

**Multiple Catalysis in the CNDO/2 Approximation. Formamidine Catalysed  
1,3-Proton Transfer in Propene**

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## Multiple Catalysis in the CNDO/2 Approximation. Formamidinium Catalysed 1,3-Proton Transfer in Propene

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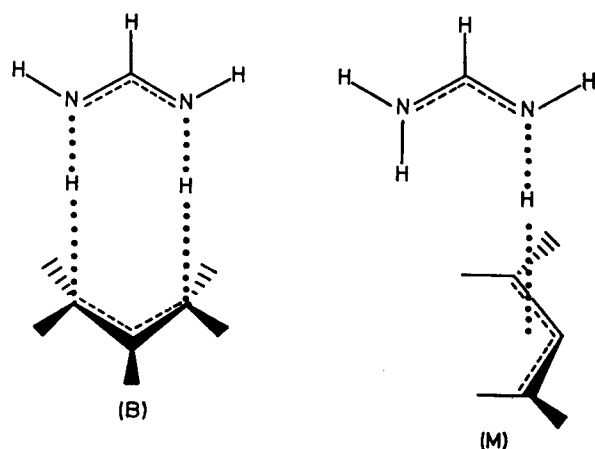
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*Summary* A CNDO/2 molecular orbital study of bifunctional and monofunctional formamidinium catalysis of 1,3-proton transfers in propene shows that the energy barrier for bifunctional catalysis is much lower than that for monofunctional catalysis.

We report here preliminary results of our comparative CNDO/2 MO study of monofunctional formamidinium base catalysis and bifunctional formamidinium acid-base catalysis of 1,3-proton transfers in propene. The activated com-

plexes for these reactions have structures (M) and (B), respectively.

The suprafacial sigmatropic reaction of hydrogen of order [1,3] is forbidden according to the Woodward-Hoffmann rules.<sup>1</sup> Experimentally no such processes are yet known. On the other hand base-catalysed 1,3-proton transfers have frequently been observed and are under certain conditions intramolecular and/or stereospecific reactions.<sup>2</sup> Thus the basic catalyst makes accessible a low energy pathway for the 1,3-proton transfer. This



pathway presumably involves a loss of orbital phase memory by the hydrogen on its travel along the reaction co-ordinate, a process which obviously needs high energy to occur in an uncatalysed thermal and suprafacial manner (Figure).

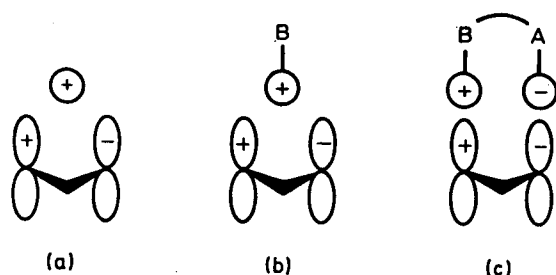


FIGURE. Main orbitals involved in uncatalysed (a), monofunctionally catalysed (b), and bifunctionally catalysed (c) 1,3-proton transfer reaction.

A potential possibility of making 1,3-proton transfers concerted and further accelerated over monofunctional catalysis is to use bifunctional acid-base catalysts.

For the sake of internal consistency of our results, the energies of formamidine, propene, and the activated complexes of bifunctional (B) and monofunctional (M) catalysis

were minimised with respect to those variables, bond distances and angles, which were found to be most important. The optimal geometries of the activated complexes were found to correspond in the positions of all atoms except those of the transferring hydrogens to allyl and formamidinium ions put together in the way shown in (B) and (M). The optimal distance between the two ionic units was found in both cases to be 26 nm measured from the plane of the allyl system to the basic N. The transferring hydrogen(s) were found to lie 12.4 nm away from the N (N's). A complete account of these and other computational details will be presented elsewhere.<sup>3</sup>

The symmetrical activated complexes (B) and (M) were found to be less stable than the initial state by 121 and 453 kJ/mol (29 and 108 kcal/mol), respectively. Energy profiles of both types of catalysis were partly studied and no reaction intermediates were found along either pathway in this rather crude investigation. The timing of the migration of the two hydrogens was studied in the bifunctional case. It was found that their movement is synchronous and lags behind all other changes along the reaction co-ordinate chosen.

It is of importance when cyclic reactions are studied to investigate how the orbitals of the initial state correlate with those of the products.<sup>1,4</sup> With such a study an erroneous prediction of a low barrier for a symmetry forbidden process can be avoided. Earlier work on bifunctional catalysis seems not to have recognised the importance of such a correlation.<sup>5</sup> We found for the bifunctional catalysis that all the bonding orbitals of the initial state correlated with the bonding orbitals of the products as well as with those of the activated complex (B). Thus this type of bifunctional catalysis is a symmetry-allowed process.

Parallel to this theoretical study we have undertaken a reaction mechanistic investigation of some amidine-catalysed 1,3-proton transfer reactions.<sup>6</sup>

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