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POSSIBLE IMPORTANCE OF AN ABNORMAL ORBITAL INTERACTION IN EXCITED-STATE REACTIONS BETWEEN ELECTRON DONORS AND ACCEPTORS

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Photochemical reactions between powerful electron donors and acceptors are likely controlled by the $(HOMO)_D$-$(LUMO)_A$ interaction involved in the D^*A-$D^{+*}A^-$ or DA^*-D^+A^{-*} interaction, the frontier orbital interaction being the same as one in usual thermal reactions.

Recent experimental results[1,2] suggest that the stereoselection rules[3,4] for photochemical reactions now require reinvestigation. For example, *trans,-trans*-2,4-hexadiene gives the 4+4 cycloadduct with anthracene[1a] but the 4+2 cycloadduct with 9-cyanoanthracene.[1b] The distribution of the 4+2, 4+4, and 4+6 cycloadducts between cycloheptatriene and anthracenes was observed to change significantly with the substitution at the 9 and 10 positions on anthracene.[2] The pioneering work of Epiotis[5] implied that the photochemical "symmetry-forbidden" reactions become allowed by the $(HOMO)_D$-$(LUMO)_A$ interaction involved in the DA - D^+A^- interaction. This interaction is, however, antibonding on the excited-state potential energy surface. We investigate this problem from a viewpoint of the configuration or orbital interaction.[4,6,7]

We restrict ourselves to the intermolecular electron density, ρ_{inter}, since the bond formation requires accumulation of electrons in the intermolecular region. Some off-diagonal elements, ρ_{IK}'s, contribute to ρ_{inter} rather than the diagonal elements, ρ_{KK}'s,[6] i.e.,

$$\rho_{inter} \simeq \sum_K C_I C_K \rho_{IK} \simeq \sum_K \frac{(H_{IK}/S_{IK}) - H_{II}}{H_{II} - H_{KK}} S_{IK}\rho_{IK}$$

where the perturbation theory[7] is applied to estimating C_K. The ρ_{IK} should contain a product of two orbitals which belong to different molecules.[6] It follows that the important configurations are D^+A^-, D^-A^+, $D^{+*}A^-$, and $D^{-*}A^+$ for $I=D^*A$, and D^+A^-, D^-A^+, D^+A^{-*}, and D^-A^{+*} for $I=DA^*$ (Fig. 1). It is evident from the equation that D^*A (or DA^*) contributes most significantly to the bonding through the interaction with the configuration which lies above and close to itself, since the interaction involves the largest positive coefficient of $S_{IK}\rho_{IK}$.[8] Is there such a configuration among the selected ones, which is responsible for the "symmetry-forbidden" reactions?

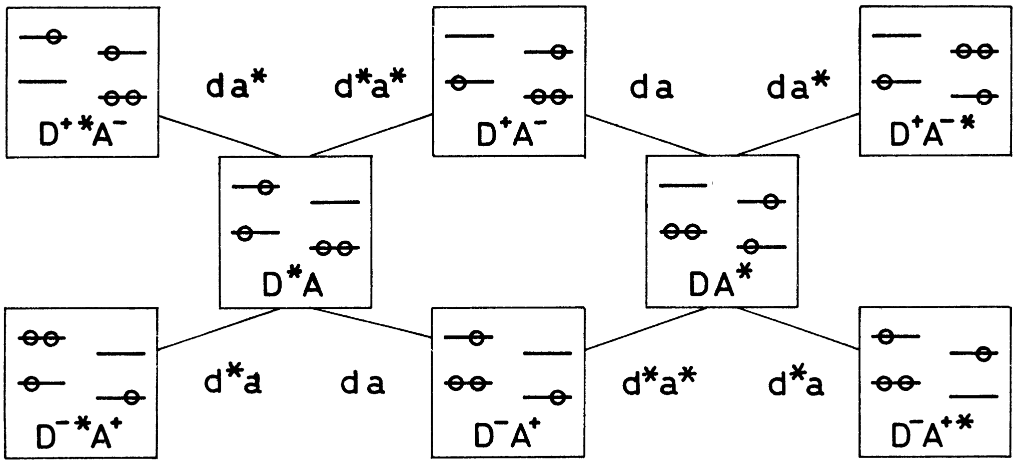

Fig. 1. The important configuration (orbital) interactions which contribute to the intermolecular electron density.

Figure 2 schematically illustrates the change in the configuration energies as a function of the donor-acceptor properties of reactants. Enhancement of the donor-acceptor properties lowers $E_{D^+A^-}$ and $E_{D^{+*}A^-}$ and elevates $E_{D^-A^+}$ and $E_{D^{-*}A^+}$, presumably resulting in the reversal of $E_{D^-A^+}$ and $E_{D^{+*}A^-}$. The D^*A - $D^{+*}A^-$ interaction then contributes most significantly to the bonding since $D^{+*}A^-$ lies above D^*A and close to it. The configuration interaction involves the d-a* interaction. The frontier orbital interaction is the same as one in most of thermal interactions. For I=DA* the corresponding configuration (orbital) interaction is the DA* - D^+A^{-*} (d - a*) interaction. We may conclude that photochemical "symmetry-forbidden" reactions possibly occur between powerful donors and acceptors if the $D^{+*}A^-$ or D^+A^{-*} configuration is significantly lowered.[9]

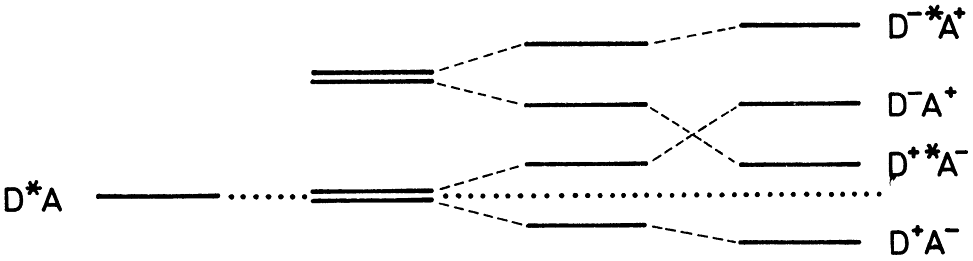

Fig. 2. The configuration energies relative to D*A as a function of the donor-acceptor properties of reactants

The preceding arguments have been limited to the excited states where D*A or DA* is the main configuration. Some photochemical reactions between donors and acceptors may occur on another potential energy surface where D^+A^- is main, in the case of $E_{D^+A^-} < E_{D*A}$ or E_{DA*}. The important configurations are DA, D*A, DA*, D*A*, and $D^{++}A^{--}$, the energy levels being in the order of $E_{DA} < E_{D^+A^-} < E_{D*A}, E_{DA*} < E_{D*A*}, E_{D^{++}A^{--}}$. The DA - D^+A^- interaction has much to do with the intermolecular electron density, but involves an antibonding d - a* orbital overlap. A bonding property is caused by the D^+A^- - D*A or D^+A^- - DA* interaction, i.e., the d* - a* or d - a orbital overlap. As a result, no symmetry-forbidden reactions are expected to occur.

Epiotis ascribed the photochemical $[4_s+2_s]$ cycloaddition reactions to the level order of $E_{D^+A^-} < E_{DA} < E_{D*A}, E_{DA*} < E_{D^-A^+}$ (Fig. 15 in ref. 5). A single configuration interaction, which involves the d - a* orbital overlap, is the DA - D^+A^- interaction. However, this interaction contains an antibonding overlap since the main configuration, DA, lies above D^+A^-. This implies that the theoretical arguments by Epiotis should be revised.

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8) It is presumed that $(H_{IK}/S_{IK}) - H_{II} < 0$.

9) Kanematsu et al.[2b)] interpreted their experimental results in terms of this orbital interaction involved in the $D{*}A - D^{+}{*}A^{-}$ interaction.

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