

A SPECTROSCOPIC STUDY OF THE
TOLAN-NAPHTHALENE PHOTOADDITION

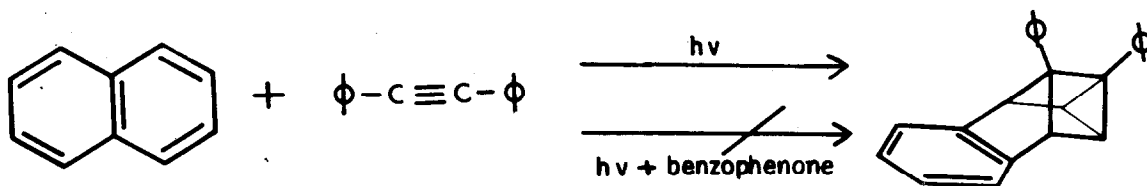
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Following the observation by Sasse (1) that photoassociation occurred between tolan (diphenylacetylene) and naphthalene in solution,



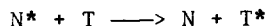
a spectroscopic study of the reaction was suggested (2).

In an investigation of the quenching properties of tolan and naphthalene it was found that the quenching in solution of naphthalene fluorescence by tolan is extremely efficient, and exhibits the following characteristics:

- (i) it increases with a decrease in solvent viscosity,
- (ii) it increases with decreasing temperature for relatively fluid solvents, although
- (iii) in solvents of high viscosity a decrease in temperature decreases the amount of quenching.

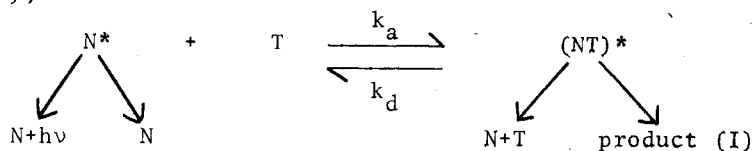
The quenching obeys Stern-Volmer kinetics.

It was also noted that naphthalene had a negligible quenching effect on tolan fluorescence, and, whereas this can be attributed to the very short lifetime of tolan in the excited state (ca. 10^{-9} seconds), it is significant that the fluorescence of tolan is not at all sensitized by the relatively long-lived (ca. 10^{-7} seconds) excited naphthalene. This rules out the possibility of straight energy transfer according to the reaction scheme



where N represents a molecule of naphthalene, T = tolan, and an asterisk denotes a molecule in an excited state.

The behaviour of the tolan-naphthalene system is most readily rationalised on the basis of the mechanism used for excimer formation, with the proviso that no fluorescence can be attributed unambiguously to the quench complex ("exciplex");



The apparent rate constant for quenching varies inversely with the solvent viscosity, and has a value of 2.4×10^9 litre mole⁻¹ sec⁻¹ in 90% ethanol at 20°. The values of C_h (the concentration of tolan which halves the fluorescence intensity of naphthalene) at room temperature are .0022M for isopentane (viscosity $\eta = 0.22$ cp), .0045M for 90% ethanol ($\eta = 1.6$ cp), and .0095M for benzyl alcohol ($\eta = 5.8$ cp), indicating that quenching is collision-dependent.

From the dependence of C_h on temperature, and after correcting for the viscosity of the solvent, we obtained a value of $\Delta H = -6.8$ kcal mole⁻¹, a value which forces us to consider the reverse reaction.

An examination of the ultraviolet absorption spectra of the two compounds shows that the 0-0 transition to the lowest excited singlet electronic level of tolan requires $2,700$ cm⁻¹ more energy than that of naphthalene (3). Thus complete energy transfer would be an endothermic process ($\Delta H = +7.7$ kcal mole⁻¹), in contrast to the exothermic formation of the exciplex which must be a different physical process. The formation of an exciplex does not allow a conclusion to be reached as to whether the degradation of electronic energy to vibrational energy is intermolecular (4), or intramolecular. In the latter case it is followed by transfer of vibrational energy to the quenching species with the dissociation of the anti-bonding electronic ground state complex.

Clearly the vibrational properties of the molecules will be critical, and in this connection it is useful to consider the excited states of acetylene.

The first excited state of acetylene is trans bent and the vibrations with this same symmetry form an anomalously strong ground-state progression in

the absorption spectrum (5) because the decrease in the population of the higher levels (as given by the Boltzmann distribution) is partially compensated by an increase in transition probability through a "more vertical" Franck-Condon transition (Fig. 1).

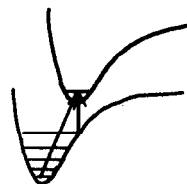


FIG.1

Whereas identical arguments do not necessarily apply to tolan, the long vibrational progressions seen in its fluorescence spectrum at low temperatures (-60°C) increasing from a small O-O band to a maximum 3200 cm^{-1} to the red, indicate that excitation causes some considerable change in geometry. The expected effect on the absorption spectrum is revealed by noting the large apparent bathochromic shift on increasing the tolan concentration, due to the intensification of a long, weak tail of the absorption spectrum (6).

The coup de grace is applied by comparing the excitation spectra of solutions (7) of naphthalene and tolan. That of naphthalene behaves quite normally, coinciding with the L_b absorption band from $330\text{ m}\mu$ to shorter wavelengths; however, the excitation spectrum of tolan extends from $300\text{ m}\mu$ ($5\text{ m}\mu$ higher than the O-O absorption band at $295\text{ m}\mu$) up to $350\text{ m}\mu$.

This means that "hot" vibrational levels in the ground state of tolan are favoured for excitation, and the effective energy of the vibronic promotion of tolan can in practice be lower than that of naphthalene. The small amount of overlap between donor emission and acceptor absorption is of the same order of magnitude as in excimer formation, and thus we assume the same energetics are involved.

As experiments have suggested that the photoaddition proceeds via an initially excited naphthalene species, it appears that the reaction mechanism proposed for quenching, explained on the basis of the hot vibrational levels of tolan, is in fact the mechanism that produces the product (I).

In molecules which are likely to have a different geometry in the excited state, the normal solution UV spectrum can mask subtleties which are of critical importance in determining the course of a photochemical reaction.

REFERENCES

1. W.H.F. Sasse, P.J. Collin and Galina Sugowdz, Tetrahedron Letters, 38, 3373 (1965).
2. We thank Dr. Wolf Sasse for suggesting the problem and supplying us with various materials.
3. For a detailed analysis of the fluorescence spectra of tolan and naphthalene in frozen solutions, see V.I. Mikhailenko, P.A. Teplyakov, V.V. Trusov and V.M. Martynchenko, Optics and Spectroscopy, 20, 29 (1966).
4. S.L. Murov, R.S. Cole and G.S. Hammond, J.Am.Chem.Soc., 90, 2957 (1968).
5. C.K. Ingold and G.W. King, J.Chem.Soc., 2725 (1953).
6. The tolan must not contain (i.e. must not be prepared from) the isomorphous trans-stilbene, which itself has considerable absorption in the region of the tolan absorption tail.
7. Excitation spectra of solutions the same concentration as those used in the photoreaction (1), i.e. 0.1M, were measured from the front surface of the cell.