Photoaddition of S_1 Naphthalene to S_0 Acrylonitrile

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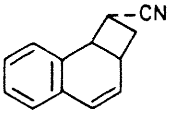
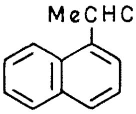
Summary The reactive state of naphthalene in a mixed photoaddition has been identified as the lowest singlet excited state, and attention is drawn to possible difficulties in studying singlet state reactions, due to triplet destruction of product.

ALTHOUGH photodimerization[1] and mixed additions[2] of arenes have been known for some time, most work has been concerned with product structures, and quantitative[3] data, particularly on the mixed photoadditions, are generally lacking.

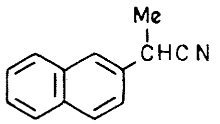
We recently reported[4] that irradiation of naphthalene and acrylonitrile in alcohol solution afforded a cyclobutane adduct (**1**) and the substituted naphthalenes (**2**) and (**3**).



(1)



(2)



(3)

We now report results which show that the reactive state involved in the cycloaddition is the lowest single excited state of naphthalene.

The characterization was achieved by relating the quenching of naphthalene fluorescence by acrylonitrile to the quantum yield of cycloaddition. The Stern–Volmer plot for the fluorescence quenching is shown in Figure 1.

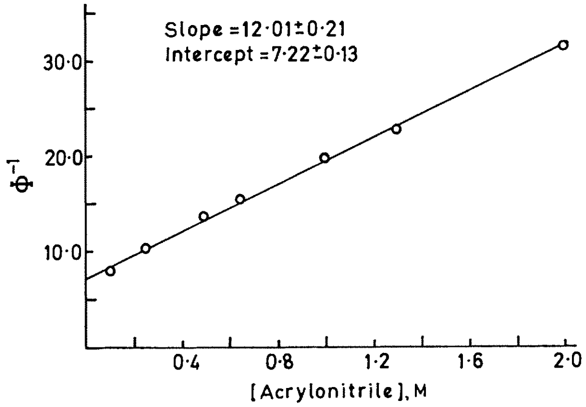


FIGURE 1. *Stern–Volmer plot for quenching of naphthalene fluorescence by acrylonitrile.*

The measurements† were performed on *tert*-butyl alcohol solutions, containing 0·1 M 2,3-dimethylbuta-1,3-diene (see below). The linear relationship between Φ_{fluor}^{-1} and acrylonitrile concentration shows that the fluorescent state is being deactivated in a bimolecular process.

The quantum yield of cycloaddition was also determined as a function of acrylonitrile concentration. In the early runs, a deviation from the expected linear plot of Φ_{addn}^{-1} *versus* [acrylonitrile]$^{-1}$ was evident, as shown by the upward curvature of curve A, Figure 2. We found that the curvature was a result of sensitized decomposition of (**1**), since (**1**) was found to decompose rapidly when photolyzed in a control experiment with benzophenone or naphthalene as sensitizer. This suggested a triplet reaction of (**1**), and it was found that the decomposition could be effectively inhibited, under the photolysis conditions and in control experiments, by the addition of 0·1 M of 2,3-dimethylbuta-1,3-diene. The diene quenches naphthalene singlets inefficiently.[5] It can be seen from plot B, Figure 2 that in the presence of the diene, Φ_{addn}^{-1} is proportional to [acrylonitrile]$^{-1}$.

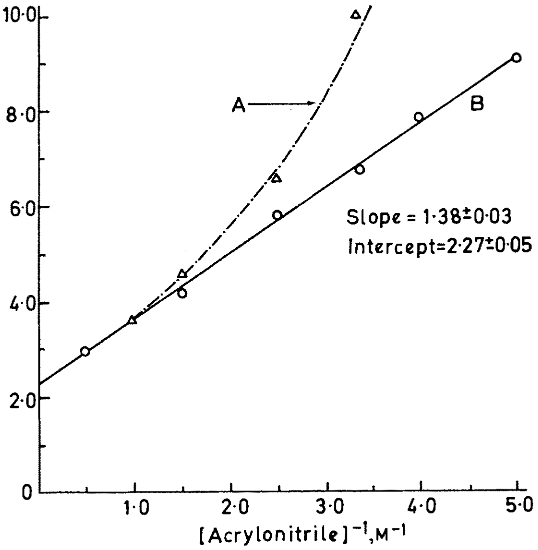


FIGURE 2. *Plots showing dependence of quantum yield of cycloaddition on acrylonitrile concentration*: A, *runs without added quencher*; B, *runs with* 0·1M *2,3-dimethylbuta-1,3-diene added.*

These results can be interpreted by the following mechanistic scheme.

$$\begin{array}{llll}
 & & \text{Rate (s}^{-1}\text{)} & \\
(\mathrm{N}) & \xrightarrow{h\nu} (\mathrm{N})^{\mathrm{S}} & & (1)\\
(\mathrm{N})^{\mathrm{S}} & \xrightarrow{-h\nu'} (\mathrm{N}) & k_{\mathrm{f}} & (2)\\
(\mathrm{N})^{\mathrm{S}} & \rightarrow (\mathrm{N})^{\mathrm{T}} & k_{\mathrm{ic}} & (3)\\
(\mathrm{N})^{\mathrm{S}} & \rightarrow (\mathrm{N}) & k_{\mathrm{d}} & (4)\\
(\mathrm{N})^{\mathrm{S}} + \mathrm{A} & \rightarrow (\mathrm{N}) + \mathrm{A} & k_{\mathrm{q}}\,[\mathrm{A}] & (5)\\
(\mathrm{N})^{\mathrm{S}} + \mathrm{A} & \rightarrow \text{Adduct} & k_{\mathrm{a}}\,[\mathrm{A}] & (6)\\
(\mathrm{N})^{\mathrm{T}} + \text{Adduct} & \rightarrow 2(\mathrm{N}) + \mathrm{A} & & (7)
\end{array}$$

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† Fluorescence intensities were measured on an Aminco–Bowman spectrofluorimeter at 339 nm, with excitation at 303 nm. Solutions were deoxygenated by purging with argon.

(N) is ground state naphthalene, $(N)^S$ and $(N)^T$ are naphthalene singlet and triplet respectively, and A is acrylonitrile: k_d includes the rate of quenching of $(N)^S$ by 2,3-dimethylbuta-1,3-diene.

The usual steady-state approximation allows us to write expressions for the quantum yields of fluorescence (process 2) and cyclo-adduct formation (process 6).

$$\phi^{-1}\ (\text{fluorescence}) = 1 + \frac{k_d + k_{ic}}{k_f} + \frac{(k_q + k_a)\,[A]}{k_f}$$

$$\phi^{-1}\ (\text{cycloaddition}) = 1 + \frac{k_q}{k_a} + \frac{(k_f + k_d + k_{ic})}{k_a} \cdot \frac{1}{[A]}$$

If the above scheme is correct, the product of the intercepts of Figures 1 and 2 should equal the product of the slopes.‡ The products were indeed found to be equal within experimental error, thus identifying the reactive state as the lowest singlet (B_{3u}^{-}) of naphthalene.

It is interesting that the intercept in Figure 2 is greater than unity. The quantum yield at infinite acrylonitrile concentration is calculated from this intercept to be 0·44, which shows that k_q and k_a are comparable. Bimolecular energy-wasting steps have been demonstrated to occur in the dimerization of 1,2-diphenylcyclobutene,[3b] the dimerization of indene,[3c] and in additions of cyclic enones.[6]

It is probable that an "exciplex" of naphthalene singlet and acrylonitrile is formed, which either collapses to form (**1**) or decays to ground state reactants. It is quite likely that triplet sensitized decomposition of a product, formed in a singlet reaction, is a general phenomenon, and the possibility should be borne in mind, particularly whenever quantitative photochemical work is undertaken.

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‡ The slopes, intercepts, and standard deviations were obtained from a least-squares fit of the data.

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[3] Reactions which have been studied include (a) the photodimerization of anthracene; E. J. Bowen, *Adv. Photochem.*, 1963, **1**, 23; (b) the dimerization of 1,2-diphenylcyclobutene; C. D. DeBoer and R. H. Schlessinger, *J. Amer. Chem. Soc.*, 1968, **90**, 803; (c) the sensitized dimerization of indene, C. De Boer, *ibid.*, 1969, **91**, 1855.

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