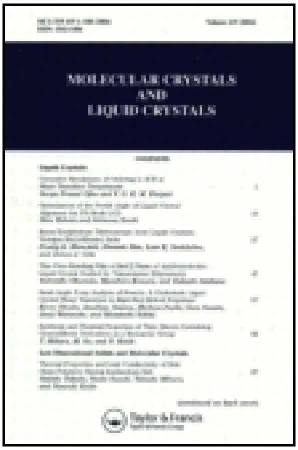

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An Organic Crystal as a Matrix for Spectroscopy and Mechanistic Studies in Photochemistry

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AN ORGANIC CRYSTAL AS A MATRIX FOR SPECTROSCOPY AND MECHANISTIC STUDIES IN PHOTOCHEMISTRY

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Abstract Advantages inherent in studying photochemical reaction mechnanisms in the solid-state are discussed. It is proven that the heterophotodimerization of 9-cyanoanthracene and 9-methoxyanthracene proceeds via an exciplex. The organic crystal matrix also permits extensive spectroscopic studies of the exciplex.

INTRODUCTION

The organic solid state, such as a doped organic crystal, can be a most convenient matrix for spectroscopy and mechanistic studies of photochemical addition reactions. This matrix has the following attractive features :

(a) Geometries of interacting molecules are fixed and may be accurately determined by various techniques such as X-ray crystallography.

(b) Studies may be performed over a wide temperature range (including very low temperatures) without significant change in the nature of the matrix.

(c) Electronic energy transfer to the reactive site is usually very efficient in organic crystals.

In this communication the role of a metastable intermediate (exciplex) in the cycloaddition (heterophotodimerization) of two anthracene derivatives is ascertained by investigating the photophysical and photochemical properties of a mixed crystal of the two components.

The problem of exciplex (or excimer) intermediacy in hetero- (or homo-) photochemical addition reactions has been studied previously in solution using two methods. In the first method[1-6] an additional quencher is added to the reaction mixture and its effect on exciplex formation and yield of photoproduct is studied as the quencher concentration is varied. If the two processes are always quenched to the same extent the exciplex is necessarily an intermediate in the photoreaction. This approach, apart from being somewhat indirect, suffers from the following limitations :

(a) The exciplex may often be difficult to observe as a result of inefficient formation and/or low fluorescence efficiency.

(b) Temperature dependence studies (e.g. for determination of activation energies) are problematic as cooling the solution inhibits kinetic processes such as diffusion and ultimately causes freezing and/or precipitation of reactants.

The second method, used by Ferguson et al[7-9] overcomes these limitations by reducing the system to a monomolecular one. The photoreaction is studied as a "photoisomeration" of linked bichromophoric molecules[8,9] or sandwich dimers[7] dissolved in a glass-forming solvent. Mechanistic information is obtained from the temperature dependence of the fluorescence decay times and quantum yields for radiative and non-radiative processes.

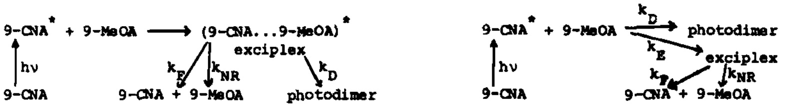
The method discussed here, namely the use of a mixed organic crystal, is very simple and retains the advantages of the latter approach while leaving the interacting species as "free" molecules in the electronic excited state.

RESULTS AND DISCUSSION

9-Cyanoanthracene (9-CNA) and 9-methoxyanthracene (9-MeOA) have been reported to photodimerize in solution giving the head-to-head heterodimer[10]. No concurrent exciplex fluorescence was observed[10]. In 9-CNA crystals doped with 9-MeOA, however, both exciplex fluorescence and heterophotodimerization were observed[11] at room temperature. The observation of the same dimer[11] as from solution[10] is consistent with the head-to-head crystal structure of 9-CNA[12] and recent force-field calculations which have shown[13] that the 9-MeOA molecules replace 9-CNA molecules substitutionally.

The two possible reaction mechanisms (that photodimerization proceeds via the exciplex or that it does not) are shown in Scheme 1. The correct mechanism can be determined from the temperature dependence of the exciplex fluorescence quantum yield (ϕ_F) and decay time (τ).

SCHEME 1



A. Photodimerization proceeds via the exciplex

$$\phi_D = \frac{k_D}{k_F + k_{NR} + k_D}$$

B. Photodimerization proceeds independently of exciplex formation

$$\phi_D = \frac{k_D}{k_E + k_D}$$

k_F = rate constant of exciplex fluorescence, k_{NR} = rate of non-radiative exciplex relaxation processes, k_D = rate of formation of photodimer, k_E = rate of exciplex formation, ϕ_D = quantum yield for formation of photodimer.

Note : (a) The excited state of 9-CNA which diffuses through the crystal is the excimer[15]

(b) The quenching of (9-CNA)* by 4% 9-MeOA is practically 100%[11]

A. Photodimerization proceeds via the exciplex

Under this mechanism it was shown[14] that

$$\phi_F = k_F (k_F + k_{NR} + k_D)^{-1} = k_F \tau \qquad (1)$$

If k_{NR} is divided into temperature independent (k^o_{NR}) and temperature dependent (k'_{NR}) parts, upon normalizing with respect to the limiting low temperature values (τ^o, ϕ^o_F) when k_D and k'_{NR} are zero, we get[14]

$$\frac{\tau}{\tau^o} = \frac{\phi_F}{\phi^o_F} = \frac{k_F + k^o_{NR}}{k_F + k_{NR} + k_D} = 1 - \frac{k'_{NR} + k_D}{k_F + k_{NR} + k_D}$$

$$= 1 - \phi'_{NR} - \phi_D \qquad (2)$$

B. Photdimerization does not proceed via the exciplex

In this case it was shown[14] that

$$\tau = (k_F + k_{NR})^{-1} \qquad (3)$$

$$\phi_F = k_E (k_F + k_D)^{-1} k_F \tau \qquad (4)$$

Normalizing as before, we get

$$\frac{\phi_F}{\phi^o_F} = \frac{k_E}{k_F + k_D} \, \frac{\tau}{\tau^o} = (1 - \phi_D) \, \tau/\tau^o \qquad (5)$$

Thus, a necessary and sufficient condition for distinguishing between the two mechanisms, as shown by (2) and (5), is that ϕ_D be larger at some temperature than the experimental error in determining the <u>relative</u> fluorescence quantum yield and lifetime.

The exciplex fluorescence decay time and quantum yield have been measured[14,15] over the temperature range 5 - 360 K (see Fig. 1). ϕ_F/ϕ^o_F and τ/τ^o show the same behaviour over the entire temperature range within experimental error (3%). This value is small compared to the measured value[14] of 0.12 for ϕ_D at 293 K ; thus it is unequivocably concluded that photodimerization proceeds via the exciplex.

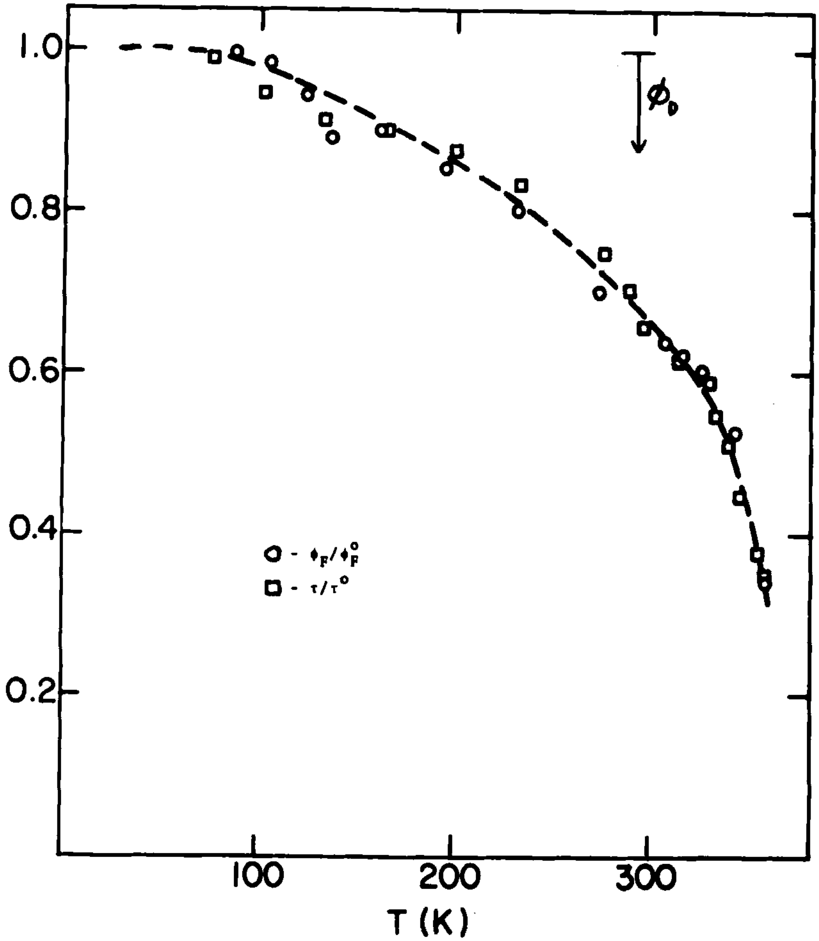


FIGURE 1. Temperature dependence of the fluorescence quantum yield and decay time for the 9-CNA - 9-MeOA exciplex. ϕ_F^o=0.3 and τ^o=78ns[14,15].

Determination of Activation Energies

We have shown[14] from the temperature dependence of ϕ_F/ϕ_F^o that there are two thermally activated processes quenching the exciplex state, with energies of activation of 5.4 and 0.95 kcal/mol. The former is assigned as the activation energy for photodimerization because it is similar to values determined for analogous photoadditions proceeding via exciplexes[7,9,16] and predicts ϕ_D and its temperature dependence in satisfactory agreement with experiment[14].

Exciplex spectroscopy

The organic crystal matrix enables us to study the spectroscopy of the exciplex at very low temperatures, something which is not possible in normal solution studies. We have reported[11] that in the 9-CNA - 9-MeOA mixed crystal system the exciplex may be directly excited at 77 K or below via a weak absorption band to the red of the pure crystal absorption edge. The resultant emission (see Fig. 2) contains some weak structure[11] (corresponding to a typical anthracene vibronic progression), something not observed at room temperature or in solution. Both these results are consistent with the exciplex ground state being less repulsive than that of excimers due to some weak charge-transfer stabilization in the former[11].

CONCLUSION

We have demonstrated the advantages of studying the mechanism of a photochemical reaction in the solid-state. This approach should be applicable to a wide range of solid-state reactions. Spectroscopic studies of the exciplex have been performed in more detail than is possible in solution.

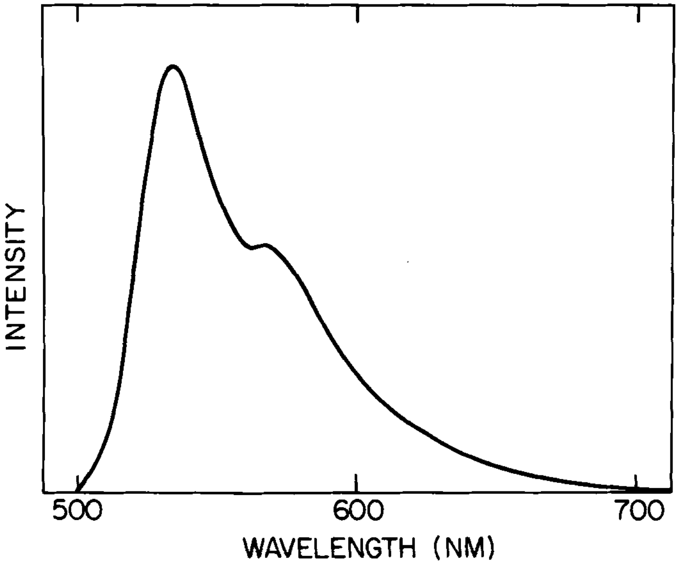


FIGURE 2. Structured mixed crystal exciplex emission from 9-CNA - 9-MeOA after direct excitation with 450 nm light at 4.2 K.

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