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REACTION POTENTIAL MAP (RPM) ANALYSIS OF CHEMICAL REACTIVITY. II. ILLUSTRATION OF THE ALLOWED/FORBIDDEN NATURE IN THE 1,n-HYDROGEN TRANSFER REACTIONS

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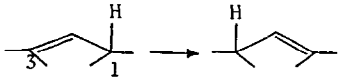
Abstract: A new kind of application of reaction potential maps to the analysis of chemical reactivity is presented in which the allowed/forbidden nature of the 1,n-hydrogen transfer reactions is clearly displayed.

Reaction potential maps (RPM) have been introduced as a guide to the study of reactive regions of molecules.[1] The RPM's are equipotential energy maps which involve not only the electrostatic potential and polarization energies generated by the interaction of two species, but also the partial charge transfer that takes place between them. Since they involve both charge and orbital interactions, a variety of chemical reactions can be analyzed by using them. For examples, the ambident mucleophilic character of the SCN^- anion,[1] and of the OCN^-, CH_2CHO^-, and NO_2^- anions[2] have been well elucidated by their RPM. In this paper, we will show that RPM's are also useful in the analysis of orbital symmetry constrained reactions and, for example, clearly display the allowed/forbidden nature of the 1,n-hydrogen transfer reactions. This clearly represents an improvement over the classical Electrostatic Potential maps.

From the Woodward-Hoffmann rules,[3] it is predicted that the suprafacial 1,3-hydrogen shift in propene is forbidden, while the 1,5-hydrogen shift in pentadiene is allowed. We considered



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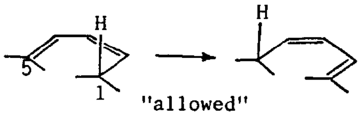

"allowed"

the allyl anion plus a proton as the model of the 1,3-hydrogen shift in propene,[4] and evaluated the RPM between the allyl anion and a proton at 1.5 Å above the molecular plane. In the present anion-proton system, the interaction energy consists of the electrostatic, polarization, and charge transfer terms; the meaning of these energy terms and the method for their practical evaluation from CNDO/2 wave functions were given elsewhere.[1,2] The only parameter involved in these equations is the orbital energy of the proton's empty 1s orbital; the value of 0.0 eV was adopted here.[5] The molecular structure employed is: R(C-C)=1.40 Å, R(C-H)=1.12 Å, bond angles= 120°. The terminal CH_3 groups were rotated in such a way as to allow one of the hydrogen atoms *to be in the proper configuration for the 1,n-shift.*

Figure 1 shows the calculated RPM of the allyl anion and its energy components. It shows (Fig. 1-a) two energy minima lying approximately above the terminal carbon atoms. These minima sit in deep potential wells separated by a large barrier at the center of the 1,3-hydrogen transfer path. This indicates that the 1,3-hydrogen shift in propene is strongly unfavorable. This forbidden nature can be well understood by analyzing the components of the RPM. It is seen that both the electrostatic potential map (Fig. 1-b) and the polarization energy surface (Fig. 1-c) are rather flat. This illustrates the fact that classical Electrostatic Potential maps are

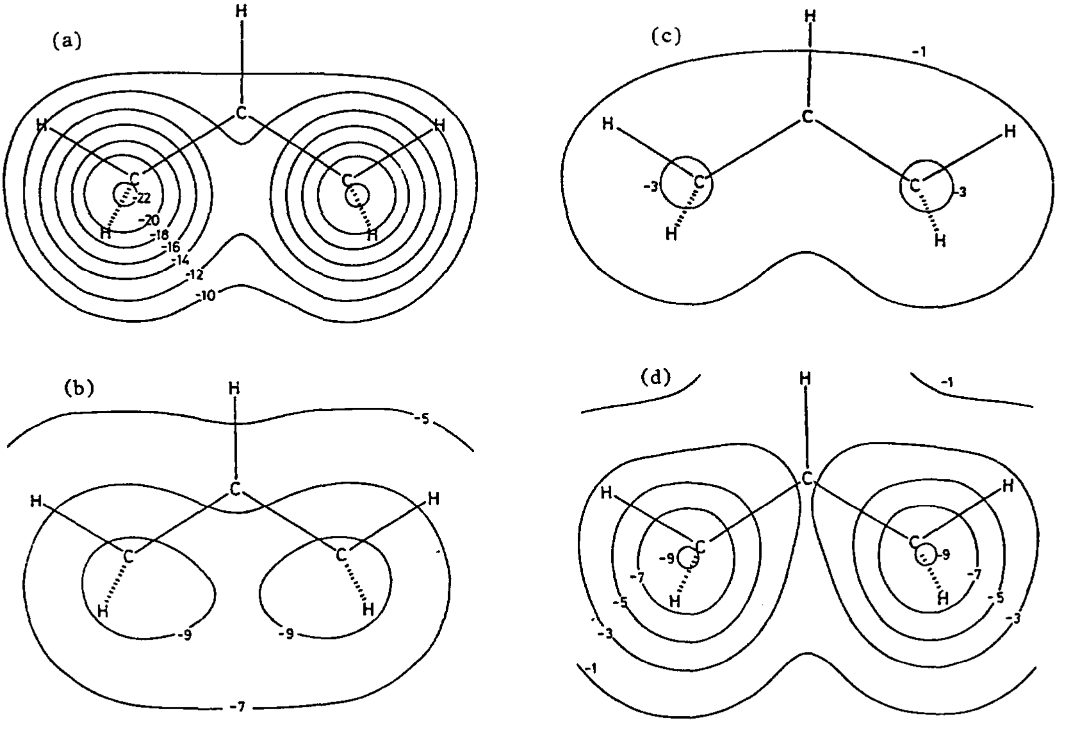

Figure 1. Reaction potential map (a) of the allyl anion against a proton, and its energy components: (b) electrostatic potential map, (c) polarization energy map, (d) charge transfer energy map. The maps were calculated 1.5 Å above the CCC plane by using the CNDO/2 wave function. The values indicated are in eV.

unable to account for orbital symmetry constraints. On the other hand, the middle point of the hydrogen transfer path has a high energy relative to the initial state in the charge transfer energy surface (Fig. 1-d). Thus the very large activation energy observed in RPM (Fig. 1-a) comes from the charge transfer interaction and it can be said that it is the orbital interaction between the allyl anion and the proton that prevents the 1,3-hydrogen shift in propene.

The 1,5-hydrogen shift in pentadiene is allowed from the Woodward-Hoffmann rules.[3] The RPM of the pentadienyl anion is thus expected to have a different shape from that of the allyl anion. Figure 2-a shows the RPM of pentadienyl.[6] The calculated activation energy of the 1,5-hydrogen shift in pentadiene (3 eV) is much lower than that of the 1,3-shift in propene (10 eV, Fig. 1-a). The absolute values of these activation energies are large, since our model consists of an anion and a proton and, since the solvation energy is not included, the electrostatic interaction energy, as well as the charge transfer one,[5] are highly overestimated. However, it is clearly seen that the 1,5-hydrogen shift in pentadiene is much more favorable than the 1,3-hydrogen shift in propene. Assuming that the solvation of the various intermediates is about the same, say 2 eV, we find 1 eV, 3 eV, and 8 eV, respectively, for the activation energy of the 1,5, the 1,7, and the 1,3 suprafacial proton transfer.

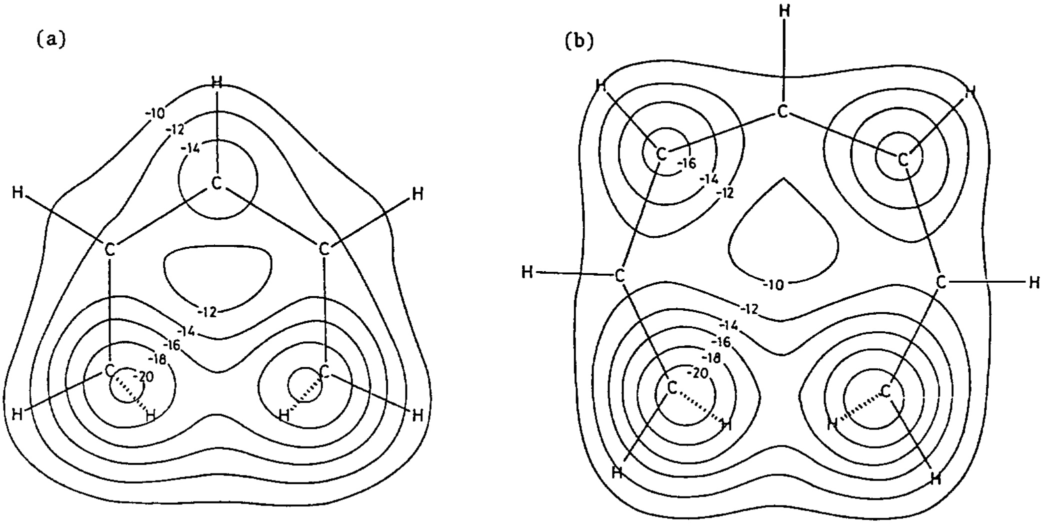

Figure 2. Reaction potential maps of (a) the pentadienyl anion and (b) the heptatrienyl anion calculated 1.5 Å above the carbon skeletons. The values indicated are in eV.

The 1,7-hydrogen shift in heptatriene is forbidden and the RPM of the heptatrienyl anion, Fig. 2-b, also shows the forbidden nature of this reaction.

The 1,5-shift is not possible either in the heptatriene configuration shown in Fig. 2-b. Indeed, in this configuration, carbon atoms 1 and 5 are too far apart. For the allowed 1,5-shift to take place, the molecule must first fold in such a way as to first bring the two carbon atoms (1 and 5) closer together. When the molecule is allowed to relax in this way, we find a low activation energy and a pattern similar to that obtained in the 1,5-shift in the pentadiene.

The difference between the allowedness of the 1,5-hydrogen shift in pentadiene and the forbidden nature of the 1,3-shift in propene and 1,7-shift in heptatriene was shown to originate from the orbital interaction between the migrating proton and the π-system of the remaining conjugated anion. Although this is anticipated from the Woodward-Hoffmann rules,[3] the RPM's of the allyl, pentadienyl, and heptatrienyl anions toward a proton illustrate more quantitatively the allowed/forbidden nature of the 1,n-hydrogen transfer reactions. This is a new kind of application of RPM and suggests a wide applicability of the RPM analysis to chemical reactivity studies.

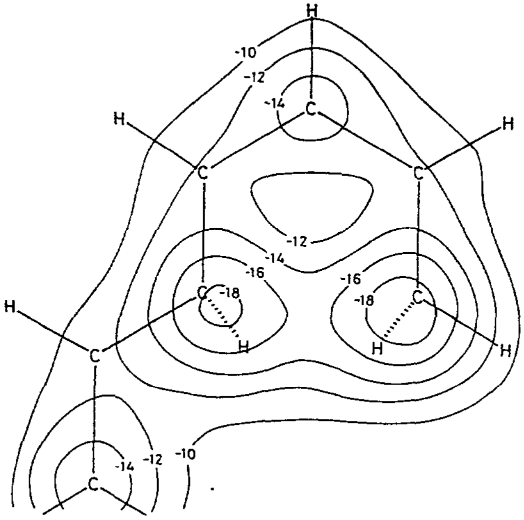

Figure 3. Reaction Potential Map for the 1-5-hydrogen shift in heptatriene

References and Notes

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2. H. Moriishi, O. Kikuchi, K. Suzuki, and G. Klopman, to be submitted.
3. R. B. Woodward and R. Hoffmann, J. Am. Chem. Soc., 87, 2511 (1965).
4. The 1,3-hydrogen shift in propene can be studied by using one of the following three model systems: an allyl anion plus a proton, an allyl radical plus a hydrogen atom, or an allyl cation plus a hydride anion. The present model is the ionic system, and it may overestimate the electrostatic interaction energy. However, the model is suitable for the present study whose objective is to compare the relative feasibility of the 1,n-hydrogen shifts in polyenes of various lengths.
5. In the RPM analysis, the orbital energy of the approaching electrophile is a measure of its softness. In our previous studies[1,2] of ambident anions, the value of 6.0 eV was employed for the model of a hard electrophile. The present model system overestimates the electrostatic interaction energy, and the value of 0.0 eV was chosen to compensate it to a certain degree. Larger values, e.g. 3.0 or 6.0 eV, for example, did not affect the qualitative conclusions obtained here.
6. All the bond lengths are 1.40 Å. The CCC bond angles of pentadienyl are 120° and those of heptatrienyl are 134.2°. These values give the same C-C distances between the terminal carbon atoms.

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