

## SUPERFICIAL PHOTOCHEMISTRY

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**Abstract** - Evidence is provided which indicates that intra- and intergranular movement of aromatic molecules adsorbed on silica gel occurs. This evidence includes the sensitized and direct dimerization of acenaphthylene and its quenching; the dimerization of 9-cyanophenanthrene; and the quenching of pyrene fluorescence by halonaphthalenes. Direct intergranular transfer is shown for acenaphthylene and pyrene in a kinetic system and, for the latter, in a static system. The effect of the surface on the behaviour of radical pairs in the Type 1 reaction is discussed.

## INTRODUCTION

Photochemistry has a long history, but it has only become a mature science in the last ten to fifteen years or so. By 'mature', used in this context, is meant that the major, initial, surprises of discovery are supposedly over, and that the workers in the field have drawn up a provisional set of rules by which to abide: the science, in short, has become respectable. Concomitant with the achievement of respectability come the assertions that the subject has lost its youthful glamour, is by way of being a little staid, and, in fact, is, as the French delicately phrase it, of a certain age. Everything new about the subject, it is implied, has an air of *déjà vu*.

And, in this sense, what follows is certainly a harking back to old times, for the first contrived photochemical experiment recorded - Scheele's discovery that violet light was the most effective in darkening silver chloride - was performed in the dry state. In the intervening years, with the exception of developments of the same reaction - photography - the overwhelming mass of work in photochemistry has been carried out in the liquid or vapour phase.

Organic photochemistry in the solid state has largely been confined to the crystal, yet the study of the photochemistry of molecules on a solid substrate can lead to at least two categories of information: that which pertains to the surface behaviour of adsorbed molecules, and which is informative about that surface, and that which reveals how the surface - molecule interaction may influence the photochemistry of the organic molecule itself (2-5). The present contribution is concerned with both aspects.

## EVIDENCE FOR TRANSLATIONAL MOVEMENT OF ADSORBED MOLECULES

There are few studies that reveal those restrictions on the motion, rotational and translational, of fair-sized organic molecules which are imposed by adsorption on a surface such as that of dry silica gel. The nature of the binding forces has been extensively studied, and in the particular case of silica gel it is generally accepted that there are two kinds of surface binding functions: the silanol (Fig. 1) and the siloxane groups. In addition, it is recognized that the silanol functions may be 'isolated', 'vicinal', or 'geminal', or may be hydrated, the water acting as a bridge in binding e.g. Fig. 1(d). The most important binding agent appears to be the hydrogen bond from the silanol to lone pair electrons or to  $\pi$ -systems. Since there is an average of about 5 silanol functions per 100 Å<sup>2</sup>, it is evident that many molecules have the possibility of binding to more than one. Highly polar materials can be considered as anchored, whereas aromatic hydrocarbons, with which we will be concerned, are more loosely held: benzene, for instance, has been claimed to show high mobility (6,7). Chromatographic behaviour gives a qualitative indication of relative binding power.

Open shell systems have also been examined (8-10). From the linewidth and shape of the E.P.R. signal it has been concluded that there is both rotational and translational movement for certain free radicals. The silica gel surface, however, is not uniform, and the effect of this non-uniformity has not been ascertained: the conclusions may be oversimplified.



The results found are shown in Fig. 2. The ratio of 2 to 3 does vary with coverage, approximately linearly up to about 15% coverage (with uniform distribution roughly equivalent to 0.4M based on molecular separation). At above 40% the curve flattens to an asymptote of about 21 for (2):(3). This might be interpreted as being indicative of the 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 neighbour' reactive molecules increases (case b). Movement required of one or both molecules of the juxtaposed pairs preliminary to dimerization or excimer formation (14) may delay reaction beyond the lifetime of the singlet (~1 ns) and allow leakage to the triplet in at least some of the pairs.

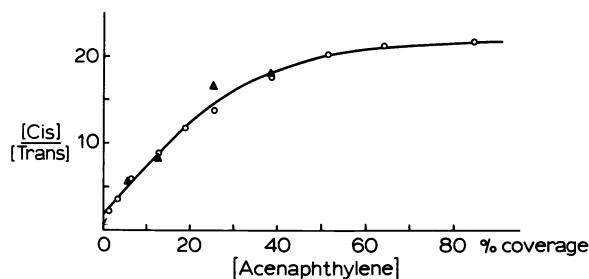


Fig. 2. Plot of (2)/(3) against acenaphthylene concentration (percentage coverage) on silica gel.

It seems improbable that the singlet can react in other than already juxtaposed pairs, which suggests that, at low coverage, these exist in greater amount than statistical, i.e., that the distribution is non-uniform. The longer-lived triplet has time for migration before reaction.

As in solution, (14) the dimerization could be sensitized. Using Rose Bengal ( $E_T = 44.6$  kcal/mole), Eosin Y ( $E_T = 46.8$  kcal/mole) or Acridine Orange ( $E_T = 49.2$  kcal/mole) at low coverages (~0.1%) with acenaphthylene 64.5% coverage, ( $1.5 \times 10^{-6}$  mole/g silica gel), as in solution, (14) a mixture of 2 and 3 was produced. Even at 10% conversion one molecule of Rose Bengal (~114 Å<sup>2</sup>;  $1.38 \times 10^{-6}$  mole/g silica gel) sensitized >57% molecules of acenaphthylene (~53 Å<sup>2</sup>). Such an efficiency cannot be attained with the closest packing possible. Assuming energy transfer is effective at 5Å, 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 on the time scale of the triplet lifetime occur.

The dimerization of acenaphthylene could be quenched by the triplet quencher ferrocene. The Stern-Volmer plots for the quenching of (2) and (3) are shown in Fig. 3. 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 ( $2.86 \times 10^{-10}$  mole (dm<sup>-2</sup>)) at a concentration of acenaphthylene of  $5.64 \times 10^{-9}$  mole (dm<sup>-2</sup>), or 13% coverage.

The lifetime in solution of triplet acenaphthylene ( $2.15 \times 10^{-6}$  s) is abnormally short, and is probably not much changed by adsorption. Using the value from solution, we obtain a value of  $k_g$  of  $7.02 \times 10^{15} (\text{dm})^2 \text{mol}^{-1} \text{s}^{-1}$ . Quenching is probable on every encounter, since diffusion apart will be slow, and so this value represents the diffusional rate constant for a molecule of ferrocene and acenaphthylene towards 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 we have found 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  $\sim 2\text{\AA}$  during the singlet lifetime, or as the singlet, whereas the triplet or in the triplet lifetime, it may move  $\sim 300\text{\AA}$ .

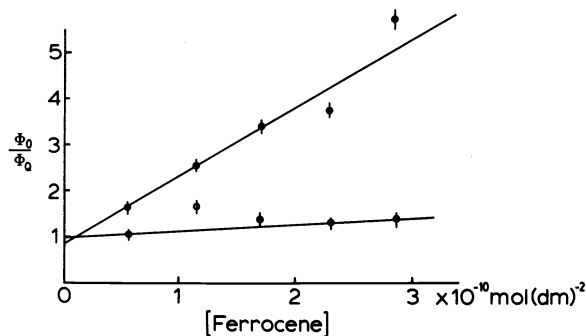


Fig. 3. The Stern-Volmer plot of the quenching of acenaphthylene is cis ( $\phi$ ) and trans ( $\blacklozenge$ ) dimer formation by ferrocene.

#### The dimerization of 9-cyanophenanthrene(9-CP)

The dimerization of 9-cyanophenanthrene in ethanolic solution has been reported (15). The reaction proceeds via the singlet state (16) and is inhibited by oxygen. Adsorbed on silica gel at 24 and 50% coverage, the dimerization was attempted by irradiation ( $\lambda > 305 \text{ nm}$ ) at  $10^\circ$  of both degassed and non-degassed samples under arbitrary but standard conditions. No product could be detected in the non-degassed samples whereas 2 and 5% dimerization was found, at 24 and 50% coverage respectively, from the degassed samples. With raised temperature ( $65\text{--}68^\circ$ ) 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 1). It was found that in propanol the quantum yield almost doubled over the range  $10\text{--}75^\circ\text{C}$ . However, the viscosity dropped also. An increase in quantum yield of dimerization was observed over the range  $10\text{--}48^\circ$  for methanol but the quantum yields in propanol at  $75^\circ$  and in methanol at  $10^\circ$ , where the viscosities are similar, were also close. We conclude that in solution the activation energy is that for diffusional motion, and assume that the same is true for the adsorbed molecules.

Table 1. Effect of temperature on the quantum yield of dimerization of 9-CP<sup>a,b</sup>

Solvent	10°	Temperature 18°	48°	75°
Propanol	0.054±0.002 (2.85cP)	0.055±0.004 (2.30cP)	0.081±.006 (1.17cP)	0.091±0.004 (0.76cP)
Methanol	0.088±.022 (0.68cP)		0.127±0.003 (0.40cP)	

<sup>a</sup>Concentration 4.0 0.2x10<sup>-3</sup>M. <sup>b</sup>Viscosity in centipoises parenthetically.

The quenching of pyrene emission by halonaphthalenes

The decay of pyrene emission adsorbed on silica gel is not a single exponential (17) but can be described by the rate law  $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ . The values of  $A_1, A_2, \tau_1, \tau_2$  varied from one measurement to another, but it was found that the mean lifetime,  $\tau$ , given by Eq. 1, was constant to within 0.5% throughout the measurement. In equation 1,  $P_i$  refers to the fraction of the emission having lifetime  $\tau_i$ . Typically,  $\tau_0 = 250$  ns. The

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

concentration of adsorbed pyrene in the quenching experiments was  $5 \times 10^{-7}$  mole/g (0.1% coverage) at which concentration there was no complicating emission (17). Both the emission yield  $\phi$  and the  $\bar{\tau}$  value were decreased in the presence of coadsorbed quenchers, 2-chloro-, 2-bromo-, and 2-iodonaphthalene. Figure 4 shows the effect of the concentration of coadsorbed 2-chloronaphthalene on  $\phi$  and  $\bar{\tau}$  at  $\lambda = 390$  nm. A reasonable straight line was obtained for the plot of  $\bar{\tau}_0/\bar{\tau}_q$  vs  $[Q]$ . In Figure 4 from the dependence of  $\bar{\tau}_q$  on  $[Q]$  and the differing slopes of  $\phi_0/\phi_q$  and  $\bar{\tau}_0/\bar{\tau}_q$  plots one may conclude that both static and dynamic quenching processes are operating on the silica gel surface, and that tumbling affects the ratio of these two processes.

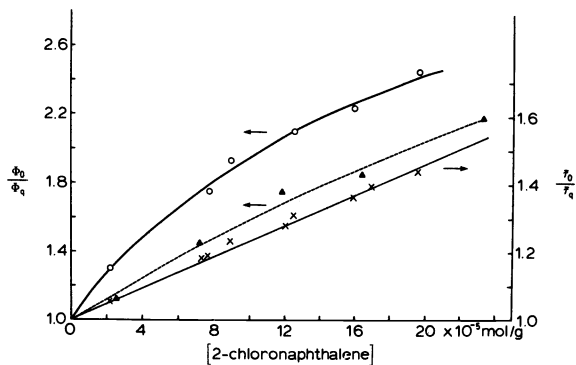
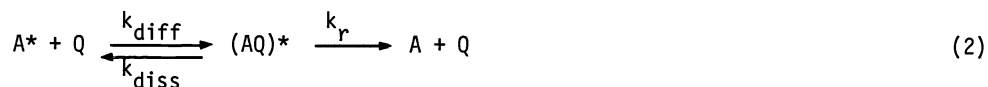


Fig. 4. The Stern-Volmer plots of quenching of pyrene fluorescence intensity (o,▲, without tumbling, after 5h tumbling, respectively) and lifetime (x) by 2-chloronaphthalene.

The quenching process can be written as in equation 2 where (AQ)\* is a complex existing for



the very short duration of a molecular encounter. If  $k_{\text{ex}}$  is the overall quenching rate it follows that equation 3 holds (18):

$$k_{\text{ex}} = \frac{k_r k_{\text{diff}}}{k_r + k_{\text{diss}}} \quad (3)$$

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

From Table 2, in cyclohexane solution  $0.08 k_{\text{ex}}(\text{2-iodo}) \approx k_{\text{ex}}(\text{2-bromo}) \approx 28 k_{\text{ex}}(\text{2-chloro})$  whereas for adsorbed molecules on silica gel  $k_{\text{ex}}(\text{2-iodo}) \approx k_{\text{ex}}(\text{2-bromo}) \approx 4.5 k_{\text{ex}}(\text{2-chloro})$ . Here it is assumed that  $\Delta(\bar{\tau}_0/\bar{\tau})/\Delta[Q] \approx \bar{\tau}_0 k_{\text{ex}}$ , i.e., that the Stern-Volmer equation holds. The most reasonable explanation for this observation is that in cyclohexane  $k_{\text{diss}} \gg k_r$ , whereas on silica gel  $k_r \geq k_{\text{diss}}$ . 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 diffusion-controlled reaction. The inversion of rate  $k_r$  and  $k_{\text{diss}}$  in cyclohexane and on silica is not surprising because  $k_r(\text{cyclohexane}) \approx k_r(\text{silica gel})$  but  $k_{\text{diss}}(\text{cyclohexane}) \gg k_{\text{diss}}(\text{silica gel})$  because of the difficulty of dissociation in (AQ)\*.

Table 2. Rate constants for the quenching of pyrene fluorescence by halonaphthalenes on silica gel and in cyclohexane solution.

Quencher	$k_{\text{ex}}$ , on silica gel [(dm) <sup>2</sup> mol <sup>-1</sup> s <sup>-1</sup> ]	$k_{\text{ex}}$ in cyclohexane (l mol <sup>-1</sup> s <sup>-1</sup> )
2-Chloronaphthalene tumbled 5h	$4.5 \times 10^{14}$ $5.6 \times 10^{14}$	$2.6 \times 10^6$
2-Bromonaphthalene tumbled 5h	$2.4 \times 10^{15}$ $2.1 \times 10^{15}$	$7.3 \times 10^7$
2-Iodonaphthalene	$2.3 \times 10^{15}$	$9.7 \times 10^8$

#### Intergranular transfer of 2-bromonaphthalene and pyrene

In the separate arms of a U-tube silica gel coated separately with pyrene ( $5 \times 10^{-7}$  mole/g) and with 2-bromonaphthalene ( $1.4 \times 10^{-4}$  mole/g) was placed and the apparatus evacuated. After sealing the pyrene adsorbed on silica was poured into an attache cell. The mean emission lifetime of this sample was 290 ns. The contents of the apparatus, the two coated silica gel samples, were mixed and shaken thoroughly for five minutes when  $\bar{\tau}$  was found to be 142 ns. Further shaking (30 minutes) only induced a change to 140 ns. A similar experiment carried out when 200 mmHg nitrogen was introduced before sealing gave equivalent results.

The quenching of pyrene by bromonaphthalene has already been described, and a value of  $\bar{\tau}$  of 140 ns corresponds to a quencher concentration of  $7 \times 10^{-5}$  mole/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 five minutes 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 fine and coarse being again separated and the acenaphthylene content analysed. The results are contained in Table 3. Similar results were obtained with pyrene, but 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.

Table 3. Intergranular transfer of adsorbed acenaphthylene and pyrene.

Adsorbed molecule on Silica gel	Time of shaking	Observed % on Silica Gel
Acenaphthylene on 35-50 mesh	5 min	82% on 35-50 mesh 18% on 50-70 mesh
Acenaphthylene on 35-50 mesh	30 min	67% on 35-50 mesh 33% on 50-70 mesh
Acenaphthylene on 50-70 mesh	5 min	32% on 35-50 mesh 68% on 50-70 mesh
Acenaphthylene on 50-70 mesh	30 min	41% on 35-50 mesh 59% on 50-70 mesh
Acenaphthylene on 35-70 mesh <sup>a</sup>	5 min	56% on 35-50 mesh 44% on 50-70 mesh
Pyrene on 35-50 mesh	5 min	95% on 35-50 mesh 5% on 50-70 mesh
Pyrene on 50-70 mesh	5 min	21% on 35-50 mesh 79% on 50-70 mesh

<sup>a</sup> Acenaphthylene was adsorbed on equal amount of mixture of 35-50 and 50-70 mesh silica gel at the same time.

Intergranular motion of pyrene was also demonstrated by another type of experiment. Two tubes were packed as shown in Figure 5 and were sealed off under 100 mm Hg nitrogen. The emission boundary was well-defined. After fifteen days the boundary in tube A had moved 3.5 mm with no change in tube B. After heating at 65° for four days, the boundary in tube A had moved 1 mm further and was observable in B below the cotton plug. After a further 34 days, both A and B had moved about 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 vapour phase.

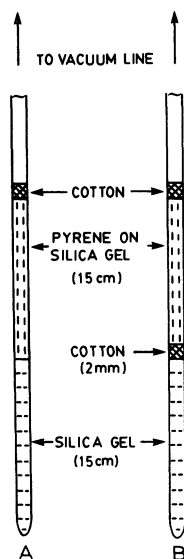
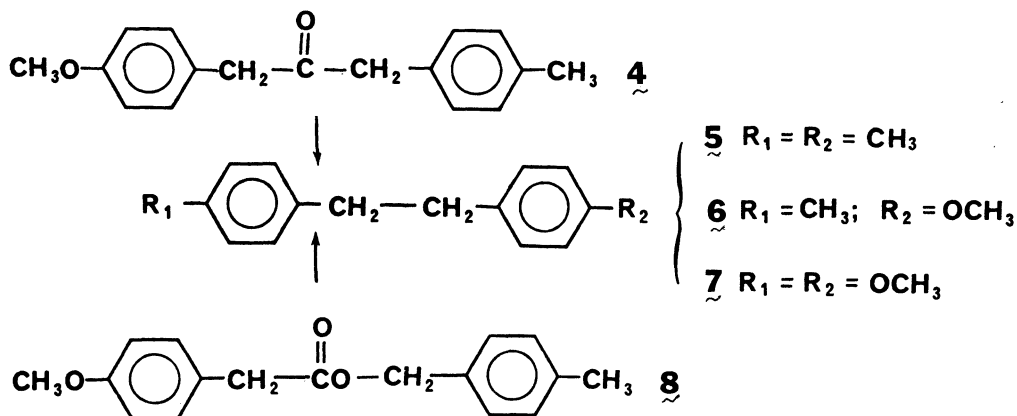


Fig. 5. Apparatus used to measure boundary shift of emission of adsorbed pyrene on silica gel.

#### ADSORPTION AND THE MODIFICATION OF RADICAL PAIR BEHAVIOUR

It is possible to conceive of a number of ways in which adsorption might influence a photochemical or photophysical process. These include restrictions on molecular transposition, modification of bimolecular reactions, and in the extreme, chemical interaction with the adsorbant, as in the case of semiconductors.

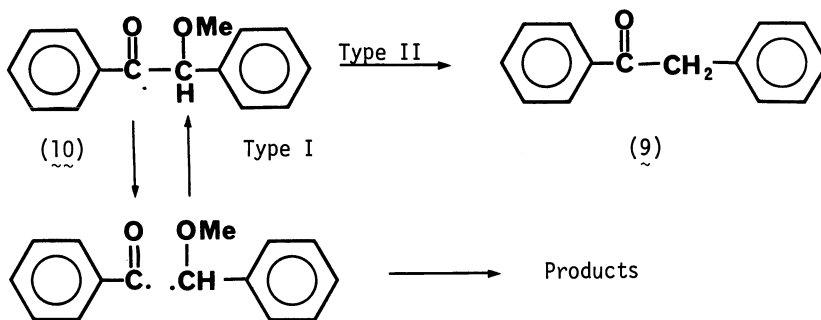
Some time ago it was found that the Photo-Fries rearrangement, could be induced on dry silica gel (11). This involves the generation of a singlet radical pair, their movement and recombination. Since the reaction proceeded more cleanly than in solution it appeared that the silica surface had a 'localising' influence rather like a solvent cage in a homogeneous system, but with a different mechanism. This was later shown, simply, in the consequences of the generation of radical pairs from the photolysis of ketone (4). This ketone on photolysis in solution generates triplet radical pairs which, after loss of CO, gives all the three possible bibenzyls (5), (6) and (7). In isopropanol these are formed in the statistical ratio of 1:2:1 and indicating efficient cage escape.





On silica gel at 20° a ratio of 1:3:7:1 was found, increased to 1:9:1 at -50° and 1: > 40:1 at -165°. Similarly, the ester (8), known from earlier work (19) to dissociate via the singlet, gave a ratio of the same bibenzyls of 1:2.5:1 in dioxan indicating the signs of an incipient cage effect. On silica gel at room temperature the ratio found was 1:6.1:1 increased to 1: > 50:1 at -50°, again indicating the resistance to diffusing apart of the radical already noted.

Such resistance implies an encouragement to recombination. One might expect that the proportion of recombination in radical pairs of, for instance, Type I homolyses might be increased before the elimination of carbon monoxide, leading to decreased product formation. This would be revealed in decreased quantum yields of reaction, but quantum yields, though measurable on silica gel, (20) present a more serious problem than in solution. We have, therefore, measured only relative yields under defined but arbitrary conditions. The reaction chosen was the photolysis of benzoin methyl ether (10). This has been extensively studied and it has been clearly shown that the primary photoreaction is a Type I cleavage (21); the potentially possible Type II reaction appeared not to occur. However, maintenance of the contiguity of the triplet radical pairs encourages their recombination and allows the Type II to occur. On silica gel at room temperature the consequences of the Type II process are found in deoxybenzoin (9) and and oxetanol, representing about 10% of the products. The proportion is increased to ~15% at low temperature because the Type II reaction on silica gel is less temperature dependent than is the Type I.



#### CONCLUSIONS

The surface of silica gel is not uniform. Except when dried under stringent conditions it contains 5 silanol groups per 100Å<sup>2</sup>. With the dimensions of a medium-sized molecule 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. The 'preferred sites' need not, however, all be identical. The energy well induced by the binding is not so deep, however, at these thermodynamically favoured positions that molecules automatically fall into them. When molecules are allowed to equilibrate by standing, heating, or better, shaking, these sites become filled.

That molecules may move in at least an intragranular fashion has been shown by (a) the changes in acenaphthylene dimers composition by irradiation at different surface coverages and to different degrees of conversion (b) the Stern-Volmer quenching of pyrene fluorescence by halonaphthalene using  $\bar{\tau}_0/\bar{\tau}$ , and (c) the quenching of acenaphthylene dimerization with ferrocene.

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 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 non-equilibrated 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 (17). 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 precisely what effect the adsorption forces have on known inter- and intramolecular photochemical processes.

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