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THE NATURE OF THE TRANSITION STATE IN HYDROBORATION REACTION : A CNDO/2 STUDY OF THE ETHYLENE BORANE COMPLEX

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There had been some controversy over the nature of the transition state in hydroboration reactions. Brown et al. first proposed a four-membered transition state[1] for the reaction. Kinetic and isotope effect studies in the solution phase with various olefins and alkyl boranes[2-5] supported this view. However, this was disputed by Streitwieser et al. on the basis of stereochemical evidences[6]. Also, the results of a gas phase kinetic study[7] and MO symmetry consideration[8] of the reaction between ethylene and borane suggested the transition state to be a loose three-membered activated complex.

As it appeared that no attempt has so far been made to study this problem by way of MO calculations, we used the CNDO/2 method[9] to obtain the minimum energy configuration of both the two proposed transition states. The geometric parameters of both the 4-center and 3-center complexes for the ethylene borane reaction have been fully optimized and the results are shown in figure I. Their CNDO/2 energies are found to be -23.483 a.u. and -23.563 a.u. respectively. Thus, the 3-center transition state is stable by about 50 Kcals/mole and may be regarded as the preferred pathway.

A clear picture of bonding in the 3-center complex has been obtained by generating a set of Localized Molecular Orbitals (LMO) by the self-energy localisation procedure[10,11]. The LMO eigenvectors interestingly indicate the existence of a three center bond between the two carbon atoms and the boron atom. The contributions from the p_z orbitals of both the C-atoms and the B-atom are most pronounced in the formation of this bond and the two C-atoms are found to contribute equally to the bonding. The atomic hybrids used by B in B-H bonds are now close to sp^3, while that in the C-B-C bond is $sp^{2.5}$. A Mulliken population analysis shows B to be -ve(0.18 e) and each C to be +ve (0.10 e).

The transfer of charge and the MO interactions involved in the complex formation are obtained by expanding[12] the MO's of the complex in terms of those of $C_2H_4(D_{2h})$ and $BH_3(C_{3v})$[13]. The changes in the occupation number of the MO's (Δn) due to the interaction are given in the table I, where it can be found that the LUMO ($2a_1$) of BH_3 has gained a net charge of 0.647 e that has been transferred mostly from the HOMO ($1b_{1g}$) of ethylene. However, the $2a_1$ occupancy is found to be much greater than the net charge transferred (0.344 e) and this excess charge comes from the low lying $1a_g$ MO of C_2H_4 which is of matching symmetry. The high occupancy of the LUMO ($1b_{2g}$) of ethylene is surprising but may be explained as arising due to some back donation from the 1e orbital of BH_3. Also, the higher lying MO's of both BH_3 and C_2H_4 that were previously unoccupied are found to be slightly populated after the interaction, probably due to self-excitation of the lower lying MO's of the adduct.

In conclusion it may be said that the reaction between C_2H_4 and BH_3, which may be regarded as a prototype of hydroboration reactions, proceeds through a 3-center intermediate rather than 4-center one; and that the 3-center complex contains a well defined C-B-C three center two electron bond.

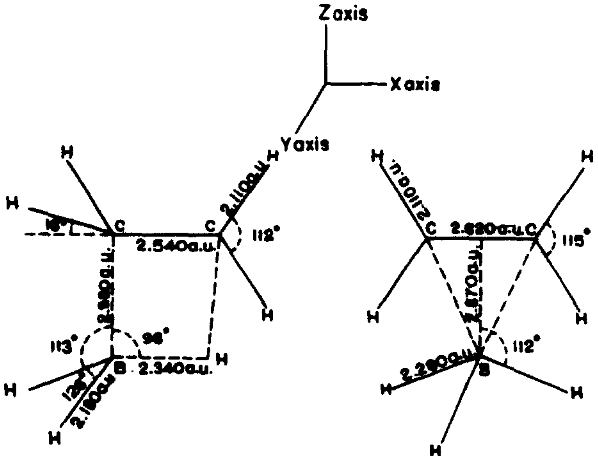

Table I

BH$_3$ MO	BH$_3$ Δn	C$_2$H$_4$ MO	C$_2$H$_4$ Δn
$1a_1$	-0.082	$1a_g$	-0.214
$1e$	-0.227	$1b_{3u}$	-0.032
$2e$	-0.046	$1b_{2u}$	-0.027
$2a_1$	0.647	$2a_g$	-0.019
$3a_1$	0.029	$1b_{1u}$	-0.001
$3e$	0.020	$1b_{1g}$	-0.337
$4e$	0.003	$1b_{2g}$	0.259
		$2b_{2u}$	0.016
		$2b_{3u}$	0.008
		$3a_g$	0.001
		$2b_{1g}$	0.001
		$3b_{3u}$	0.0
Total	+0.344	Total	-0.345

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13. It may be noted (Figure I) that during the complex formation the BH_3 moiety changes from D_{3h} to C_{3v} symmetry.
14. The calculations were carried out in Burroughs 6700 system at the Regional Computer Center, Jadavpur University.