

INTERMOLECULAR EXCIPLEX FORMATION BETWEEN BENZENE AND SOME OLEFINIC COMPOUNDS

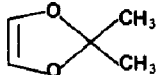
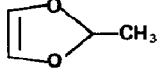


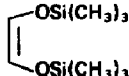
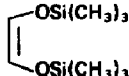
H. LEISMANN, J. MATTAY and H.-D. SCHARF

Lehrstuhl II und Institut für Organische Chemie der RWTH Aachen, Prof.-Pirlet-Strasse 1, D-5100 Aachen (F.R.G.)

Exciplex formation has been postulated as a first step in photochemical reactions of S_1 benzene with olefins [1, 2], dienes [3] and amines [1, 4]. We now report that exciplex fluorescence can be observed with S_1 benzene in the presence of particular olefinic compounds (I - V, Table 1).

TABLE 1

Data concerning exciplex formation of I - V with S_1 benzene in acetonitrile

| No. |  | I_p^a (eV) | K_{sv}^b (M^{-1}) | λ_{max}^c (nm) |
|-----|-------------------------------------------------------------------------------------|--------------|-------------------------|------------------------|
| I |  | 7.92 | 119.0 | 390 |
| II |  | 8.36 | 133.0 | 390 |
| III |  | 8.54 | 57.0 | 380 |
| IV |  | 8.56 | 117.0 | 390 |
| V |  | 9.7 | 51.0 | 393 |

^aVertical ionization potential.

^bStern-Volmer quenching constant of benzene fluorescence.

^cWavelength of maximum fluorescence intensity (the detector was phototube R 446, uncorrected).

Since there is no obvious correlation between the ionization potentials, the Stern-Volmer constants and the fluorescence emission energies, the observed exciplexes are interpreted to be "weak exciplexes" [5] with dipole-dipole rather than charge transfer stabilization.

- 1 D. Bryce-Smith and A. Gilbert, *Tetrahedron*, **33** (1977) 2459.
- 2 J. Cornelisse, V. Y. Merritt and R. Srinivasan, *J. Am. Chem. Soc.*, **95** (1973) 6197.
- 3 N. C. Yang and J. Libman, *Tetrahedron Lett.*, (1973) 1409.
- 4 M. Bellas, D. Bryce-Smith, M. T. Clarke, A. Gilbert, G. Klunkin, St. Kretonosich, C. Manning and S. Wilson, *J. Chem. Soc. Perkin Trans. 1*, (1977) 2571.
- 5 V. Hershberger and R. W. Lumry, *Photochem. Photobiol.*, **23** (1976) 391.