# Unfavourable Orbital Overlap at the Transition State of a Symmetry Allowed Reaction: a Theoretical Analysis

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The most favourable reaction path for the approach of $CH_3^+$ to acetylene to give cyclo-$C_3H_3^+$ + $H_2$ goes through a $\pi$ transition state leading from the corner-protonated cyclopropene to the products in agreement with experimental evidence; this transition structure presents a null HOMO–LUMO overlap which prevents electron density rearrangement from taking place by HOMO–LUMO interaction.

Since the pioneering work of Woodward and Hoffmann,[1] the symmetry properties of reactive systems have been used to predict reaction mechanisms having small energy barriers.[2–6] Chemical reactions consist of the breaking of some bonds and the formation of new bonds. In order to form new bonds and break old ones a rearrangement of electron density has to take place through charge transfer interactions. The increase in electron density in the intermolecular region originates from the overlap of the occupied molecular orbitals (MOs) (particularly the HOMO) of the reactant and the unoccupied MOs (particularly the LUMO) of the reagent and *vice versa*. Fukui and colleagues have shown that the nodal properties of the HOMO and LUMO are important in predicting the evolution of reactants in a chemical reaction.[7,8] Electron flow between two orbitals cannot occur unless they have a net overlap.

Fukui and colleagues have also shown that certain reactions hindered by the orbital phase relation of the HOMO and LUMO may proceed *via* pseudoexcitation, so that the paradoxical HOMO–HOMO or LUMO–LUMO overlap largely control the stabilization of the system.[7,9]

Here, we report a theoretical analysis of the formation of cyclo-$C_3H_3^+$ from the reaction of $CH_3^+$ with acetylene. *Ab initio* calculations were carried out with the GAUSSIAN 90 series of programs[10] using the 6-31G* basis set.[11] Full geometry optimization of stable structures and direct location of transition structures on the potential hypersurface were performed by means of Schlegel's algorithm.[12] MP2/6-31G*// 6-31G* calculations were carried out for the chemically important structures along the reaction coordinate. *Ab initio* wave functions were analysed using the theoretical method developed by Fukui[13] and extended recently by us,[14,15] based on the expansion of the MOs of a complex system in terms of those of its fragments[16] and configuration analysis. This method has proved useful for understanding the chemical features of complex formation from two[13,16,17] or three[14] chemically interacting systems.

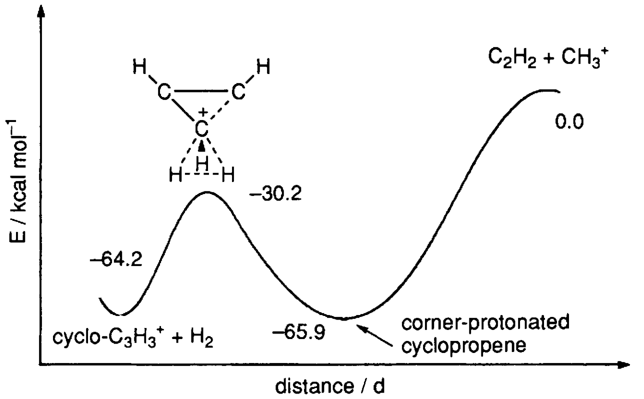

**Fig. 1** MP2/6-31G*//HF/6-31G* energy profile (kcal mol$^{-1}$; 1 cal = 4.184 J); corresponding to the π attack of $CH_3^+$ on acetylene. The distance between the carbon atom of $CH_3^+$ and one of the carbon atoms of acetylene, *d*, is taken as the reaction coordinate. Both corner-protonated cyclopropene and the TS have $C_s$ symmetry with a plane of symmetry passing through the mid-point of the C–C bond in the acetylene moiety and the central C–H bond in the $CH_3^+$ moiety.

**Table 1** Changes in the 6-31G* electronic population, Δv, of the frontier MOs of $CH_3^+$ and $C_2H_2$ at the π TS

| Fragment | MO | Δv |
|---|---|---|
| $CH_3^+$ | HOMO | −0.95 |
| | LUMO | 1.21 |
| | NLUMO | 0.11 |
| $C_2H_2$ | HOMO | −0.89 |
| | NHOMO | −0.19 |
| | LUMO | 0.59 |

**Table 2** Coefficients of the most important fragment electronic configurations for the 6-31G* π TS. (D = $C_2H_2$; A = $CH_3^+$)

| Configuration | Coefficient |
|---|---|
| $D^{2+}A^{2-}$ (HOMO–LUMO/HOMO–LUMO) | 0.1125 |
| $D^{2-}A^{2+}$ (HOMO–LUMO/HOMO–LUMO) | 0.0334 |
| DA** (HOMO–LUMO/HOMO–LUMO) | 0.1035 |
| D**A (HOMO–LUMO/HOMO–LUMO) | 0.0363 |
| $D^+A^{-*}$ (HOMO–LUMO/HOMO–LUMO) | 0.1763 |
| $D^{-*}A^+$ (HOMO–LUMO/HOMO–LUMO) | 0.0569 |
| $D^{+*}A^-$ (HOMO–LUMO/HOMO–LUMO) | −0.1004 |
| $D^-A^{+*}$ (HOMO–LUMO/HOMO–LUMO) | −0.0924 |

In a theoretical study of the formation of $C_3H_3^+ + H_2$ from the reaction of $CH_3^+$ with acetylene we have found that the most favourable path proceeds through a π-type ($C_s$) transition state (TS) leading from the corner-protonated cyclopropene to the formation of the cyclopropenyl cation, $C_3H_3^+$ ($D_{3h}$), and $H_2$ (see Fig. 1).[18] This is consistent with the experimental results obtained using a triple quadrupole mass spectrometer.[19]

Although this process is allowed by orbital symmetry according to an ordinary application of the symmetry rules, we report here an analysis of the wave function of the π TS which clearly shows that, contrary to expectations, this symmetry favoured situation does not remain the same all along the reaction coordinate. This could go unnoticed because a mechanism analogous to pseudoexcitation[7,9] seems to be a very effective alternative way to render this π channel as the most favourable route from $C_2H_2 + CH_3^+$ to cyclo-$C_3H_3^+ + H_2$.

Table 1 shows the changes in the occupation numbers of the frontier MOs of the two fragments $CH_3^+$ and $C_2H_2$. The HOMOs of $CH_3^+$ and $C_2H_2$ decrease in electronic population; the LUMO of $C_2H_2$, the NLUMO and particularly the LUMO of $CH_3^+$ become populated.

Table 2 shows the coefficients of the most important electronic configurations of $CH_3^+$ and $C_2H_2$ for the π TS. The zero configuration and all the monotransfers and monoexcitations have practically null coefficients. This is a consequence of the relative energies of the MOs of $CH_3^+$ and $C_2H_2$ with the same geometry as in the TS, and their mixing to form the MOs of the combined system. From the analysis of the $CH_3^+$ fragment we see that as a result of the change in shape of $CH_3^+$ along the reaction pathway (from planar $D_{3h}$ in reactants to $C_s$ in the π TS), its $D_{3h}$ HOMO (e′) correlates with the $C_s$ LUMO (a″) and its $D_{3h}$ LUMO (a″) correlates with the $C_s$ HOMO (a′). The $C_s$ LUMO of $CH_3^+$ has zero net overlap with the HOMO of $C_2H_2$ (a′ in the $C_s$ symmetry of the TS), and the $C_s$ HOMO of $CH_3^+$ has zero overlap with the LUMO of $C_2H_2$ (a″ in the $C_s$ symmetry of the TS), in contrast with the early steps where a favourable HOMO–LUMO overlap is found. As a consequence, no electron flow can occur between the two fragments *via* a direct HOMO–LUMO interaction. The NLUMO of the $CH_3^+$ fragment can interact with the NHOMO of *cis*-bent-acetylene (both are a′ orbitals in the $C_s$ symmetry of the TS) but the effect of this interaction does not appear in the coefficients of the most important configurations (Table 2), so it must not be a very important one. From the coefficients in Table 2 we see that local excitations, particularly those at $CH_3^+$, play an important role. Figures in Table 2 then allow us to interpret the electron loss of the HOMO of $CH_3^+$ and the increase in the population of the LUMO of $C_2H_2$ mainly in terms of local excitations. This was to be expected in view of the impossibility of a stabilizing HOMO–LUMO interaction. It has been reported that the interaction of a strong electron-acceptor and a strong donor brings about unusual reactivity as a result of a paradoxical HOMO–HOMO

**Table 3** Analysis of AO overlap population along the two C($CH_3^+$)-C(acetylene) new bonds in the π TS; the total C–C overlap population is 0.2444

| | | | C($CH_3^+$) | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | 2s | | $2p_x$ | | $2p_y$ | |
| | | | HOMO | LUMO | HOMO | LUMO | HOMO | LUMO |
| | 2s | HOMO | 0.0458 | 0.0 | 0.0401 | 0.0 | 0.0 | 0.0 |
| | | LUMO | 0.0 | 0.0001 | 0.0 | 0.0 | 0.0 | 0.0028 |
| C($C_2H_2$) | $2p_x$ | HOMO | 0.2416 | 0.0 | 0.1117 | 0.0 | 0.0 | 0.0 |
| | | LUMO | 0.0 | 0.0001 | 0.0 | 0.0 | 0.0 | 0.1143 |
| | $2p_z$ | HOMO | −0.0303 | 0.0 | −0.0367 | 0.0 | 0.0 | 0.0 |
| | | LUMO | 0.0 | −0.0001 | 0.0 | 0.0 | 0.0 | 0.2003 |

and LUMO–LUMO orbital control.[7,9] In our case an analogous circumstance is confirmed by data in Table 3, which displays the most important components of the electronic overlap population along the two new C–C bonds in the π TS, obtained from a Mulliken population analysis.[20] These figures plainly show that the HOMO–LUMO interaction directly leads to an unstable situation, and that bonding has to be established by HOMO–HOMO and LUMO–LUMO interactions.

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