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HYBRID MOLECULAR ORBITALS FOR REACTING SYSTEMS. ELUCIDATION OF REACTIVE DOMAINS

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Abstract: A pair of orbital transformations is suggested to provide a simple criterion to interpret the pathway of nonpolar reactions and to elucidate the reactive domains for competitive reactions.

It appears to be a problem of vital concern to the majority of chemists to look for the factors influencing reaction pathways. A number of theoretical studies have been attempted on reacting systems and, thus, fascinating aspects of various elementary processes are being brought to light.[1,2] On the one hand calculations will be applied to more complicated systems; on the other hand development of more succinct but reliable methods for analyzing the calculated results should be kept on. We wish to present in this letter presumably one of the simplest orbital pictures concerning the reactive domains and reaction pathways.

Aside from the Coulombic interaction between net charges, the progress of chemical transformations is described most distinctly by the appearance and disappearance of chemical bonds. Particularly in nonpolar reactions, observed selectivities are related directly with the growth of new covalent bonds between the reagent and reactant. It seems to be important, therefore, to study how the reaction pathway is controlled by the formation of bonds. A pairwise orbital transformations within each of the reagent and reactant so as to condense the intermolecular overlap density into a set of paired fragment orbitals may be useful for our purpose.[3,4] The interaction is described virtually by a pair of reagent and reactant orbitals, each given by a hybrid of canonical MO's within each fragment.

Figure 1 shows the interactive hybrid MO's of fragments which participate in the formation of new C-C sigma bond in the recombination of methyl radical. Methyl fragments were assumed to be pyramidal with tetrahedral H-C-H angle and the C-C distance was taken tentatively at 1.8Å. The calculation was carried out within the STO-6G level with the simplest 3 × 3 configuration interaction. The hybrid MO's obtained point nicely at each other, as expected. The electron population in these orbitals was calculated to be 1.046 for each of them, characterizing unpaired electrons. Facile recombination of methyl radical to give ethane is displayed in terms of the shape and electron population of the hybrid MO's.

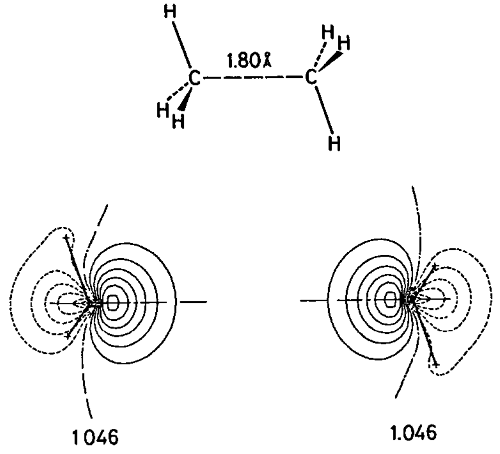

Fig. 1 Interactive hybrid MO's in recombination of methy radical.

It is interesting to examine next how the interactive hybrid MO's respond to the deviation from the most likely pathway. For this purpose, we carried out calculations by tilting methyl radicals by 30° in a conrotatory or disrotatory manner, as shown in Fig. 2. It is astonishing to see that the hybrid MO's scarcely change against pitching and/or yawing of methyl fragments. Though this may be related to the stasis of bond orbitals found in stable molecular systems,[6] we should note here that the interactive hybrid MO's are determined in order to maximize their contribution in a pair to the intermolecular overlap density and, therefore, the electron distribution within each methyl fragment has never been referred to in the orbital transformations. Accordingly, the hybrid orbitals are not subject directly to the structural constraint of fragments. The result of calculation presented in Fig. 2 seems to indicate an important aspect of

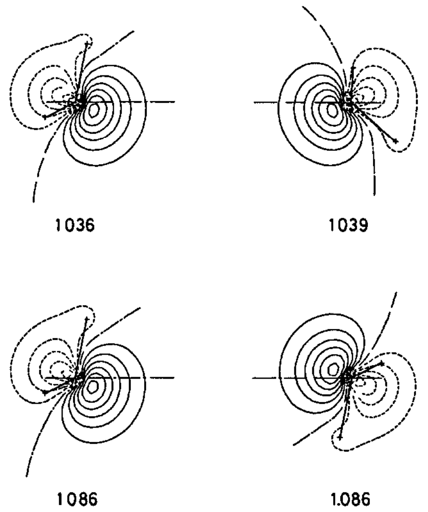

Fig. 2 Changes in the interactive hybrid MO's associated with tilting.

chemical reactions. The reagent should recognize its relative position and orientation in space by observing the reactant and reckon the most favourable course to attack it. Tilting of a methyl fragment is depicted as a change in the intermolecular overlap density not only between the reaction sites but also between all the constituent atoms of fragments and this, in turn, is manifested as a change in the direction of maximum extension of the interactive hybrid MO. Thus, the path of nonpolar reactions is most likely to be defined in such a manner as to maximize the overlap between the interactive hybrid MO's of the reagent and reactant. The hybrid MO's may be adopted, therefore, as the basis orbitals for utilizing the "principle of maximum overlap" and/or "overlap and orientation principle" as the simplest theoretical guides to discuss possible paths of chemical reactions.[7,8]

Figure 3 shows the cases in which deviation from the symmetric path gets appreciably large. The possibility of another chemical process, i.e., disproportionation, seems to arise. The localization of the interactive hybrid MO at the hydrogen atom under attack is not remarkable, however, suggesting that the removal of hydrogen is not necessarily facile in this system. The carbon-hydrogen bond shares a certain region in space with the radical lobe at the carbon atom in methyl radical and, therefore, competition between recombination and disproportionation would favour the former.

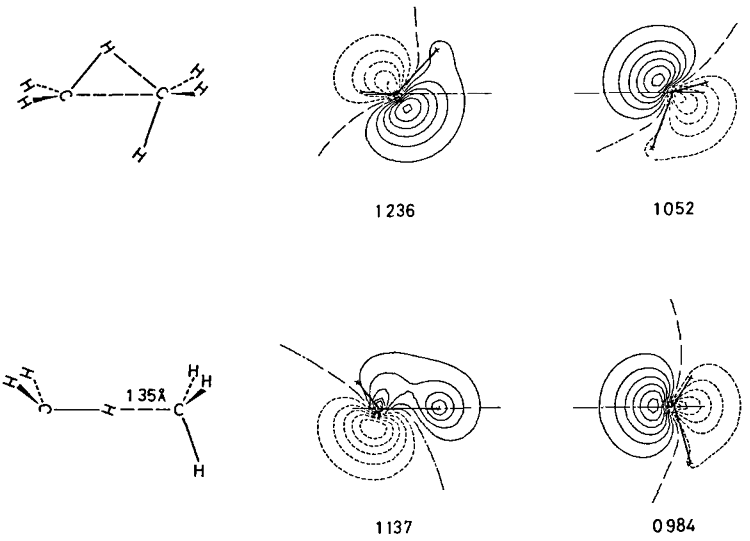

Fig. 3 Interactive hybrid MO's of methyl radicals indicating the competition between recombination and disproportionation.

The interactive hybrid MO of ethyl fragment in a system consisting of ethyl radical and methyl radical was found also to be delocalized over the radical center as shown in Fig. 4. The orbital possesses, however, a node between the hydrogen atom under attack and the carbon atom with an unpaired electron. The interaction between the attacking methyl and the radical center of ethyl is repulsive. This means that, once the attacking radical begins to interact with a methyl hydrogen of ethyl radical, it should continue to approach the hydrogen. The reactive channel for disproportionation is separated distinctly from that for recombination, notwithstanding that the localization is not effective at the hydrogen atom in the interactive hybrid MO. Disproportionation may be more probable in the case of larger odd electron systems, since the hybrid MO will localize more efficiently in the region around a hydrogen atom to be removed by an attacking radical.

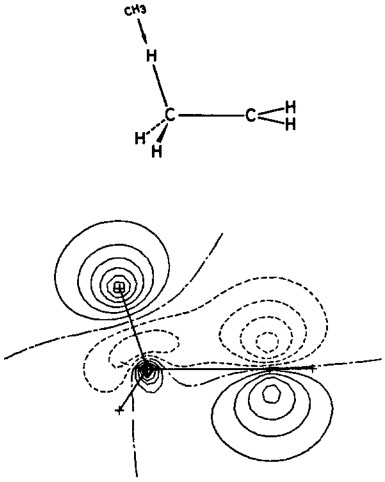

Fig. 4 Interactive hybrid MO of ethyl radical in disproportionation.

By carrying out similar calculations, we may be able to see how the reaction pathway would be influenced by a variation in reagents and by an introduction of substituents. The extent of localization and direction of extension of the hybrid MO's will offer hopefully a clear and simple distinction between favourable and unfavourable reactions.

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