HYBRID MOLECULAR ORBITALS FOR INTERACTING SYSTEMS.

REACTIVE REGION AND REACTION SITES

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Abstract: It is shown how the reactive region is determined in a molecule and
how the reaction sites are specified in the reactive region by the use of hybrid
molecular orbitals.

Chemists have long been accustomed to think of chemical bonds in terms of an electron
pair shared by a pair of orbitals.   The concept of hybridization introduced by Pauling[1] has
been imaginative.   In the MO theory, however, electrons are populated in orbitals which are
delocalized, in general, over the whole molecular framework.   Then, a chemical bond is
expressed by defining a certain quantity, such as the Mulliken overlap population, which adds
up the contributions of all the occupied MOs.   On the other hand, chemical reactions are
frequently discussed by taking some particular MOs, e.g., the highest occupied MO of the
electron donating molecule and the lowest unoccupied MO of the electron accepting molecule.
Other MOs also take part in interactions significantly as the reagent and reactant get to
be sizable.   With a view to connecting the results of sophisticated MO calculations with
our elementary notion of electron pairs in directed valence orbitals, we started a study of
hybrid MOs to describe chemical interactions between two molecular systems.[2-5]   Here we report
an important aspect of orbital interactions.

Let us assume that a proton is placed 1.5Å above the molecular plane of hexatriene and
that it moves from the position above the terminal carbon C_1 to the position above the midpoint
of the C_3-C_4 bond along the C_1-C_2, C_2-C_3 and C_3-C_4 bond axes.   The occupied π MOs, as well
as the occupied σ MOs, of hexatriene molecule participate in the electron donation to proton.
Then, by recombining the occupied MOs of hexatriene properly, we can single out an orbital

which represents by itself the electron-transfer interaction with the proton 1s orbital.

Figure 1 shows the hybrid of occupied MOs mentioned above with regard to several positions of proton. The calculation was performed within the ab initio STO-3G level. First of all, it is seen that the hybrid MO does not change significantly when the proton is retained in the C_1-C_2 bond region (I, II, III). The hybrid orbital is perceived to be essentially a C=C π MO. Thus, the C_1-C_2 bond is suggested to have a strong ability for electron donation to the proton and the bond is specified as a reactive region for protonation to hexatriene.
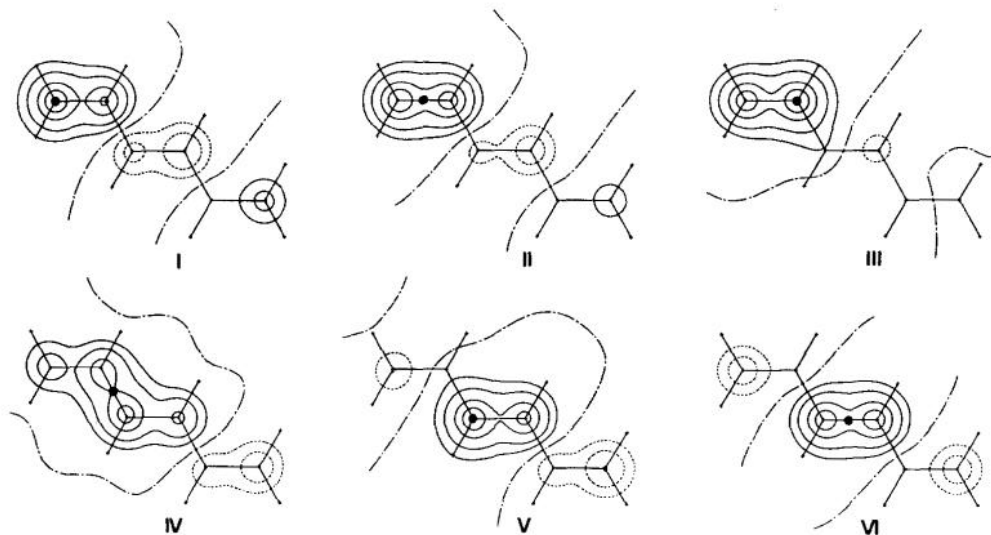

Figure 1. The occupied hybrid MO of hexatriene. The location of proton is indicated by a dot.

When the proton migrates in the C_2-C_3 bond region, however, the hybrid MO shows no more an effective localization (IV). This indicates that protonation to the C_2-C_3 bond is unfavourable. When the proton moves further on to the C_3-C_4 bond region, a nicely localized orbital is obtained again (V, VI). The change in the shape of the orbital is not conspicuous as far as the proton stays within the C_3-C_4 bond. The C_3-C_4 bond is specified as another reactive region of hexatriene for protonation.

The calculation has revealed that the region of molecules participating in the delocalization interaction is confined to a certain structural unit in favourable interactions, while no specific part of molecule is defined as the reactive unit in unfavourable interactions.

One may note that the reactive unit as determined
by the occupied hybrid MO is connected directly
with our elementary chemical concept, "functional
groups". Though hexatriene is a conjugated mole-
cule, the C_1-C_2, C_3-C_4 and C_5-C_6 bonds are recog-
nized essentially as double bonds, while the C_2-C_3
and C_4-C_5 bonds are not.

In hexatriene, the highest occupied MO is
bonding in the C_1-C_2, C_3-C_4 and C_5-C_6 bond regions
and antibonding in the C_2-C_3 and C_4-C_5 bond
regions. Thus, one may derive immediately the
same conclusion as mentioned above only by looking
at the highest occupied MO. However, if one refers
to larger molecular systems, particularly to satu-

Figure 2. The occupied hybrid MO of
an aromatic system.

rated systems, one may soon be aware of the significance of other MOs. In Figure 2 is shown
the occupied hybrid MO of a large condensed aromatic system which donates the electron density
to a proton placed 1.0Å above the midpoint of the central C-C bond. The orbital is seen
to be localized in the region of interaction, though the highest occupied MO tends to show
the maximum amplitude not in the C-C bond region but in the peripheral area of the system.

The delocalization interaction was found above to have an important ability to determine
the reactive region in molecules. According to our chemical intuition, a C-H sigma bond
should be formed when proton attacks a carbon atom. We show next that the determination
of reaction sites in the reactive region is ascribed to other sort of orbital interactions.

In Figure 3 are illustrated the interactive hybrid MOs obtained for protonation to
propene. The C_3H_7 cation optimized by means of the energy-gradient technique[6] was partitioned
tentatively into a deformed propene and a proton and the hybrid MO of propene was calculated
by taking not only the delocalization interaction but also the polarization interaction into
account in this case. It is seen that the polarization interaction specifies the reaction
site, C_1 or C_2, in the reactive unit, the C_1-C_2 bond. By watching the orbitals carefully,
one will find that the hybrid MO is localized around the reaction site more effectively in
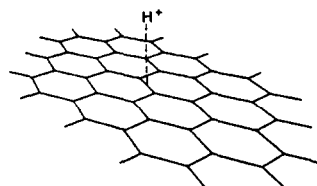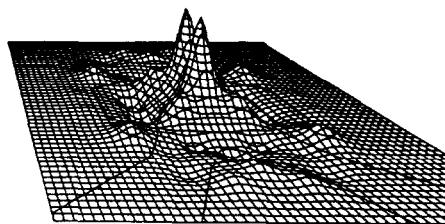the C_1 protonation than in the C_2 protonation. The slight difference in the hybrid MOs is

responsible for the calculated energy difference and, thus, may lead to the well-known Markownikoff rule.[7]

We have shown above that our familiar concepts in chemistry are reproduced in theoretical calculations. The molecular orbital calculations will be applied more and more frequently in future. It will be helpful, therefore, to know what regions of reagent and reactant are actually involved in interactions and how the reaction sites are
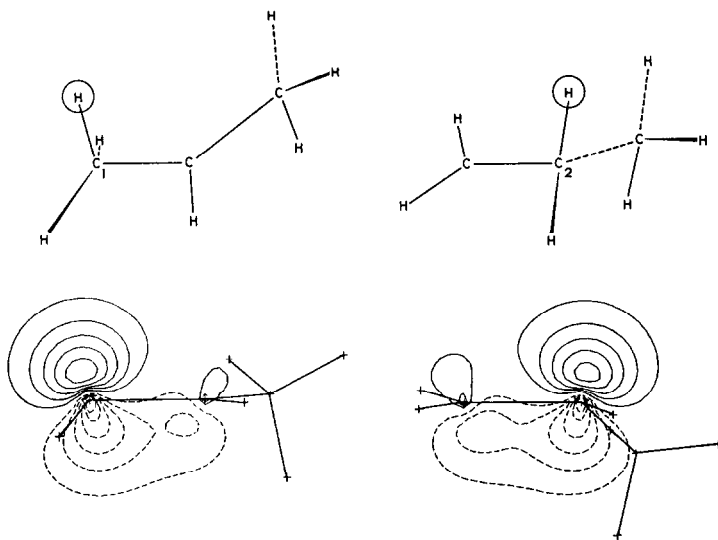

Figure 3. The interactive hybrid MO of propene for proton addition. C_1 protonation on the left and C_2 protonation on the right.

defined in the course of reactions. We believe the concept of orbital localization in interactions may provide a guide to make good use of calculated results for practical purposes.

References

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7. See, for instance, C. K. Ingold, "Structure and Mechanism in Organic Chemistry", 2nd ed., Cornell University Press, Ithaca, 1969, pp. 942-1097.