

Role of Exciplex in the Photocycloaddition of 2,5-Dimethylhexa-2,4-diene to Anthracene

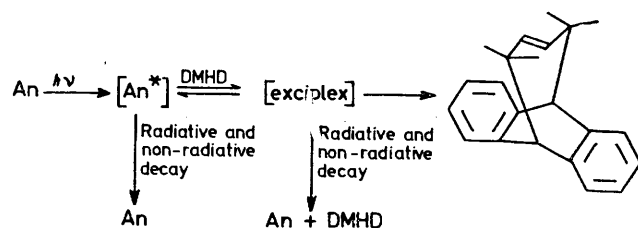
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Summary The photocycloaddition between anthracene and 2,5-dimethylhexa-2,4-diene is demonstrated to proceed via the exciplex.

EXCIPLEXES are frequently observed in systems which undergo photochemical reactions and have been commonly invoked as reactive intermediates,¹ although compelling evidence for this assumption is rare.² Exciplex fluorescence has been observed from solutions of 2,5-dimethylhexa-2,4-diene (DMHD) and various anthracenes, including unsubstituted anthracene.³ The systematic correlation between the solvent shifts of these exciplex emissions and the photochemistry observed suggests that the exciplex plays a role in the photocycloadditions of dienes to anthracenes.⁴ We present here kinetic evidence which demonstrates that the exciplex between anthracene and DMHD is an intermediate in the photocycloaddition process.

One characteristic feature of exciplex systems is the reversibility of exciplex formation, indicative of the partial establishment of equilibrium between the exciplex and the isolated components.^{4,5} In the case of the anthracene-DMHD system, this equilibrium is clearly revealed by a 68% increase in the Stern-Volmer quenching constant (K_{sv}) as the temperature decreases from 50 to -10°C (Table).⁶ A similar change in the quantum yields with temperature occurs for the photocycloaddition of DMHD to anthracene. The quantum yield for this reaction increases by 83% from 50 to -20°C . Thus there is clearly a reversible step which precedes the photocycloaddition. Our results also suggest that it may be advantageous experimentally to carry out photocycloadditions at lower temperatures.



An = Anthracene; DMHD = 2,5-Dimethylhexa-2,4-diene

Under the conditions in which the quantum yields were measured, it is possible to determine the fraction of the excited anthracene which is quenched by DMHD, and thus one can calculate the limiting quantum yield, which is the fraction of the quenched excited anthracene which results in product formation [equation (1)]. The significant result,

$$\phi_{lim} = \phi \{1 + [K_{sv}(\text{DMHD})]^{-1}\} \quad (1)$$

shown in the Table, is that the limiting quantum yield is constant with temperature, 0.44 ± 0.04 .

TABLE
Photochemical interaction between anthracene and DMHD in methylcyclohexane.

Temp./ $^\circ\text{C}$	$K_{sv}^a/l \text{ mol}^{-1}$	ϕ^b	ϕ_{lim}^c
-20	—	0.33 ± 0.01	—
-10	15.8 ± 0.7	0.26 ± 0.01	0.44
0	15.6 ± 0.2	0.28 ± 0.03	0.48
10	15.1 ± 0.5	0.26 ± 0.01	0.45
20	14.9 ± 0.3	0.22 ± 0.03	0.39
30	13.6 ± 0.1	0.22 ± 0.02	0.40
40	11.5 ± 0.3	0.23 ± 0.01	0.46
50	9.4 ± 0.8	0.18 ± 0.01	0.39

^a Stern-Volmer quenching constant for the quenching of anthracene fluorescence by DMHD, measured with a Perkin-Elmer MP-4 Spectrofluorimeter. ^b Quantum yield of anthracene consumption in degassed solutions at 365 nm, measured at $0.0008 \text{ mol l}^{-1}$ anthracene and 0.09 mol l^{-1} DMHD with a conventional merry-go-round apparatus. A correction factor has been applied to account for incomplete light absorption. ^c See text.

The fact that both the quantum yield and K_{sv} increase with decreasing temperatures rules out any mechanism which does not involve a reversible step prior to product formation. On the other hand, if a second exciplex were formed preceding the photocycloaddition which was significantly different in energy from the exciplex, the two equilibria between excited anthracene, DMHD, and the two exciplexes would respond differently to changes in temperature, resulting in differing limiting quantum yields at different temperatures. The absence of any change implies that only one exciplex is the precursor to quenching, exciplex fluorescence, and product formation.⁷

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† Our experimental data do not exclude other complex mechanisms, such as the formation of two thermodynamically indistinguishable exciplexes or two exciplexes in rapid thermoneutral equilibrium. Such possibilities will be discussed in a future publication.

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⁶ See also F. D. Lewis and C. E. Hoyle, *J. Amer. Chem. Soc.*, 1975, **97**, 5950.