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Semiempirical Quantum Chemical Calculations of Intermediate Complexes in Catalytic Reactions

VII. Butene Isomerization over Basic Catalysts

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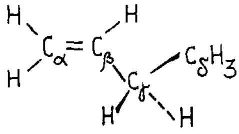
The nature of chemical activation of the 1-butene molecule due to dissociative adsorption on basic catalysts is analyzed within the scope of an approximate SCF MO method.

1. INTRODUCTION

Catalytic isomerization of olefins can occur over both acidic and basic oxides. Investigations of mechanisms of this reaction are carried out, usually, for the simplest case of catalyzed isomerization of 1-butene (M).



(M)

When strong acidic catalysts (e.g., silica–alumina) are employed, one generally proposes the formation of the 2-butyl-carbonium cation playing the role of a common surface complex (CSC) via which the isomerization of butenes occurs (*1*, *2*). The electronic structure of CSC was theoretically investigated in our previous paper (*3*) where it was demonstrated that the selected activation of chemical bonds in the M, caused by proton addition to the C_α atom, is indeed favorable for realizing the 1-butene isomerization in accord with the reaction scheme (1) including the cleavage of a C_γ–H bond and the formation of the double bond $C_\beta{=}C_\gamma$.

On the contrary, in the case of strong basic catalysts (MgO, CaO, ZnO, etc.) the isomerization is believed (*4–8*) to proceed via a carbanion mechanism which includes a stage of dissociative adsorption of butene molecules with subsequent stabilization of protons and π-allylic carbanions on the O^{2-} ions and metal cations, respectively. Such a picture of the butene isomerization on a strong basic substrate implies that the electronic structure of a coordinated intermediate tremendously resembles that of a free butene carbanion [cf. Ref. (*12*) for particulars] and a catalyst is mainly responsible for creating and stabilization of the corresponding ionic species. With this in mind one should recognize the opportunity of realizing the ensuing stages of the catalytic isomerization on basic catalysts to be closely connected with the electronic properties of the assumed carbanions.

The heterolytic cleavage of a C_γ–H bond in the course of the M adsorption can lead to the formation of both *syn* and *anti* isomers of the π-allylic anion, and the subsequent addition of protons to the C_α atoms of these species must then complete the M isomerization and yield the corresponding *trans* and *cis* butenes. This

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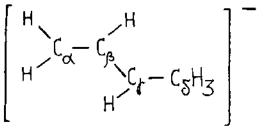
reaction scheme of the catalytic isomerization of 1-butene over strong basic oxides may be presented as follows:

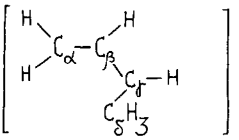
$$\begin{array}{c} \text{1-butene} \\ \upharpoonleft\!\downharpoonright \qquad\qquad \downharpoonleft\!\upharpoonright \\ \textit{cis}\text{-2-butene} \rightleftharpoons \textit{anti-}\pi^- \rightleftharpoons \textit{syn-}\pi^- \rightleftharpoons \\ \qquad\qquad\qquad\qquad \textit{trans}\text{-2-butene.} \end{array}$$

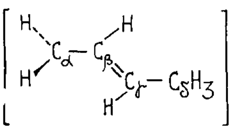
Seeing that the π-allylic carbanions play the important role of intermediate complexes in the proposed reaction scheme, it is of interest to examine theoretically and compare their electronic structures as, undoubtedly, it can help gaining of a more profound insight into the mechanism of the butene isomerization over basic catalysts. For this purpose the quantum chemical calculations of some geometrical conformations of the π-allylic carbanion were carried out within the scope of the CNDO/2 approximations (*9*). The methodology of calculating the electronic properties of intermediate complexes was discussed in detail elsewhere (*3*) and, therefore, the introduction concerning this point is not presented in this paper.

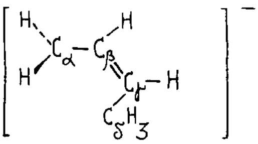
2. GEOMETRICAL STRUCTURES OF π-ALLYLIC CARBANION

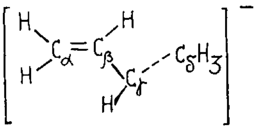
To supply a more detailed picture of the selected activation of chemical bonds in the 1-butene molecule due to the formation of the π-allylic carbanion under the dissociative adsorption, we have considered several species (S, A, T, C, D) represented below:


(S)


(A)


(T)


(C)


(D)

The first two intermediates (S) and (A) present, respectively, the *syn* and *anti* conformations of the π-allylic carbanion wherein the carbon skeleton and the nonmethyl H atoms are in the same plane. The structures (T) and (C) are formed from the (S) and (A) by means of turning the H_2C_α group through 90° around the C_α–C_β bond while the (D) structure corresponds to turning the HC_γ–$C_\delta H_3$ fragment through 90° around the C_β–C_γ bond. The values of chemical bond lengths and angles were standard (*10*) for all species (S, A, T, C, D, M).

3. RESULTS AND DISCUSSION

The calculated magnitudes of the excess charges Q^A of atoms and the relative total energies E^- (kcal/mole) of the π-allylic carbanions as well as indexes $i_{AB}\%$ $= \Delta E_{AB}/E_{AB}\%$ (*3*) of changing the strength of chemical bonds A–B due to the dissociative adsorption of the 1-butene molecule are summarized in Table 1. The results of calculations indicate that differences in the electronic properties of the (S) and (A) intermediates are small. Likewise, the electronic configurations of the (T) and (C) structures are almost identical.

According to the CNDO/2 calculation, the distribution of the excess electron in the *syn* and *anti* forms of the π-allylic carbanion corresponds to the nearly 70% concentration of the negative charge in the C_α and C_γ atoms. It follows that stabilization of the *syn* and *anti* conformations in the electric field of surface

TABLE 1

CNDO/2 Results for π-Allylic Carbanions

Structure	S	A	T	C	D
$Q_{C\alpha H_2}{}^{H}$	−0.07	−0.08	−0.07	−0.07	−0.07
$Q_{C\alpha H_2}{}^{H'}$	−0.05	−0.04	−0.07	−0.07	−0.03
$Q_{C\alpha H_2}{}^{C}$	−0.35	−0.35	−0.56	−0.56	−0.16
$Q_{C\beta H}{}^{C}$	0.09	0.08	0.14	0.13	0.13
$Q_{C\beta H}{}^{H}$	−0.07	−0.08	−0.15	−0.15	−0.13
$Q_{C\gamma H}{}^{C}$	−0.32	−0.31	−0.14	−0.12	−0.47
$Q_{C\gamma H}{}^{H}$	−0.04	−0.07	−0.03	−0.08	−0.06
$Q_{C\delta H_3}{}^{C}$	0.05	0.05	0.01	0.02	0.10
$\bar{Q}_{C\delta H_3}{}^{H}$	−0.08	−0.07	−0.04	−0.03	−0.10
$i_{H-C\alpha}\%$	−1.0	−1.1	−2.7	−2.6	−2.2
$i_{H'-C\alpha}$	0.6	0.7	−2.1	−2.1	0.4
$i_{C\alpha-C\beta}$	−14.2	−14.3	−26.1	−26.3	−0.7
$i_{H-C\beta}$	0.1	−0.2	−4.7	−4.8	−4.4
$i_{C\beta-C\gamma}$	26.4	26.6	47.7	48.0	10.2
$i_{H-C\gamma}$	2.0	0.9	1.6	−0.5	−0.1
$i_{C\gamma-C\delta}$	7.0	7.3	3.3	4.6	8.9
$\bar{i}_{H-C\delta}$	−1.6	−1.5	−0.9	−1.0	−2.0
E^-	≡0	2.0	28.8	27.7	14.4

ions must be expected, first of all, to be due to electrostatic interactions with these atoms. It is worth mentioning at this point that the energy of interactions between the negatively charged carbon atoms and the lattice surface may strongly depend on geometry of the carbanion adsorption and, therefore, the explicit consideration of a substrate is obligatory for reliably predicting the more energy-stable intermediate on a surface. At the same time, the above interactions seem to be unable to create appreciable alterations in the electronic configurations of free π-allylic carbanions.

As one can see from Table 1, the formation of the (S) and (A) intermediates under the heterolytic cleavage of a C_γ–H bond in the 1-butene molecule is connected with the noticeable activation of the $C_\alpha{=}C_\beta$ double bond, and owing to it the chance arises for a relatively free internal rotation around the C_α–C_β axis. In contrast, because of strengthening the single bonds C_β–C_γ and C_γ–C_δ, the rotations around them must be more hindered than in the case of the noncoordinated molecule (M). Special attention should be given to the calculated energies of the (T) and (C) structures as well as to the indexes $i_{CC}\%$ of changing the strength of carbon bonds which testify that restrictions on the internal rotations are rather severe for the π-allylic carbanion but insignificant for the almost fully saturated 2-butyl-carbonium cation involved as the CSC in the acid-catalyzed reaction (*3*). This structural difference does seem to be important for realizing a greater kinetic selectivity of the butene isomerization over basic oxides as compared to acidic ones.

The results, presented in Table 1, indicate that, owing to the structural reorganizations caused by turning the H_2C_α group under the formation of the (T) and (C) species, further strengthening of the C_β–C_γ bond and activation of the C_α–C_β bond take place. It is also interesting to note that the chemical bonds H–C_α and C_γ–C_δ in the (C) and (T) conformations are weaker than in the (A) and (S). As before, the negative charge concentration in the C_α and C_γ atoms is nearly 70% but now these atoms possess the strongly unequal portions of 56 and 14%, respectively. Thus, the charge distributions in the (T) and (C) anions are favorable for the preferable addition of protons to the C_α atoms which is required for completing the isomerization reaction. Hence, the (T) and (C) structures have electronic configurations highly resembling those of the corresponding *trans* and *cis* conformations of 2-butene as the final product of the 1-butene isomerization. Therefore, it seems justifiable to draw the following conclusion that the (T) and (C) forms of the π-allylic carbanion may present either true transition states or rather like intermediates participating in conclusive stages of the butene isomerization over strong basic catalysts.

On the other hand, the structural reorganizations, connected with the formation of the (D) species of the π-allylic carbanion, may help the occurrence of the competitional reaction of the 1-butene dehydrogenation as in this case the tendencies of activating the $C_\delta H$ bonds and strengthening the C_γ–C_δ bond are more pronounced. For removal of a H^- ion from the (D) structure it is also favorable that the negative charge concentration in the H atoms of the $C_\delta H_3$ group and in the closely to them situated C_γ atom is about 80%. At the same time it is necessary to pay attention to the considerable negative charge of the H atom in the $C_\beta H$ group as well as to noticeable weakening the C_β–H bond in the (D) form. Thus, the results of the performed quantum chemical calculations reveal the possibility of a more complicated mechanism of dehydrogenation including the heterolytic cleavage of the C_β–H bond and the subsequent transfer of a hydrogen atom from the $C_\delta H_3$ group to the C_β atom. It must be emphasized that the (T) and (C) conformations of the π-allylic carbanion are also inclined to a similar removal of the H^- ion by virtue of the same activation of the C_β–H bond in them as in the (D) species.

As a final point it is interesting to note that the calculated relative energies E^- (Table 1) of the (C) and (T) free intermediates do not contradict the experimental data on a high kinetic selectivity of the catalyzed isomerization of butenes over basic oxides for which the *cis/trans* ratio is usually about 10. However, one should bear in mind that the difference in total energies of the (C) and (T) structures, as well as of the (A) and (S) forms, is rather small and in such cases, as was already emphasized (*3*), the relative order of stability of the corresponding complexes on catalyst surfaces may be reverse. Moreover, other stages of catalytic isomerization, which probably are not connected with internal rotations in π-allylic systems, may prove to be important in determining the high kinetic selectivity (*11*).

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