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Quantum Chemical Study of Catalytic Isomerization of Olefins

II. Intramolecular Hydrogen Shift in the Presence of a Basic Center

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The intramolecular hydrogen shift via an allyl-like intermediate was examined as the mechanism for olefin isomerization by means of a semiempirical molecular orbital (CNDO/2) calculation. The energy barrier for the hydrogen shift is very high for the allyl–hydrogen system, but with a strong base present at an appropriate position the height of the barrier decreases sharply. The effect of the basic center was analyzed in terms of two-center interactions, and was discussed in relation to the orbital symmetry rule. The present calculation suggests that the hydrogen-shift process becomes either a two-step or single-step mechanism depending on the basic strength of the catalytic center.

INTRODUCTION

Allylic species (cations, anions, and radicals) are important reaction intermediates in various catalytic reactions such as isomerization and oxidation. Experimental evidence for the existence and roles of the intermediates in the reactions has been reported for several catalyst systems (*1–3*). For double bond isomerization catalyzed by basic reagents, allylic intermediates having an anionic character have been assumed both for homogeneous and heterogeneous systems (*3–6*). We have shown previously, on the basis of quantum chemical calculations, that anionic 1-methylallyl tends to assume the *anti* (*cis*) configuration and that cationic 1-methylallyl is stable in the *syn* (*trans*) configuration, conforming to the trend suspected from experimental results (*7*). Tracer studies have revealed that this reaction proceeds effectively via the intramolecular 1,3-shift of a hydrogen atom, in both homogeneous and heterogeneous systems (*3*). For example, for a CaO catalyst, a deuterium atom at the allylic position of 1-butene migrates to the terminal carbon during isomerization to 2-butene (*3b*). This intramolecular mechanism has been observed over several metal oxide catalysts, e.g., MgO (*3c*), $MgFe_2O_4$ (*3d*), and Al_2O_3 (*4*). If this process proceeds via an allylic intermediate having a sufficiently long life, hydrogen–deuterium exchange between the catalyst and the olefin may occur. On the other hand, the direct 1,3-shift of a hydrogen atom in a single step, which is sometimes considered as a possible mechanism (*4, 5*), should be an entirely intramolecular mechanism.

However, the 1,3-hydrogen shift in the *supra* mode for an allyl anion and a proton system is a process forbidden by the Woodward–Hoffman rule and the conservation of symmetry of frontier orbitals (*8*): The highest occupied molecular orbital of

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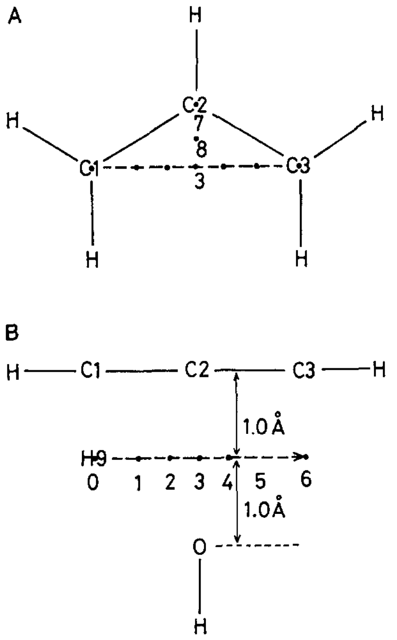


FIG. 1. The model adopted for the calculations of the 1,3-allyl hydrogen shift. (A) Top view, (B) front view.

the allyl anion possesses opposite signs at the 1 and 3 carbons. This rule may also be related to some extent to other concerted mechanisms proposed for olefin isomerization (*9*).

The aims of the present study are to extend the previous calculation and to elucidate the effect of a basic catalyst on this process. The principal questions are how the process, which is forbidden by the symmetry rule, takes place when a basic catalytic center exists and what happens when the basic strength of the center is changed.

RESULTS AND DISCUSSION

The procedures for the molecular orbital (CNDO/2) calculation (*10*) and the partition of energies into two-center terms are the same as given in the previous paper (*7*). Due to the simplification and assumption involved in the calculation, the CNDO method exhibits certain weaknesses, e.g., in the calculation of the absolute energy values. However, this method has been reasonably successful in the prediction of equilibrium geometry (*10*), charge distribution (*10*), and relative stability of geometrical and conformational isomers (*7*, *10*), and has been applied to the study of catalysis (*12*). Therefore, the CNDO method was chosen for this work. The model adopted for calculation is shown in Fig. 1. A hydrogen atom, which is located 1 Å below the allyl plane, moves from the position right below C1 (position 0) to the position below C3 (position 6), so that the double bond of the pseudopropylene migrates from C2–C3 to C1–C2 during the process. Although this model may appear to be too simple, it is a suitable model for clarifying the symmetry aspects of the intramolecular hydrogen shift.

An OH^-, having the oxygen atom situated 2 Å below C2, is taken as the model of the basic center. The OH^- may represent a strong base similar to an oxide ion on the surface having a low coordination number. This position is the same as that used in Ref. (*7*) and renders the system stable. When the oxygen of OH^- is moved on the plane lying 2 Å below the allyl plane, with H9 fixed at position 3, the energy of the system increases in the order, position 3 < position 8 < position 7 (see Fig. 1A). This change is due to the attractive interaction between the $2p_z$ of C2 and the oxygen atom.

When the hydrogen (H9) moves along the 0–3–6 line, the total energy changes as is shown in Fig. 2. In the absence of OH^-, there appears a high energy barrier for the 1,3-shift, as is expected from the symmetry rule. When OH^- is present at the appropriate position, the height of the barrier is lowered sharply and the system becomes a little more stable than the initial configuration. It must be remarked that the initial system resembles propylene, but is slightly less stable than the system which consists of actual propylene and OH^-. However, it may be stated that the hydrogen transfer proceeds only over a small energy barrier,

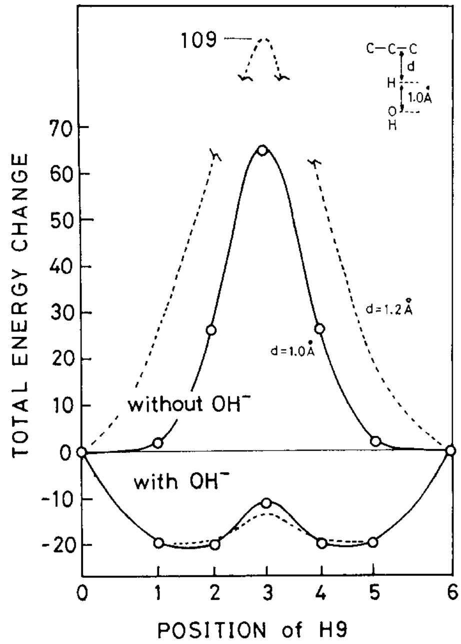


FIG. 2. The change in the total energy (in kcal/mol) during the 1,3-hydrogen shift in the absence and in the presence of OH^- (from position 0 to 6 in Fig. 1).

after the allyl and H are formed from propylene on the surface basic center. This trend essentially does not change, even if the C–H9 and C2–OH distances are changed, as is shown by the example in Fig. 2. In the absence of OH^-, the height of the barrier increases when the allyl–H9 distance is increased, but the barrier remains essentially unchanged for the system containing OH^-.

The contrast found between the two cases is analyzed in more detail in terms of two-center energies. In Fig. 3, the variation of the covalent bond energies and the charge distribution during the course of the hydrogen shift are plotted against the position of hydrogen shift. Only the first half (0–3) is presented, since the second half is the mirror image of the first half. This figure shows that the covalent interaction for H9–C1 and C2–C3 bonds decreases from positions 0 to 3, while, for H9–C2 and H9–C3, the covalent interaction becomes stronger. The C1–C2 bond is strengthened only slightly for the case without OH^-, but its strength increases considerably when OH^- is present. It is most remarkable that the H9–OH interaction becomes significant as H9 approaches OH^-. In the initial system, the C1–C2 and C2–C3 bonds are respectively of single- and double-bond character. As for the allyl alone, these two bonds are approximately of 1.5-fold character, covalent energy for the C–C bond calculated by CNDO being approximately 1.43 to 1.45 a.u. However,

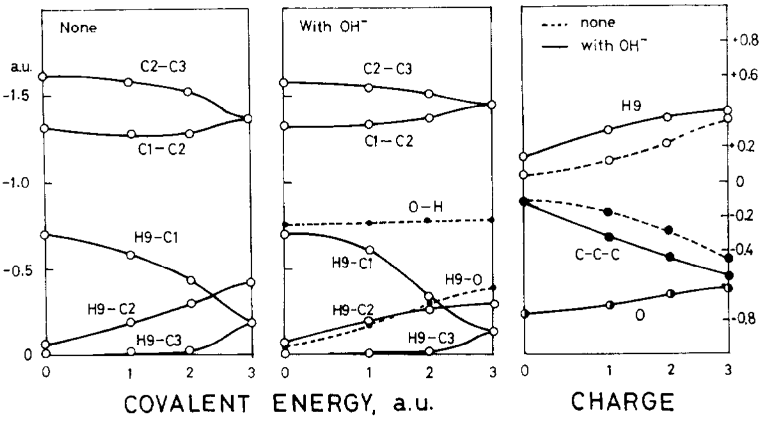
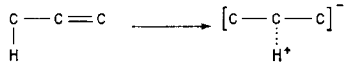


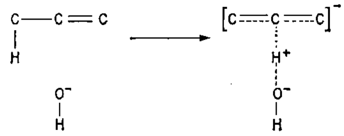
FIG. 3. The covalent energies (in a.u.) and charge distribution plotted against the position of the hydrogen shift in the absence and in the presence of OH^- (positions 0 to 3 are the same as in Fig. 1).

without OH^-, two C–C bonds become nearly single bonds when H9 is at position 3, indicating a destructive effect of H9 on C–C–C bonds. In the presence of OH^-, C_3H_5 actually exhibits this allylic character at the same H9 position. This is the reason why there is a high energy barrier in the absence of OH^-, in conformity with the symmetry rule. The barrier is lowered to some extent by the increase in the attractive C2–H9 force (σ type).

Regarding the charge distribution, considerable polarization takes place, with the allyl becoming more anionic and H9 more like a proton, in both cases. However, at position 3, the interactions of H9 with the allyl and with OH^- are mainly of covalent character on the basis of the present CNDO calculation. The processes (for shifting H9 from position 0 to 3) with and without OH^-, therefore, may be illustrated, respectively, by reactions (1) and (2).



$$\underset{H}{C}-C=C \longrightarrow [C-\underset{H^+}{C}-C]^- \quad (1)$$



$$\underset{\underset{H}{O^-}}{\underset{H}{C}}-C=C \longrightarrow [C\text{---}\underset{\underset{\underset{H}{O^-}}{H^+}}{C}\text{---}C]^- \quad (2)$$

In Fig. 4, the changes in several two-center terms important to this process are presented. It may be seen that, as described above, the high barrier in the absence of OH^- is mainly due to a weakening of the C–C bonds (E^{c+k}, which is the sum of the covalent and exchange energies, changes by about 163 kcal/mol). The C–H interaction changes much less during the hydrogen shift. The large loss in the C–C bond energies is partly compensated for by the gain in the C–H9 electrostatic interaction (ca. 100 kcal/mol). The difference between these energy changes (163 − 100) is comparable to the total energy change (65 kcal/mol). When OH^- is present, H9 interacts strongly with OH^-, leaving the allyl system little altered [E^{c+k}(C–C) changes by ca. 15 kcal/mol]. Since the E^{elec}(C–H9) varies similarly for both cases, the reason why the system containing OH^- becomes stable is that the loss of the allyl–H9 bond energy is overcome by the strong H9–OH interaction, the destructive effect of H9 on the allyl part being very small.

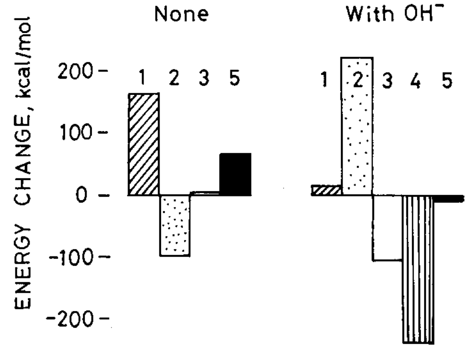


FIG. 4. The change in several two-center energies for shifts from positions 0 to 3 in Fig. 1. (1) E^{c+k}(C–C): covalent and exchange energies among the carbon atoms; (2) E^{c+k}(C–H9): covalent and exchange energies between H9 and the carbon atoms; (3) E^{elec}(C–H9): electrostatic energy between H9 and the carbon atoms; (4) E^{c+k} (O–others): covalent and exchange energies between the oxygen atom and other atoms (mainly H9); (5) Total energy.

The effect of a water molecule in place of OH^- was studied as a model of a weak base. H_2O may represent M–O–M or M–O–H on the surface. The oxygen atom is

TABLE 1

Energy Changes for the Hydrogen Shift Process in the Presence of Bases (in kcal/mol)[a]

Basic center	Sum of the two-center terms for				Total energy change
	C–C	allyl-H9	O–H9	All	
None	+152	−83	—	+46	+65, +109[b]
H_2O	+90	−22	−47	+21	+75, +94[b], +65[c]
OH^-	+21	+105	−273	−61	−10

[a] The differences in the energies for H9 at positions 0 and 3 for standard geometry (Fig. 1) are given, except for those values with superscripts b and c. Plus signs indicate that the energies increase from 0 to 3.

[b] Allyl plane–H9 = 1.2 Å; allyl plane–O = 2.2 Å.

[c] Allyl plane–H9 = 1.0 Å; allyl plane–O = 2.1 Å.

fixed 2 Å below C2, since this position renders the system most stable as before. Two hydrogen atoms are located below the oxygen with the H–H line parallel or perpendicular to the C1–C3 line. No substantial difference in energy was observed between the two water configurations. Some of the results are given in Table 1, together with the previous two cases. It is seen that H_2O is intermediate between the two previous cases as for the two-center terms. For instance, H9 at position 3 has a destructive effect on the C–C bonds as in the hydrocarbon-only system, although to a lesser extent. The oxygen atom interacts attractively with H9 but is less effective than OH^-. As for the total energy change, H_2O has a rather small effect, although it varies slightly for a small change in distance (Fig. 2 and Table 1). Probably the one-center terms contribute more in this case, owing to the extensive polarization of the system. However, the reason for this was not investigated further. Nevertheless, the changes in the two-center terms appear to illustrate well the effect of the difference in the basicity of the catalytic center. The present calculation suggests that the oxygen basicity in *M*–O–*M* or *M*–O–H is not strong enough to be effective in the hydrogen transfer process. The effect of LiOH lies between H_2O and OH^-, indicating that their basicities increase in the order $H_2O < LiOH < OH^-$ (*11*).

SUMMARY

(i) There is a high energy barrier for the 1,3-hydrogen shift in the allyl system, in accord with molecular orbital symmetry considerations. The hydrogen atom shifting (H9, Fig. 1) interacts destructively with the allyl part at the top of the barrier, donating electrons to allyl system. The barrier is partly lowered by the σ-type attractive interaction between H9 and C2.

(ii) The barrier becomes very low when a strong base, like OH^-, is present at an appropriate position. This effect is mainly due to the rather strong interaction between H9 and the basic center. Besides the energy gain from this interaction alone, there is an indirect gain in energy due to a decrease in the destructive effect of H9 on the allyl skeleton.

(iii) A water molecule, chosen as the model of a weak base, exhibits an intermediate effect on this process for the two-center terms.

(iv) In the transition state (position 3, Fig. 1), in the presence of OH^-, the system is strongly polarized, although considerable allyl–H9 interaction of covalent character occurs. Further calculations show that the entire system becomes slightly more stable as the allyl–H9 distance is increased and as H9 approaches OH^- more closely. This indicates that the system tends to dissociate to allyl and water. These results suggest that the hydrogen transfer process becomes more like a stepwise mechanism in the presence of a strong base.

$$C_3H_6 + OH^- \rightarrow C_3H_5^- + H_2O \rightarrow \text{“isomerized” } C_3H_6 + OH^-$$

On the contrary, the reaction $C_3H^6 + H_2O \rightarrow C_3H_5^- + H_3O^+$ is endothermic, so that the 1,3-hydrogen shift resembles a concerted one-step mechanism if it does occur. The actual process catalyzed by bases may exhibit either the one-step or the two-step mechanism depending on the basic strength of the catalytic center and other factors, such as the ability of the cationic center to coordinate with the allyl.

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REFERENCES

1. Voge, H. H., Wagner, C. D., and Stevenson, D. P., *J. Catal.* 2, 58 (1963); Adams, C. R., and Jennings, T. J., *J. Catal.* 2, 63

(1963); Sachtler, W. M. H., *Rec. Trav. Chim.* **82**, 243 (1963).

2. Kokes, R. J., and Dent, A. L., *Advan. Catal.* **22**, 1 (1972); Kondo, T., Ichikawa, M., Saito, S., and Tamaru, K., *Bull. Chem. Soc.. Japan* **45**, 1580 (1972); Tanabe, K., Yoshii, N., and Hattori, H., *Chem. Commun.* 464 (1971).

3. (*a*) Bank, S., Rowe, C. A. Jr., and Schriesheim, A., *J. Amer. Chem. Soc.* **85**, 2115 (1963); (*b*) Tani, N., Misono, M., and Yoneda, Y., *Chem. Lett.* **1973**, 591; (*c*) Shannon, I. R., Kemball, C., and Leach, H. F., *in* "Symposium on Chemisorption and Catalysis." Institute of Petroleum, London, 1970. (*d*) Gibson, M. A., and Hightower, J. W., *J. Catal.* **41**, 420 (1976).

4. Gerberich, H. R., and Hall, W. K., *J. Catal.* **5**, 99 (1966).

5. Baird, M. J., and Lunsford, J. H., *J. Catal.* **26**, 440 (1972).

6. Haag, W. O., and Pines, H., *J. Amer. Chem. Soc.* **82**, 387 (1960); Foster, N. F., and Cvetanovic, R. J., *J. Amer. Chem. Soc.* **82**, 4274 (1960).

7. Grabowski, W., Misono, M., and Yoneda, Y., *J. Catal.* **47**, 55–61 (1977).

8. Woodward, R. B., and Hoffman, R., "The Conservation of Orbital Symmetry." Academic Press, New York, 1970; Anh, N. T., "Les Regles de Woodward–Hoffman." Ediscience, Paris, 1970.

9. Turkevich, J., and Smith, R. K., *J. Chem. Phys.* **16**, 466 (1948); Corado, A., Kiss, A., Knözinger, H., and Müller, H. D., *J. Catal.* **37**, 68 (1975).

10. Pople, J. A., and Beveridge, D. L., "Approximate Molecular Orbital Theory." McGraw-Hill, New York, 1970.

11. Grabowski, W., Misono, M., and Yoneda, Y., unpublished results.

12. Baetzold, R. C., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 25, p. 1. Academic Press, New York, 1976; Blyholder, G., *J. Chem. Soc. Chem. Commun.* **1973**, 625; Chuvylkin, N. D., Zhidomirov, G. M., and Kazansky, V. B., *J. Catal.* **44**, 76 (1976); Yoshida, S., Tai, S., and Tarama, K., *J. Catal.* **45**, 242 (1976).