aldrich) was purified by column chromatography and recrystallized from ethanol (mp 112.5 °C). Cyclohexane and methylene chloride were spectral grade. For emission spectra or kinetics, cyclohexane was further purified by passing through a silica gel column. The silica gel surface area (560 m²/g) was determined using the method of Hoffman et al.⁴²

Direct Irradiation of Adsorbed Acenaphthylene on Dry Silica Gel. A cyclohexane solution containing a suitable amount of acenaphthylene (2.40, 6.00, 12.0, 24.0, 36.0, 48.0, 71.8, 96.0, or 158.0 mg) was adsorbed on 500 mg of activated silica gel by simply evaporating the solvent in the specially designed cell. Each of the above concentrations corresponds to the respective monolayer surface coverage following: 1.29, 3.23, 6.45, 12.9, 19.4, 25.8, 38.6, 51.6, or 84.9% (100% monolayer coverage corresponds to 372 mg of acenaphthylene per g silica gel). The cell is shown in Figure 14. After activating 500 mg of silica gel in B, stopcock E was closed to protect the silica gel from moisture. A cyclohexane solution of acenaphthylene was added to C and evacuated with a pump for a short

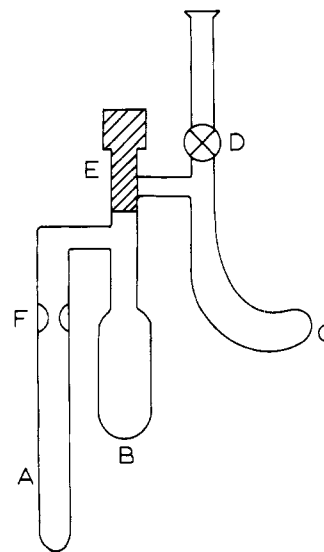


Figure 14. Reaction cell used for acenaphthylene direct irradiation.

time (2 or 3 min) to fill the space from C to D with the vapor of the solvent. Then D was closed and E was opened. The solvent was transferred from C to B and acenaphthylene was adsorbed on activated silica gel by simply evaporating the solvent. Finally, the prepared sample was degassed (10^{-5} mmHg) at liquid nitrogen temperature; the cell was filled with oxygen-free nitrogen and F was sealed off. The rotated quartz tube A was irradiated with a 150-W xenon lamp through a 0-52 Corning filter ($\lambda > 350$ nm) for 1 h while cooling with running water. The reaction mixture was eluted with methylene chloride (ca. 150 mL), and tetracosane (~0.1–0.3 mg) was added as an internal standard. After concentration, the products were analyzed on a Varian 3700 GC (column OV 101, 1 m; retention times: cis dimer, 15 min; trans dimer, 30 min; internal standard, 9 min). A similar procedure was used to prepare and analyze the samples in the presence of acenaphthene. The amount of acenaphthene was regulated to keep the total molarity of acenaphthylene (plus acenaphthene) on the surface constant at 1.46 mmol/g (60% coverage).

Sensitized Irradiation of Adsorbed Acenaphthylene on Silica Gel. A solution of dry methanol (3 mL) containing a small amount (0.7 mg) of sensitizer, Rose Bengal, Eosin Y, or Acridine Orange was added to 500 mg of silica gel and the dye was adsorbed by evaporating the solvent. The silica gel was dried by pumping (0.3 mmHg) for 12 h at room temperature to remove methanol completely. A cyclohexane solution (ca. 2–3 mL) of acenaphthylene was added to the sensitizer-silica gel and the solvent was removed under reduced pressure. The sample was then transferred to a quartz tube and the system was evacuated (10^{-5} mmHg) at 77 K, filled with oxygen-free nitrogen, and sealed off. The rotating quartz tube was irradiated with a 150-W xenon (3-68 Corning filter) for ca. 5 min. The reaction mixture was submitted to a similar analytical procedure as for direct irradiation. The dye was not eluted at all by methylene chloride.

Quenching of Acenaphthylene Dimerization with Ferrocene. A cyclohexane solution containing 24.0 mg of acenaphthylene and a suitable amount of ferrocene (0.0, 0.298, 0.596, 0.894, 1.192, or 1.490 mg) was added to activated silica gel (500 mg), followed by evaporation of the solvent in the cell shown in Figure 14. After preparing samples, the rotated quartz tubes (6) were irradiated at the same on a merry-go-round for 3 h with a 150-W xenon lamp (0-52 Corning filter). The reaction was analyzed as already described.

Direct Irradiation of Adsorbed Acenaphthylene on Dry Silica Surface without Rotation. All samples were prepared as described under direct irradiation. A round cell with a flat face (diameter 30 mm, depth 10 mm) was used instead of a round tube in place of A (Figure 14), and silica gel (ca. 100 mg) was spread on the bottom of the quartz cell in a thin layer. The sample was irradiated with a 150-W xenon lamp (0-52 Corning filter) using a light pipe (20 min–1 h). To get a high conversion to the corresponding dimers, a 1-kW lamp (0-52 Corning filter) was used as a light source for 5 h. The irradiated sample was treated and analyzed as described above.

Photodimerization of 9-Cyanophenanthrene. The quantum yields of dimerization in solution were determined at 334 ± 6 nm with a JASCO spectroirradiator calibrated with the ferrioxalate actinometer. The optical densities used were >1.8. The disappearance of 9-cyanophenanthrene was followed by the optical adsorption change in solution.

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The results are summarized in Table III. 9-Cyanophenanthrene was adsorbed at 24 (36 mg/g of silica gel) and 50% (76 mg/g of silica gel) coverage on degassed dried (200 °C; 0.3 mmHg) silica gel. It is believed that dimerization did not proceed from microcrystals because (a) the dimerization in the crystals was very inefficient both at +10 and +70 °C, (b) crystals could not be observed by microscope ($\times 128$), (c) crystals in contact with silica gel gradually disappeared, and (d) the lifetimes (air) of the nitrile in the crystal (τ_1 , 29 ns; τ_2 , 25 ns) were longer than in the adsorbed state (24% coverage; τ_1 , 4.8 ns; τ_2 , 17 ns). Dimerization was induced by irradiation with a 150-W xenon lamp through a Corning 0-52 filter. The tube containing the nitrile was rotated for 7 h. Disappearance of the starting material was monitored by the UV absorption in a cyclohexane-silica gel slurry by comparison with a nonirradiated blank. The dimer was thermally unstable at GC injection temperature (250 °C) but is stable at 80 °C.

Emission Spectra and Decay Kinetics of Adsorbed Pyrene on Dry Silica Gel. A cyclohexane solution (ca. 15 mL) containing a suitable amount of pyrene and the quencher was adsorbed on activated silica gel by simply evaporating the solvent slowly. The sample was transferred into a Suprasil cell with 2-mm optical path length. Then the system was degassed (10^{-5} mmHg) at room temperature or 60 °C for ~ 40 min. The weight loss of pyrene is negligible under these conditions, although a small amount (ca. 2×10^{-6} mol) of 2-chloro- or 2-bromonaphthalene is lost when heated. The degassed cell was sealed off. Emission spectra were recorded on a Perkin-Elmer MPF-4 emission spectrophotometer with a cell holder specially designed to hold the cell at a ca. 45° angle to the incident excitation light beam. The emission from the front surface of the cell was monitored with a slit width of the monochromator of 0.75 nm. For the comparison of emission intensity, the mean value of at least three measurements on the same sample were used. Emission decay profiles were measured with a PRA 3000 single photon lifetime apparatus with excitation and emission monochromators (slit width 8 nm). Deconvolution was performed with PRA software which employs iterative least-squares deconvolution. A similar procedure was used for the decay kinetics of anthracene and 9-cyanophenanthrene.

Full (100%) monolayer surface coverages correspond to 97, 28, and 152 mg/g of silica gel for pyrene, anthracene, and 9-cyanophenanthrene.

Intergranular Transfer of 2-Bromonaphthalene and Pyrene. Equal amounts (ca. 500 mg) of silica gel were coated with pyrene (7×10^{-7} mol/g) and 2-bromonaphthalene (1.4×10^{-4} mol/g) and placed in the branches A and B, respectively, of the apparatus shown in Figure 9. After evacuation for 2 h ($\sim 10^{-5}$ mmHg) the system was sealed from the vacuum line. The "pyrene" sample was then carefully introduced into the sample cell avoiding contamination by the "bromonaphthalene" sample. The pyrene mean lifetime was 290 ns. After standing for 1 day the samples were mixed and shaken vigorously for 5 min. The lifetime of the pyrene was 142 ns reduced to 140 ns after 30 min of shaking. A similar experiment carried out under nitrogen (200 mmHg) gave the same results.

Intergranular Transfer of Acenaphthalene and Pyrene. Silica gel (35-70 mesh, Merck) was divided into coarse and fine fractions using a 50-mesh sieve. Acenaphthylene (ca. 12 mg) was adsorbed onto 500 mg of either coarse or fine silica gel by evaporation of a cyclohexane solution. The silica gel was then mixed with an equal amount of uncoated silica gel of opposite grain size and shaken for 5 or 30 min. The mixed powder was again separated into coarse and fine. The error in the separation was <15%. Each portion of the separation silica was extracted with methylene dichloride and the acenaphthylene estimated spectroscopically. The same procedure was used with pyrene; the results are given in Table V.

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Registry No. 1, 208-96-8; 2, 15065-28-8; 3, 14620-98-5; 4, 83-32-9; 5, 2510-55-6; pyrene, 129-00-0; 2-bromonaphthalene, 580-13-2; anthracene, 120-12-7.

Naphthonitrile-Alkene Exciplexes. Comparison of Bimolecular and Bichromophoric Cases: Effects of Linking on Fluorescence and Photochemistry

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Abstract: The fluorescence quenching and photochemistry of 2-methyl-, 4-methyl-, and 6-methyl-1-naphthonitrile with tetramethylethylene have been studied in nonpolar solvents. Stern-Volmer constants (benzene solvent) are 10.1, 15.7, and 7.2 M^{-1} , respectively, showing that quenching is insensitive to the position of the methyl group. Exciplex emission was observed in each case, and exciplex lifetimes were measured by single photon counting techniques. The methyl-naphthonitriles react with tetramethylethylene to give 1-cyano-7,7,8,8-tetramethyl-2,3-benzobicyclo[4.2.0]-2,4-octadiene derivatives, and limiting quantum yields were measured. In the case of 4-methyl-1-naphthonitrile, quenching with biacetyl showed that the exciplex is an intermediate in the cycloaddition reaction and no triplets are formed in the exciplex decay. Rates of exciplex collapse to cyclobutane products were derived. The bichromophoric molecules **1**, **2**, and **3**, in which the chromophores are linked by a three-atom chain, were synthesized. All three show strong quenching of the monomer (naphthonitrile) fluorescence, and weak exciplex emission. Compounds **1**, **2**, and **3** also react on irradiation, giving internal cycloaddition products. The structures of the latter were determined, and the structure work is described. Comparison of quantum yields for internal cycloaddition with limiting quantum yields for the bimolecular cases shows that the three-atom chain greatly facilitates collapse of the exciplexes to products in these systems. Exciplex formation and decay are discussed in terms of current theory. The structure of one photoproduct, 7-cyano-5,6,6-trimethyl-8,9-benzo-3-oxatricyclo[5.4.0.0^{1,5}]-8,10-undecadiene (**10**), was determined by X-ray diffraction, and the structure is described.

Exciplex formation was proposed some time ago by Hammond and co-workers² to account for the quenching of fluorescence of aromatic compounds by dienes.² The observation of exciplex fluorescence from 1-naphthonitrile and electron-rich alkenes by

Taylor³ showed that exciplexes are indeed formed in fluorescence quenching by ethylene derivatives. A kinetic analysis of the 1-naphthonitrile-olefin system has been carried out.^{4,5} Exciplex formation was found to be reversible, and rate constants for the

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