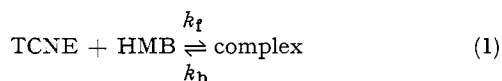


## Kinetics of the Formation of the Donor-Acceptor Complex between Tetracyanoethylene and Hexamethylbenzene in Solution studied by a Microwave Temperature-jump Method

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**Summary** The rate constant for the formation of the donor-acceptor complex between tetracyanoethylene and hexamethylbenzene in 1-chlorobutane at  $-83^\circ$  is  $(1.45 \pm 0.3) \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ , about 10 times less than the value calculated for diffusion control.

EQUILIBRIA in the formation of donor-acceptor complexes in solution have been much studied.<sup>1,2</sup> There has so far been no direct determination of rates, but evidence from dielectric relaxation<sup>3,4</sup> indicates that they are very high. In the most favourable cases, at low temperatures, they are within the range of the temperature-jump technique. We have determined the rate constant at  $-83^\circ \text{C}$  for the formation of the complex between tetracyanoethylene (TCNE) and hexamethylbenzene (HMB) [equation (1)] by a



microwave temperature-jump method,<sup>5</sup> modified for use at low temperatures. The method requires a polar solvent; we have used 1-chlorobutane. It is necessary to know equilibrium concentrations at  $-83^\circ \text{C}$ , which were obtained by extrapolation from measurements of the equilibrium constant in the temperature range  $+50$  to  $-20^\circ \text{C}$ . We have assumed that the complex has the composition TCNE-HMB; the presence of a small amount of a 2:1 complex<sup>6</sup> would not greatly affect the results.

The value of  $k_f$  at  $-83^\circ \text{C}$  is  $(1.45 \pm 0.3) \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ , the uncertainty being the estimated limits of error. If the reactant molecules are assumed to be structureless spheres of comparable size in a homogeneous fluid of viscosity  $\eta$ , then the value calculated for a diffusion-controlled reaction at the same temperature ( $k_D = 8RT/3000\eta$ ) is  $1.7 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ . The observed rate constant is smaller than this by a factor of 12.

This difference is probably due to solvation changes. It is unlikely to be due to steric requirements of the reactant molecules, since the attractive forces in the complex are not highly directional. Nor is there likely to be any appreciable energy barrier to complex formation once the reactant molecules have come together in an encounter; no bonds are stretched, and the contributions from repulsion and charge-separation are small, since the 'bonds' in such complexes are exceptionally long, and the dipole moment small (1.35 D). It appears that the complex is somewhat less solvated than the reactants; a comparison of equilibrium constants for similar systems in solution and in the gas phase suggests that this is so,<sup>7</sup> and our value of  $\Delta S^\ddagger$  at  $25^\circ$  ( $-14 \text{ cal mol}^{-1} \text{ deg}^{-1}$ ) is rather smaller than would otherwise be expected. If the reactants have to be partly desolvated before the transition state can form, there may well be an activation energy (*ca.*  $1 \text{ kcal mol}^{-1}$ ) which will lead to an effective encounter rate constant lower than the calculated value of  $k_D$  by an order of magnitude.

A full report of this work is in preparation.

(Received, September 7th, 1971; Com. 1570.)

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<sup>7</sup> Ref. 2, p. 185.