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Semiempirical Quantum Chemical Calculations of Intermediate Complexes in Catalytic Reactions

VI. Butene Isomerization

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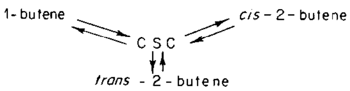
The nature of chemical activation of the 1-butene molecule due to the addition of a proton is analyzed within the scope of an approximate SCF MO method.

1. INTRODUCTION

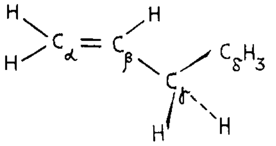
The isomerization of olefins belongs to the simplest type of chemical reactions in which unsaturated hydrocarbons can participate. Under some conditions this reaction may be catalyzed by a variety of chemical compositions and occurs in both homogeneous and heterogeneous phases [See, e.g. (*1*)]. The results of numerous experimental studies served as a basis for several proposed mechanisms of the catalyzed olefin isomerization (*2–5*). Hence, it will not be suggested that a single mechanism can be general for all catalysts.

The reaction mechanisms of the *n*-butene isomerization over alumina and silica–alumina were discussed in detail by Hightower and Hall (*1*). They came to the conclusion that in the case of alumina no single mechanism, advanced in the literature, can account for the whole set of their experimental observations, i.e., the various reaction paths may be practicable on different active sites and are probably strongly dependent on the butene geometry over alumina. In contrast, the mechanism of the butene isomerization over silica–alumina was presented in (*1*) with the help of the following reaction scheme:



(1)

Here the abbreviation CSC denotes some common surface complex. All the observed selectivities and their temperature dependencies as well as the relative reactivities of the isomers and certain other kinetic and thermodynamic data can be accounted for, at least semi-quantitatively, if a 2-butyl-carbonium ion is identified as CSC. Such a surface complex can be formed by addition of a proton to the C_α atom of a 1-butene molecule (M):



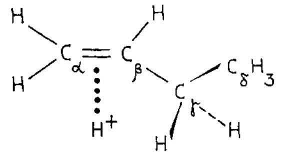
(M)

The subsequent loss of a proton due to the C_γ–H bond cleavage must then complete the reaction of the 1-butene isomerization.

Seeing that the role of CSC in the proposed reaction scheme (1) is rather significant, it is of interest to verify whether the qualitative alterations in the electronic structure of M, caused by CSC formation, are indeed favorable for realizing the isomerization in accord with the above scheme. For this purpose the quantum chemical calculations of the influence of coordinating by H^+ on the chemical activation of M were carried out within the scope of the CNDO/2 method (*6*). This paper continues our previous theoretical work (*7–11*) concerning similar problems of changing the reactivity of H_2 and C_2H_5OH molecules due to the formation of complexes with some active species.

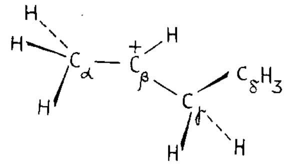
2. GEOMETRICAL STRUCTURES OF COMPLEXES

For the purpose of a more complete analysis of the influence of the proton addition on the chemical activation of 1-butene there were examined both a π-complex

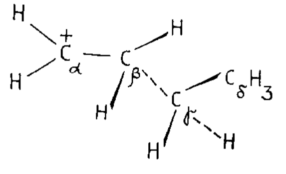


(π)

and "classical" butyl-carbonium ions (σ-complexes) which can be naturally formed from the π-complex:



(σ_1)



(σ_2)

The proton in the π-complex was under the plane of the $H_2C_\alpha = C_\beta HC_\gamma$ fragment at 1.09 Å distance from each of the C_α and C_β atoms.

The values of chemical bond lengths and corresponding angles were standard (*12*) for all structures (M, π, σ_1 and σ_2).

3. METHOD OF CALCULATION

The electronic properties of 1-butene as well as of its complexes were calculated within the scope of the generally accepted CNDO/2 approximations. At present there is already a massive quantum chemical literature (*13–18*), where the methodology and adequacy of these approximations have been examined. In this context it is only worth mentioning the possibility of partitioning the total molecular energy E, obtained by CNDO/2 method, into mono and bicentric physical components (*13*):

$$E = \sum_{A} E_A + \sum_{A > B} \sum E_{AB}.$$

The E_{AB} energy of the A–B bond correlates closely with the contribution of the resonance integrals (*19*)

$$E^R_{AB} = 2 \sum_{\mu \in A} \sum_{\nu \in B} P_{\mu\nu} \cdot \beta_{\mu\nu} \cdot S_{\mu\nu},$$

where $P_{\mu\nu}$ are the elements of the bond order matrix, $\beta_{\mu\nu}$ are the energy factors and $S_{\mu\nu}$ are the overlap integrals of the slater-type orbitals.

This partitioning makes it possible to gain an insight into the electronic structure of chemical bonds, as it was proposed (*20*) that a connection exists between the two-center terms and the concept of the chemical bond. Moreover, it was noted (*19*) that the two-center energy components are a measure of the strength of chemical bonds even in the case of nonclassical bonds in carbonium ions.

The E_{AB} values and the corresponding E^R_{AB} magnitudes are well suited to describe the relative strength of chemical bonds in molecules. However, to characterize the selected activation of these bonds due to the formation of intermediate complexes with any active centers, it may be more convenient to define indexes (*9–11*),

$$i_{AB}\% = \frac{\Delta E_{AB}}{E_{AB}} \% \approx \frac{\Delta E^R_{AB}}{E^R_{AB}} \%,$$

where $\Delta E_{AB} = E^c_{AB} - E_{AB}$ is the difference in energies of a chemical bond A–B in a complex and in a free molecule.

It is also worth noting at this point that in this work we examine only the influence of the proton addition on the selected activation of chemical bonds in 1-butene and do not consider the energy of hydrocarbon adsorption. In this case the lack of a treatment of the substrate is reasonable, as the appreciable activation of chemical bonds will be mainly caused by closely situated proton, while the influence of the distant surface atoms must be rather small.

When qualitatively considering the activation of chemical bonds in coordinated molecules, i.e., their "preparation" for chemical reactions, it is justifiable to make use of such an approach as regards any other adsorbate–adsorbent systems. However, to determine the more energy-stable molecular conformation on a surface as well as the reaction pathway, it is necessary to carry out a thorough investigation of the substrate.

4. 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, σ_1 and σ_2 complexes as well as indexes $i_{AB}\%$ of changing the strength of chemical bonds A–B due to coordinating M by H^+ are summarized in Table 1. The electronic charge belonging to the acidic center H^+ in the π, σ_1 and σ_2 complexes is denoted by Q_{Kt}.

In all cases the value of Q_{Kt} is near −1, i.e., the addition of the proton evokes the intense polarization of the butene molecule owing to which almost a whole electron turns out to be removed from M to H^+. As is to be expected, the excess charges of the C_{α} and C_{β} atoms alter within the widest limits. Note that the calculated electron distributions in the σ_1 and σ_2 complexes agree qualitatively with the simplified chemical conceptions of the structure of the "classical" butyl-carbonium ions.

TABLE 1

CNDO/2 RESULTS FOR THE ISOLATED AND COORDINATED 1-BUTENE MOLECULE

Structure	M	π	σ_1	σ_2
$Q^{H}_{C_{\alpha}H_2}$	0.01	0.11	0.15	0.12
$Q^{H'}_{C_{\alpha}H_2}$	0.01	0.12	0.10	0.12
$Q^{C}_{C_{\alpha}H_2}$	−0.06	0.05	−0.08	0.35
$Q^{C}_{C_{\beta}H}$	0.02	0.14	0.33	−0.04
$Q^{H}_{C_{\beta}H}$	0.01	0.10	0.10	0.10
$Q^{C}_{C_{\gamma}H_2}$	0.02	0.00	−0.01	0.03
$Q^{H}_{C_{\gamma}H_2}$	0.00	0.04	0.07	0.03
$Q^{H'}_{C_{\gamma}H_2}$	−0.01	0.06	0.08	0.05
$Q^{C}_{C_{\delta}H_3}$	0.00	−0.01	0.01	−0.02
$Q^{H}_{C_{\delta}H_3}$	0.00	0.04	0.05	0.03
Q_{Kt}	—	−0.73	−0.90	−0.83
$i_{H-C_{\alpha}}\%$	0	−0.6	−5.5	0.1
$i_{H'-C_{\alpha}}$	0	−0.7	−3.2	0.1
$i_{C_{\alpha}-C_{\beta}}$	0	−15.2	−30.4	−29.6
$i_{H-C_{\beta}}$	0	−0.4	0.6	−3.4
$i_{C_{\beta}-C_{\gamma}}$	0	−1.1	5.0	−6.4
$i_{H-C_{\gamma}}$	0	0.1	−0.6	0.2
$i_{H'-C_{\gamma}}$	0	0.3	−0.5	0.5
$i_{C_{\gamma}-C_{\delta}}$	0	−1.0	−4.2	0.3
$i_{H-C_{\delta}}$	0	0.1	0.1	0.0
E^+	—	13.4	≡0	46.5

Essential weakening of the C_{α}–C_{β} bond in the σ_1 complex together with tendencies of strengthening the C_{β}–C_{γ} bond and weakening the H–C_{γ} and H′–C_{γ} bonds are 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 $C_{\beta}{=}C_{\gamma}$. At the same time, noticeable weakening the C_{γ}–C_{δ} bond apparently shows that the corresponding reaction of cracking may take place. Thus, the theoretically obtained picture for the specific activation of chemical bonds in the σ_1 complex does not appear to be in qualitative contradiction to the choice (*I*) of a 2-butyl-carbonium ion as CSC in the proposed reaction scheme (1).

On the contrary, the reverse tendencies of changing the strengths of the C_{β}–C_{γ} and C_{γ}–H bonds in the π-complex indicate that there is no reason to consider this complex as CSC.

As one can see from Table 1, the activation of chemical bonds in the butene molecule due to the addition of a proton to the C_β atom is more favorable for cracking than for isomerization, Hence, it is also unlikely that the σ_2 complex could serve as the model of CSC in the reaction scheme (1).

As a final point it must be emphasized that, in the above calculations, the influence of the catalyst surface on chemical bond energies and charge distributions in complexes was considered negligible in comparison with the proton influence. Such is the case when a proton is much closer to a butene molecule than other surface atoms. However, even in this case, the explicit consideration of the lattice surface is obligatory for reliably predicting the more energy-stable complex. It is especially important when the difference in total energies of free complexes is rather small (cf. relative energies of σ_1 and π structures). At the same time, when the energy difference for free complexes is large enough (cf. σ_1 and σ_2 structures) then the interaction with the surface will probably not reverse the obtained relative order of their stability.

In conclusion, we see that the results of the performed quantum chemical calculations of the electronic structure of the 1-butene molecule coordinated by H^+ confirm the assumption (*1*) that a 2-butyl-carbonium ion is capable of playing the role of a common surface complex via which the isomerization of butenes occurs over silica–alumina.

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