Excited Complex Formation between Aromatic Hydrocarbons and Heterocyclic Compounds

By R. STEPHEN DAVIDSON, ANDREW LEWIS, and (in part) TERENCE D. WHELAN
(*Department of Chemistry, The University, Leicester* LE1 7RH)

Summary Many excited singlet aromatic hydrocarbons form fluorescent exciplexes with furans, thiophens, pyrroles, and indoles.

THERE have been a number of reports of photoreactions of aromatic hydrocarbons with heterocyclic compounds, *e.g.* reaction of benzene with furan[1] and pyrrole,[2a,b] naphthalene with pyrrole,[3] and 1-cyanonaphthalene with furan.[4] Since the ionisation potentials of these heterocyclic compounds lie in the region 8—10 eV[5] there is the possibility that they will quench the first excited singlet state of the hydrocarbons by an electron transfer process. The occurrence of such a process will not only affect the physical decay processes of the excited hydrocarbon but also the type of products formed in the reaction.[6] We now present unequivocal evidence for the formation of singlet exciplexes between aromatic hydrocarbons and heterocyclic compounds.

Quenching of the fluorescence of 1-cyanonaphthalene, 9-cyanophenanthrene, and 9-cyanoanthracene by furans, thiophens, pyrroles, and 1-methylindole in non-polar solvents is accompanied by the appearance of a new structureless fluorescence band to the red of the hydrocarbon fluorescence (see Table). These emission bands are attributed to fluorescence of exciplex intermediates. The emitting species has considerable charge-transfer character since the wavelength for maximal emission is particularly sensitive to changes in solvent polarity. In the majority of cases, increase in the polarity of the solvent is accompanied by a shift of the emission band to the red with a concomitant decrease in quantum yield of exciplex fluorescence. No exciplex emission from any of the systems was observed when ethanol and acetonitrile were used as solvents. The wavelength of exciplex emission for a number of the complexes was determined for a variety of solvents and from these data dipole moments for the complexes were calculated.[7] Exciplexes of 1-cyanonaphthalene with 2-methylfuran, 2,5-dimethylfuran, 1-methylpyrrole, and 1-methylindole were found to have dipole moments of *ca.* 8—9 Debye,[†] *i.e.* these complexes have considerable charge-transfer character.

From a study of the effect of temperature upon the relative intensity of aromatic hydrocarbon and exciplex fluorescence bands in the 1-cyanonaphthalene–2-methylfuran and –1-methylpyrrole systems it was calculated[8] that the enthalpy of exciplex formation in the two systems was 2·5 and 9·0 kcal mol^{-1} respectively. The lower stability of the exciplex derived from 2-methylfuran is to be expected

TABLE

Wavelength (nm) of exciplex emission in benzene solution or rate constant (l mol^{-1} s^{-1}; ± 0·5) for fluorescence quenching[a]

	Naphthalene	1-Cyanonaphthalene	Anthracene	9-Cyanoanthracene	9-Cyanophenanthrene
Furan (8·89 eV)[b] ..	c	4×10^{7}[d] 1×10^{9}[e]	c	1×10^{7}[d] 1×10^{7}[e]	c
2-Methylfuran (8·39 eV)[b]	c	414 nm	c	c	c
2,5-Dimethylfuran (8·01 eV)[b] ..	c	432 nm	c	3×10^{9}[d] 5×10^{9}[e]	437 nm
Thiophen	c	c	c	1×10^{7}[d] 1×10^{7}[e]	c
1-Methylpyrrole .. (8·2 eV)[b]		452 nm 9×10^{9}[e]	8×10^{8}[e]	2×10^{9}[d] $6{\cdot}5 \times 10^{9}$[e]	452 nm
1,2,5-Trimethylpyrrole	430 nm	520 nm	500 nm		515 nm
1-Methylindole		455 nm			455 nm

[a] In none of the systems investigated could association between the hydrocarbon and heterocycle be detected by u.v. spectroscopy. [b] Ionisation potentials; see ref. 5. [c] Exciplex emission not observed in these systems. [d] Cyclohexane solvent. [e] Acetonitrile solvent.

[†] After an examination of molecular models of these complexes a value of 5·0 Å was chosen for the cavity radius of the complex.

from the fact that the ionisation potential of this heterocycle (8·39 eV[5]) is higher than that of 1-methylpyrrole (8·2 eV[5]). The enthalpy of formation of the exciplex containing pyrrole is similar to that for the naphthalene–triethylamine exciplex (8·0 kcal mol^{-1}).[9]

Many of the heterocyclic compounds studied do not form fluorescent exciplexes with excited singlet polycyclic aromatic hydrocarbons although they quench the fluorescence of the hydrocarbon. The rate constants for the quenching process increase as the ionisation potential of the heterocyclic compound is decreased (see Table). In those cases where quenching in cyclohexane solution is relatively inefficient, change of solvent to acetonitrile leads to an increase in the rate constants. This increase may indicate that either quenching in this solvent involves complete electron transfer to give radical ions or else the exciplex is sufficiently stable in this solvent to prevent its dissociation into the hydrocarbon excited snglet state and ground state heterocycle.

The behaviour of the aromatic hydrocarbon–heterocyclic systems is very similar to the well known aromatic hydrocarbon–amine systems.[10] One would therefore expect that the photoreactions of these systems should show a dependence upon solvent polarity[7,11] and sensitivity to the presence of proton donors.[2b,7]

We thank S.R.C. for research studentships to A. L. and T. W. and the Royal Society for an equipment grant.

(*Received*, 19*th December* 1974; *Com.* 1548.)

---

[1] T. S. Cantrell, *Tetrahedron Letters*, 1974, 3959; J. Berridge, D. Bryce-Smith, and A. Gilbert, *J.C.S. Chem. Comm.*, 1974, 964.

[2] (a) M. Bellas, D. Bryce-Smith, and A. Gilbert, *Chem. Comm.*, 1967, 263; (b) D. Bryce-Smith, M. T. Clarke, A. Gilbert, G. Klunklin, and C. Manning, *ibid.*, 1971, 916.

[3] J. J. McCullough, C. W. Huang, and W. S. Wu, *Chem. Comm.*, 1970, 1368; J. J. McCullough and W. S. Wu, *Tetrahedron Letters*, 1971, 3951; J. J. McCullough, W. S. Wu, and C. W. Huang, *J.C.S. Perkin II*, 1972, 370.

[4] T. Sugioka, C. Pac, and H. Sakurai, *Chem. Letters*, 1972, 667.

[5] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Hesson, K. Draxl, and F. H. Field, 'Ionisation Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions,' National Bureau of Standards, Washington, 1969.

[6] R. S. Davidson in 'Molecular Association,' Vol. I, ed. R. Foster, in the press.

[7] H. Knibbe, Ph.D. Thesis, University of Amsterdam, 1969; B. Stevens, *Adv. Photochem.*, 1971, **8**, 161.

[8] J. B. Birks, M. D. Lumb, and I. H. Munro, *Proc. Roy. Soc.*, 1964, *A*, 280, 289.

[9] M. G. Kuzmin and L. N. Guseva, *Chem. Phys. Letters*, 1969, **3**, 71.

[10] H. Leonhardt and A. Weller, *Ber. Bunsengesellschaft, Phys. Chem.*, 1963, **67**, 791.

[11] R. S. Davidson, *Chem. Comm.*, 1969, 1450.