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MEDIUM EFFECTS ON THE PHOTO-ADDITION OF NAPHTHALENE AND PYRROLE

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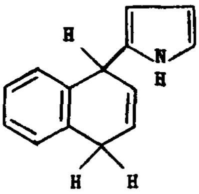
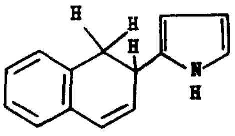
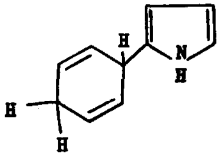
We recently reported that naphthalene and pyrrole react on irradiation,[1] and the products formed, (I) and (II) are homologous with the benzene-pyrrole photoadduct (III).[2]



(I)



(II)



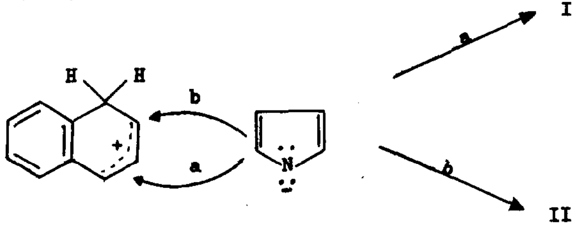
(III)

In this paper we report studies of solvent effects on this reaction, from which we conclude that (i) the reaction is initiated by an "exciplex" of naphthalene singlet[1] (S_1) and pyrrole, which resembles the familiar excited complexes of amines,[3-7] and (ii) the final step in the sequence of processes leading to (I) and (II) is ionic. The study included determination of solvent effects on the quenching of naphthalene fluorescence by pyrrole and by N-methylpyrrole, and on the ratio of the major adducts, (I) and (II).

The results of the quenching experiments are given in Table I. The measurements were made on an Aminco-Bowman Spectrofluorimeter; excitation was at 322 nm, monitoring at 343 nm, and solutions were deoxygenated by purging with argon. The Stern-Volmer plots were linear over the range of pyrrole concentrations studied. The slopes of these plots, the fluorescence lifetimes of naphthalene, and the derived bimolecular rate constants for quenching, in each of the three solvents, are given. The calculated diffusion-limited rate constants are also given for comparison. The quenching constants, kq, are similar in the three solvents, and are close to the diffusion limit. This indicates that the mechanism for quenching resembles that proposed[3-7] for similar processes involving various amines.

The dependence of the ratio of the major products (I) and (II) on solvent polarity is shown in Table II. The fraction of the more stable isomer (II)[8] increases with increasing polarity of the medium, and it is noteworthy that a similar trend is observed in the medium effects on certain ground state, ionic reactions. In particular, about equal amounts of 1,2- and 1,4-dibromides are formed from bromine and 1,3- dienes in polar media, but the 1,4- dibromide (more stable) is favoured under more polar conditions.[9] Also, the capture of unsymmetrical allylic carbonium ions (from silver ion and allylic halides) by solvent shows a similar dependence to that given in Table II.[10] The cinnamyl cation, for example, gives the two possible solvolysis products in about equal amounts in ethyl alcohol.[10] The parallel is striking and we suggest that (I) and (II) are formed from an ion pair, as follows:

(IV)



The charge-transfer interpretation of fluorescence quenching, proposed by Weller[3] and substantiated by him[4] and by others[5-7] can be used as the basis for the following mechanism which explains our results.

$$Ns_1 + Py \longrightarrow [\overset{\delta-}{N}\text{--------}\overset{\delta+}{Py}] \qquad \text{Rate } kq\,[Py]$$

charge-transfer
exciplex

$$[\overset{\delta-}{N}\text{------}\overset{\delta+}{Py}] \xrightarrow{H^+\ \text{shift}} [\overset{+}{NH}\text{------}Py^-]$$

ion-pair

$$[\overset{+}{NH}\text{-----}\overset{-}{Py}] \xrightarrow{\text{a or b}} \text{(I) or (II)}$$

Ns_1 is naphthalene singlet, Py is pyrrole, and $\overset{+}{NH}$ is the 1-H naphthalenonium ion shown in (IV). This mechanism is consistent with our deuterium labelling experiment using N-dueteriopyrrole,[1] and with the observation that N-methylpyrrole quenches Ns_1 efficiently, but does not undergo reaction.[1,2]

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Table I. Quenching of Naphthalene Fluorescence by Pyrroles.

Solvent	Quencher	k^{a} diff x 10^{-9} M^{-1} sec^{-1}	Lifetime n sec	Slope x 10^{-2}, M^{-1}	kq x 10^{-9} M^{-1} sec^{-1}
Ethanol	Pyrrole	8.5	85[b]	2.07	2.43
	N-Methylpyrrole			0.86	1.01
Acetonitrile	Pyrrole	10.0	118[c]	3.85	3.26
	N-Methylpyrrole			1.95	1.65
Benzene	Pyrrole	5.0	96[b]	2.43	2.53

[a] P.J. Wagner and A.E. Kemppainen, *J. Amer. Chem. Soc.*, 1969, **91**, 3085.

[b] D. Schulte-Fröhlinde and R. Pfefferkorn, *Ber. Bunsengesellschaft Phys. Chem.*, 1968, **72**, 330.

[c] N. Mataga, M. Tamura and H. Nishimura, *Mol. Physics*, 1965, **9**, 367.

Table II. Solvent Effects on the Naphthalene-pyrrole Reaction.

Solvent	Dielectric Constant[a]	Fraction (%)[c] of I	Relative Reaction Rates
Hexane	1.9	82	-
Benzene	2.3	74	1.45
Dichloromethane	9.1	66	1.08
95% Ethanol[b]	24.3	60	1.04
Acetonitrile	37.5	62	1.00
Methanol[b]	32.6	52	0.89
80% Methanol[b]	$>$ 32.6	49	0.59

[a] A.A. Maryott and E.R. Smith "Table of Dielectric Constants of Pure Liquids". National Bureau of Standards, Circular 514, Washington, D.C. 1951.

[b] The effects of these solvents are probably due in part to their hydrogen bonding properties.

[c] These ratios were measured by g.l.c. on 1.5 m x 3.0 mm of 5% QF-1 at 153°; p-bromobenzophenone was used as an internal standard.

References

1. J.J. McCullough, C.W. Huang and W.S. Wu, Chem. Comm., 1970, 1368.
2. M. Bellas, D. Bryce-Smith and A. Gilbert, Chem. Comm., 1967, 263; D. Bryce-Smith, Pure Appl. Chem., 1968, 16, 47.
3. H. Leonhardt and A. Weller, Z. Physik. Chem., N.F., 1961, 29, 277; idem., Ber. Bunsengesellschaft Phys. Chem., 1963, 67, 791.
4. A recent account is given in D. Rehm and A. Weller, Israel J. Chem., 1970, 8, 259.
5. T. Miwa and M. Koizumi, Bull. Chem. Soc. Japan, 1966, 39, 2588; K. Kaneta and M. Koizumi, ibid., 1967, 40, 2254.
6. W.R. Ware and H.P. Richter, J. Chem. Phys., 1968, 48, 1595.
7. R.S. Davidson, Chem. Comm., 1969, 1450.
8. 1,4-dihydronaphthalenes isomerize to the 1,2-dihydronaphthalene derivatives on equilibration with base: A.J. Birch, Quart. Rev., 1950, 4, 69, and references cited. See also D.J. Cram "Fundamentals of Carbanion Chemistry", Academic Press, New York, N.Y. 1965. Ch. V.
9. C.K. Ingold "Structure and Mechanism in Organic Chemistry", G. Bell and Sons Ltd., London, 1953, p. 673.
10. R.H. Dewolfe and W.G. Young, Chem. Rev., 1956, 56, 797.