JOURNAL OF CATALYSIS 47, 55–61 (1977)

Quantum Chemical Study of Catalytic Isomerization of Olefins

I. Allylic Intermediate in the Presence of a Base

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Received June 21, 1976; revised November 30, 1976

Semiempirical molecular orbital calculation by CNDO/2 has been carried out to clarify the 1-butene isomerization which takes place in the presence of basic solid catalysts, such as CaO and MgO. The method of calculation was verified by applying it to the rotational barrier of alkanes as well as the relative stability of conformational or geometrical isomers of 1-butene and 2-butene. The calculation predicts that 1-methylallyl anion, a plausible intermediate in base-catalyzed isomerization, is more stable in *anti* (or *cis*) form, while cation is stable in *syn* (or *trans*) form. These results are in agreement with the experimental results that *cis*-2-butene is preferentially formed in base-catalyzed isomerization and *trans* form is favored in the reaction which proceeds via a cationic intermediate. Barrier of rotation about central C–C bond of anion has been calculated to be 40 kcal/mole, while it is much smaller for cation (13 kcal/mole). Cooperation of 1-methylallyl anion with water molecule increases a little the energy difference between *cis* and *trans* form: 1.3 kcal/mole in the presence of water and 0.9 kcal in its absence. Involvement of a lithium ion into the system makes this difference larger. Mechanism of base-catalyzed isomerization is discussed in the light of these calculations.

INTRODUCTION

1-Butene isomerization to 2-butene has been studied as a model reaction to classify catalysts, to compare the activity, and to elucidate the mechanism of olefin isomerization (*1*). The *cis*/*trans* ratio of 2-butene formed varies from a few to more than 10, depending on the kind of catalysts (*1*). Over basic solid catalysts, *cis*-2-butene usually predominates (*1*b). Also, in the base-catalyzed isomerization of 1-olefin in liquid phase, the *cis*/*trans* ratio is at least 10, although the rate depends on the catalyst and solvent (*2*). It has recently been reported that hydrogenation of butadiene over MgO results in predominant formation of *cis*-2-butene probably via an allyl intermediate (*3*). In the light of these facts it is reasonably assumed that in the reaction, which proceeds via an 1-alkylallyl anion, *cis*-2-olefin is formed in excess, because of the higher stability of *anti* (or *cis*) form than *syn* (or *trans*) form. On the other hand, it was suggested that *trans* form is more stable in the case of cation (*4*). It has been attempted in this work to examine this phenomenon from a quantum chemical viewpoint. Quantum chemical study has been little applied to the heterogeneous acid–base catalysis, although a few works have been reported for metal catalysts (*5*).

RESULTS AND DISCUSSION

Method of Calculation and Its Examination

CNDO/2 with original parameterization is used. Test calculations gave essentially

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ISSN 0021-9517

TABLE 1

Barriers of Rotation and Relative Stability for Several Hydrocarbons

Molecule	Energy (kcal/mole)		Remarks
	Calcd (CNDO/2)	Exptl	
n-Butane	4.29	6.5[a]	*gauche–gauche* barrier
	2.46	3.6[b]	*trans–gauche* barrier
	0.30	0.8[c]	*trans–gauche* difference
Ethane	2.20	2.9[d]	*gauche–gauche* barrier
1-Butene[g]	0.38	1.74[e]	*cis–trans* difference
	2.26	0.15[e]	*cis–skew* difference
2-Butene[h]	0.50	1.1[f]	*cis–trans* difference

[a,b,c,d,e,f] See Ref. *8*a, b, c, d, e, and f, respectively.

[g] The stability decreases in the order of *skew* > *cis* > *trans*.

[h] *Trans* is more stable than *cis* form.

the same results as was reported by Pople and Beveridge (*6*). In order to examine the interatomic interactions, energy was partitioned according to the literature (*7*). Two-center terms are divided into five parts:

$$E_{\mathrm{AB}}{}^{v} = -P_{\mathrm{A}}V_{\mathrm{AB}} - P_{\mathrm{B}}V_{\mathrm{BA}},$$

$$E_{\mathrm{AB}}{}^{c} = 2\sum_{\mu\in\mathrm{A}}\sum_{\nu\in\mathrm{B}} P_{\mu\nu}\cdot S_{\mu\nu}\cdot\beta_{\mu\nu},$$

$$E_{\mathrm{AB}}{}^{j} = P_{\mathrm{A}}P_{\mathrm{B}}\cdot\gamma_{\mathrm{AB}},$$

$$E_{\mathrm{AB}}{}^{k} = -\tfrac{1}{2}\gamma_{\mathrm{AB}}\sum_{\mu\in\mathrm{A}}\sum_{\nu\in\mathrm{B}} P_{\mu\nu}{}^{2},$$

$$E_{\mathrm{AB}}{}^{n} = Z_{\mathrm{A}}Z_{\mathrm{B}}/R_{\mathrm{AB}}.$$

$E_{\mathrm{AB}}{}^{v}$ is the sum of the potential energy of the electrons on atom A in the field of nucleus B and that of the electrons on atom B in the field of nucleus A. $E_{\mathrm{AB}}{}^{c}$, which is called covalent energy, is the contribution of the resonance integrals to the energy of the A–B bond. $P_{\mu\nu}$ is the charge density and bond-order matrix, $S_{\mu\nu}$ being the overlap integral between atomic orbitals μ and ν. $E_{\mathrm{AB}}{}^{j}$ is the repulsion of the electrons on the atoms A and B. $E_{\mathrm{AB}}{}^{k}$ corresponds to electronic exchange interaction, and $E_{\mathrm{AB}}{}^{n}$ represents nuclear repulsion energy. Sum of E^{v}, E^{j}, and E^{n} expresses the electrostatic interaction (E^{elec}).

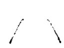
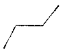
The validity of CNDO method was checked particularly for the application to the relative stability of conformational or geometric isomers of hydrocarbons. Table 1 shows that barriers of rotation as well as the relative stabilities can be estimated correctly. Relative stability of three conformers of 1-butene was correctly predicted by calculation, although the calculated *skew–cis* energy difference is too large. Energies of interaction between two terminal methyls or methyl-methylene expressed in two-center terms are collected in Table 2. It is remarked that covalent energies of 1-butene and *n*-butane become lower when two groups face with each other. This is in contrast to the case of 2-butene where *trans*-2-butene is slightly more stable as for the covalent energy.

TABLE 2

Energies in Two-Center Terms for Terminal CH_3---CH_2 or CH_3---CH_3 Interaction (kcal/mole)

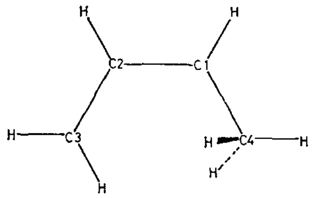
Molecule		E^{c}	E^{k}	E^{elec}
1-Butene[a]	*cis*	−3.046	−0.616	3.822
	trans	−1.398	−0.404	−0.182
2-Butene	*cis*	−1.233	−0.707	2.967
	trans	−1.712	−0.776	0.101
n-Butane[b]	*cis*	−6.453	−1.021	6.694
	trans	−1.379	−0.478	0.007

[a]  (*cis*) and  (*trans*).

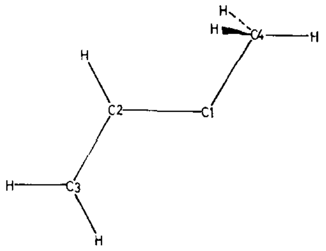
[b]  (*cis*) and  (*trans*).

1-Methylallyl Ions

Removal of a hydrogen atom from the carbon in allyl position produces 1-methylallyl ion. The geometry predicted by *ab initio* calculation was used in the present calculation (*9*). Angle of methyl rotation is important in *cis* form, so that it was chosen so as to make the *cis* anion most stable. Allyl ions, whose C2–C3 and C1–C2 bond distances are 1.34 and 1.53 Å, respectively, and whose bond angles are characteristic of the parent hydrocarbon, were calculated in some cases for comparison (called hereafter a "classical" ion). In Fig. 1, the total energy is plotted against the rotational angle about C1–C2 bond for anion and cation. A high barrier of rotation is found for anion. This barrier may be lowered to some extent by changing the structure to a "classical" one (curve 1). As for the *cis* and *trans* forms, *cis* form is more stable in the case of anion, although the difference is small (0.9 kcal/mole). On the other hand, *trans* cation is found to be more stable than *cis* isomer by 4 kcal/mole.



ANTI (CIS) FORM



SYN (TRANS) FORM

The reason why the stable form of 1-methylallyl is reversed from anion to cation is considered in the rest of this section. Table 3 shows the interaction energy between terminal CH_3 and CH_2, which is divided into E^c, E^k, and E^{elec}. The electrostatic energy, E^{elec}, makes the *cis* form less stable both for anion and cation, while it is less repulsive for *cis* anion than *cis* cation. Differences of E^{elec} between *cis* and *trans* are 3.0 kcal (anion) and 4.6 kcal (cation), difference of these differences being 1.6 kcal. On the other hand, the covalent energy, E^c, favors *cis* form for anion by 0.4 kcal and *trans* form for cation by 4.8 kcal, in conformity with the trend found in the total energy calculated. Difference in differences for the covalent energies is 5.2 kcal = 4.8 − (−0.4). Therefore, it may be interesting to examine the covalent energy in more detail.

The covalent interaction between terminal CH_3 and CH_2 is split into four components in Table 4: (i) C3- - -C4, (ii) C3- - -H4, (iii) C4- - -H3, and (iv) H3- - -H4, where H3 and H4 denote hydrogen atoms attached to C3 and C4, respectively. The contribution of the last component is omitted, since it is negligible. Regardless of the number of electrons, the

TABLE 3

Energies in Two-Center Terms for CH_3- - -CH_2 Interaction in 1-Methylallyl Ions (kcal/mole)

Molecule	E^c	E^k	E^{elec}	Total energy[a]
Anion *cis*	−1.986	−1.923	9.449	
trans	−1.584	−1.418	6.495	0.9
cation *cis*	3.603	−2.884	10.821	
trans	−1.160	−2.385	6.225	−4.0
Cis anion + H_2O	−1.820	−1.680	9.800	
Trans anion + H_2O	−1.570	−1.240	6.600	1.3

[a] Difference in total energy: energy of *trans* form minus energy of *cis* form.

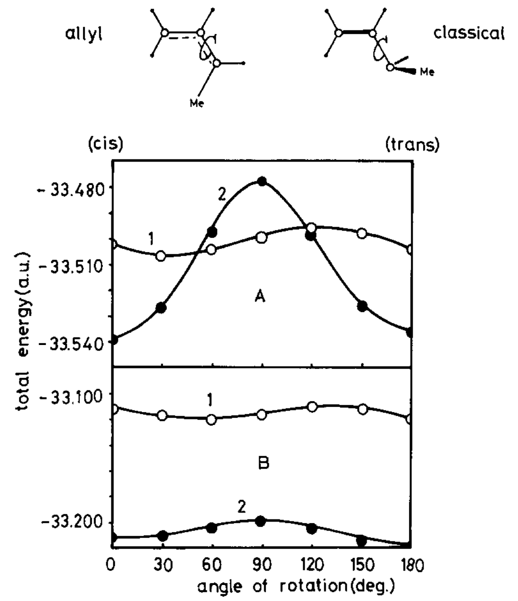


FIG. 1. Total energy of 1-methylallyl ions plotted against the angle of rotation about C1–C2 bond. (A) Anion; (B) cation; (1) classical; (2) allyl.

C3---C4 interaction (i) is repulsive in *cis* form in contrast to *trans*. The interaction (ii) is significantly repulsive for cations, while this is attractive for anions. As for the interaction (iii), little difference is found between cation and anion. It is attractive for all cases, but smaller for *trans* isomer. Thus, *cis* anion is more stable than *trans* anion, because of the attractive C3---H4 and C4---H3 interactions [(ii) and (iii)]. On the other hand, *cis* cation is less stable than *trans*, since repulsive C3---H4 interaction (ii) exists in addition to C3---C4 repulsion (i).

Following the Mulliken's population analysis, we can scrutinize the $P_{\mu\nu} \cdot S_{\mu\nu}$ terms. The C4---H3 interaction (iii) results from the attractive mixing of 1*s* of H3 and 2*s*, $2p_x$, $2p_y$ of C4, which is always greater for *cis* form owing to larger overlapping. The C3---H4 interaction exhibits distinct difference between *cis* anion and *cis* cation; $P_{\mu\nu} \cdot S_{\mu\nu}$ is positive for anion, but negative for cation. The signs of orbitals of p_z(C3) and pseudo *p* orbital of CH_3 in the highest occupied molecular orbital (HOMO) match in the case of anion, but they are opposite in HOMO of cation (Fig. 2). This interaction becomes stronger in *cis* form because of the shorter distance, so that *cis* anion and *trans* cation are the more stable forms. This explanation essentially agrees with that given qualitatively by Hoffmann and Olson (*10*).

The methyl-substituted allyl anion is conformationally more stable than cation (Fig. 1). This fact could be attributed to a small contribution of $2p_z$(C2) of the same sign as $2p_z$(C1) in HOMO which reinforces the C1–C2 bond of anion. Similarly, lower barrier of rotation in a "classical" anion can be explained as $2p_z$ at C2 in HOMO bears opposite sign to the adjacent $2p_z$ atomic orbitals.

1-Butene and 1-Methylallyl Anion in the Presence of Basic Center on the Surface of Solid Catalysts

In the first step of the isomerization of 1-butene, a basic center attracts a proton from allyl position to make C–H bond looser. The basic center on the surface of basic catalysts was represented by OH^- group located 2 Å below allyl plane. Calculations for various positions of OH^-, as well as for various angles of rotation about C1–C2 axis, were carried out, keeping O–H bond perpendicular to butene plane. The results indicated that shorter H(allyl posi-

TABLE 4

Components of Covalent Energy for Terminal CH_3---CH_2 Interaction in 1-Methylallyl Ions[a]

$E^c{}_{AB}$ (kcal/mole)	Cation		Anion	
	cis	*trans*	*cis*	*trans*
(i) $E^c{}_{C3,C4}$	3.84	−1.37	2.19	−1.39
(ii) $E^c{}_{C3,H4}$	3.04	0.13	−1.89	−0.17
(iii) $E^c{}_{C4,H3}$	−2.35	−0.01	−1.85	−0.03

[a] $E^c{}_{C3,C4}$, etc., are the covalent interaction energies between C3 and C4, etc. H3 and H4 denote the hydrogen atoms attached to C3 and C4, respectively.

tion)---OH distance makes the system more stable. In the next step, a methyl-substituted allyl anion (*cis* or *trans*) was placed close to a water molecule, which may be formed by a proton transfer from butene to OH^-. Projection of the allyl is shown in Fig. 3. Oxygen atom of water is placed 2 Å below the allyl with one hydrogen (H_A) of water oriented downward, while the second (H_B) is directed toward terminal sp^2 carbon. The results show that negatively charged oxygen interacts attractively with positive C2, but repulsively with negative terminal C3 (see Fig. 4), so that the system becomes most stable when the oxygen is located exactly below C2. For such location of basic catalyst center, *cis*-1-methylallyl anion is 1.3 kcal/mole more stable than *trans* isomer, energy difference being a little larger than that in the gas phase (0.9 kcal/mole). Hydrogen (H_B) connected to oxygen, which can be regarded as an atom attacking C3 to form 2-butene, interacts attractively with C3. Terminal methyl group interacts with oxygen repulsively, but there is no difference in this energy between *cis* and *trans* forms. The methyl–methylene interaction energies divided into E^c, E^k, and E^{elec} are given in Table 3. The covalent methyl–methylene interaction is more attractive for *cis* anion than for *trans* isomer. This result is essentially the same as that in the gas phase. Slightly enhanced stability of *cis* form results from changes in various kinds of interactions among atoms.

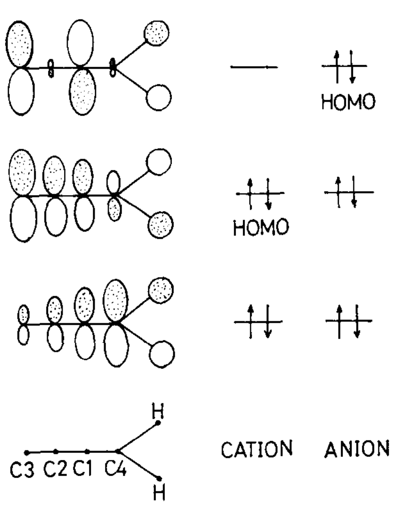


FIG. 2. Molecular orbitals of 1-methylallyl ions near the highest occupied orbital.

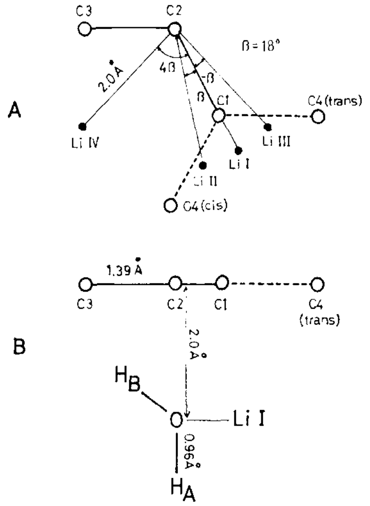


FIG. 3. The projection of the system consisting of a 1-methylallyl ion, a water molecule, and a lithium ion at various positions. (A) Top view; (B) front view.

Therefore, it seems acceptable to state that the *cis* transition state is preferred both in the gas phase and in the presence of a basic catalyst center, as speculated from the experimental results. Although several other factors characteristic of the solid surface, e.g., the effects of metal ion and surface geometry, may also affect the selectivity, difference of 1.3 kcal/mole found between *cis*- and *trans*-1-methylallyl anion is sufficient to make the *cis*/*trans* ratio about $10[= \exp(1.3/RT)]$ at room temperature.

The basic properties of typical basic catalysts, such as MgO, CaO, BaO, and hydroxides like LiOH and NaOH, may be associated with lattice oxygen bearing negative charge. A hydroxyl anion is the simplest model of a basic catalyst center containing oxygen. As a more advanced model, lithium hydroxide was examined. A lithium ion was added to the system calculated above, the ion being placed 2 Å from oxygen. Li–O–H_A

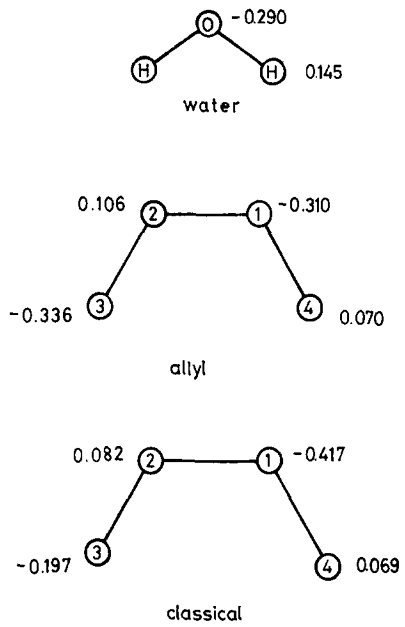


FIG. 4. Charge distribution in the water molecule and two forms of 1-methyallyl anion.

angle was fixed at 90° as has been found by CNDO to be the most stable geometry (Fig. 3). The energies for a few positions of Li tested are shown in Fig. 5. *Cis–trans* energy difference becomes 2.2 kcal/mole for the most stable hypothetical geometries (Li II for *cis* and Li I for *trans* in Fig. 3). The stability of the system mainly depends on the distance between lithium and carbons. Increase in energy for Li IV position results from the decrease in the interactions of Li- - -C1 and C4, which are only partially compensated by the increase in Li- - -C3 attraction. Examination of the charge distribution indicates that metal collects to some extent electrons which are originally carried by hydrocarbon. These results indicate that attractive interactions of methylallyl with metal ion is also very important in olefin isomerization, in addition to the interaction with basic centers.

SUMMARY

Among the main problems in catalysis are the elucidation of the interaction between molecules and active centers and to find out what is the essential factors determining the catalytic activity and selectivity. In this work it has been attempted by use of quantum chemistry to elucidate the selectivity in a simple catalytic process, viz, isomerization of olefin. The results obtained are in satisfactory agreement with experimental data. The calculation shows that 1-methylallyl anion is more stable in *cis* form and that the stability is even enhanced in the presence of a basic catalyst. It was also demonstrated that higher stability in *cis* anion is mainly due to the attractive covalent interaction between terminal C3 and H of CH_3 (Fig. 2).

The choice of model is very important and it is always a problem how far the model is valid. In base-catalyzed isomerization in liquid phase, OR^- is the active species (R = alkyl) (*2*). Therefore, it may be reasonable to accept hydroxyl anion as a simple model of a base. Similar basic centers may be found on solid surface, e.g., oxide ion exposed on the surface. The results when lithium is incorporated into the model suggest that attractive cooperation between metal ion and hydrocarbon is also important. Although the models adopted in the present calculations are rather simple, they seem to simulate quite well the actual reaction which takes place in base-catalyzed olefin isomerization.

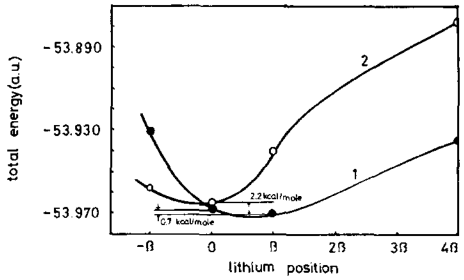


FIG. 5. Total energies of 1-methylallyl–H–LiOH systems for various Li positions. (1) *cis* form; (2) *trans* form.

ACKNOWLEDGMENT

The authors express their gratitude to Dr. T. Okada for his valuable suggestions. One of us (W.G.) gratefully acknowledges the financial support from the Japan Society for the Promotion of Science.

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