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NEGATIVE TEMPERATURE DEPENDENCE OF THE PHOTOCHEMICAL (4 + 4) CYCLOADDITION OF FURAN TO α-NAPHTHONITRILE: EVIDENCE FOR EXCIPLEX INTERMEDIACY[1)]

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The photochemical (4 + 4) cycloaddition of furan to α-naphthonitrile (α-NN) giving 1-cyano-9,10-benzo-11-oxatricyclo[4,2,2,$1^{2,5}$]undeca-3,7,9-triene (I) showed negative temperature dependency. An identical Arrhenius plot of $\gamma k_r \tau$ was obtained from both quantum yield and fluorescence quenching experiments. These results were interpreted as caused by reversible dissociation of an exciplex.

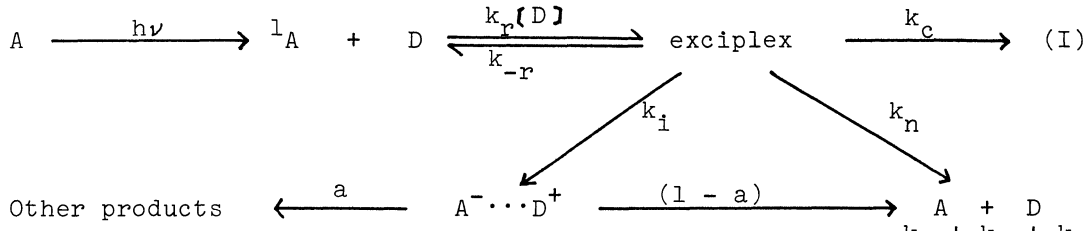
In a previous paper,[2)] we reported a novel photochemical (4 + 4) cycloaddition of furan to α-NN and suggested an exciplex mechanism on the basis of appearance of new emission and solvent dependent character of the photochemical reaction as well as fluorescence quenching. However, this suggestion is not conclusive, since it is left to be solved whether or not the (4 + 4) cycloaddition reaction is a mode of exciplex decay as a chemical process.

Recently, much attention has been paid on exciplex intermediacy in organic photochemical reactions,[3)] but direct and confirmative evidences are lack for the most part. Although negative temperature dependency has been regarded as a strong evidence for exciplexes or excimers, a few examples have been so far reported.[4)] In the present paper, we wish to report negative temperature dependence of the photochemical reaction of α-NN with furan.

Quantum yields for the disappearance of α-NN[5)] were determined by potassium ferrioxalate actinometry using a merry-go-round apparatus at 313 nm in a temperature regulated water bath. Fluorescence measurements were carried out with a Hitachi MPF-2A fluorometer equipped with a temperature regulated cell compartment. When the reciprocals of the quantum yields were plotted with the reciprocals of furan concentrations, it was found that the intercept (90) was independent on temperature, while the slopes increased with the increase of temperature. Thus the intercept-to-slope ratios were determined to be 0.86 at 1.5 °C, 0.69 at 15 °C, 0.35 at 30 °C, and 0.11 M^{-1} at 60 °C, indicating negative temperature dependency. The adduct (I) was so stable under the conditions to decompose into α-NN and furan in no appreciable amount.

The fluorescence behavior of α-NN in the presence of furan was also temperature dependent (Fig. 1). The slopes of Stern-Volmer plots for the fluorescence quenching were determined to be 0.77 at 5 °C, 0.62 at 22 °C, and 0.36 M^{-1} at 40 °C, showing again negative temperature dependency.

These results are consistent with the exciplex mechanism[2] modified by taking account of reversible dissociation of an exciplex, from which the rate equations (1) and (2) are derived by steady-state assumption.



$$F_0/F = 1 + \gamma k_r \tau [D] \quad \cdots\cdots \quad (1); \qquad 1/\phi_{-A} = \left(1 + \frac{1}{\gamma k_r \tau [D]}\right)\left(\frac{k_n + k_i + k_c}{k_c + a k_i}\right) \quad \cdots \quad (2)$$

$$\gamma = (k_n + k_i + k_c)/(k_n + k_i + k_c + k_{-r}); \quad A = \alpha\text{-NN and } D = \text{furan}$$

An Arrhenius plot of $\gamma k_r \tau$ obtained from the quantum yield measurements is superimposable on that from the fluorescence quenching experiments within experimental errors (Fig. 2). This result indicates with no doubt that a common intermediate, i.e. an exciplex, is operative in both the fluorescence quenching and the cycloaddition.[6] It is of interest to note that the exciplex is not only emissive, but also reactive to undergo the cycloaddition as a mode of the non-radiative decay. Detailed discussion will be published in a separate paper.

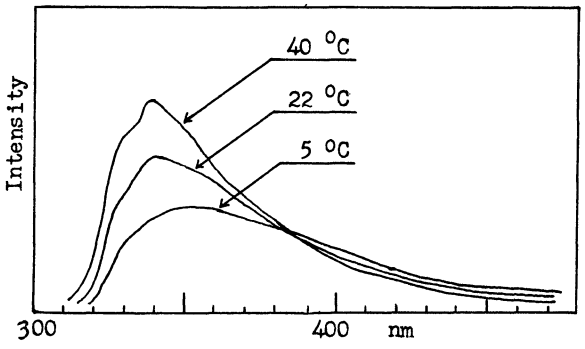


Fig. 1. Fluorescence spectra of a furan solution of α-NN (1.7×10^{-4} M).

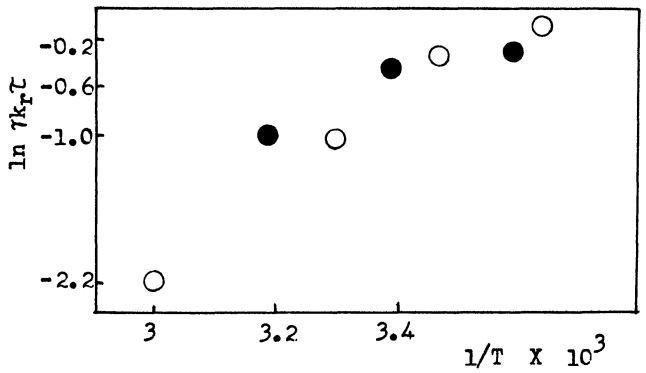


Fig. 2. An Arrhenius plot of $\gamma k_r \tau$ from quantum yield (-○-) and fluorescence quenching (-●-) runs.

References

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5) Unless otherwise noted, degassed cyclohexane solutions were used for quantum yield and fluorescence measurements.
6) Since the fluorescence intensity of α-NN was found to be approximately constant within the temperature range investigated, the life time (τ) may be constant.

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