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Fragmentation and Isomerization of 1,2-Dimethylcyclobutane

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The potential surface of 1,2-dimethylcyclobutane is investigated with respect to fragmentation and isomerization by the semiempirical MO method SINDO1. Energy and geometry of eight transition states and four intermediates are determined for the nonconcerted fragmentations under optimization of all internal coordinates. We find that symmetric cleavage of *cis*-dimethylcyclobutane is the most favored process leading to fragmentation. Whereas the symmetric elimination involves two different barrier heights, the asymmetric elimination involves only two equal barrier heights. The possibility of isomerization of *cis*- to *trans*-dimethylcyclobutane was also studied and revealed two different barrier heights lower than the corresponding heights for fragmentation.

Key words: Fragmentation and isomerization of 1,2-dimethylcyclobutane.

1. Introduction

The semiempirical method SINDO1 [1] was developed to study chemical reaction surfaces. In two previous investigations [2, 3] the method was used for elimination reactions involving unsubstituted and substituted four- to seven-membered ring systems. In particular, we were successful in locating small minima of a few kcal/mol on the potential surfaces which may be passed during fragmentation processes. The question of experimental significance of such potential wells as chemically interceptable intermediates was raised.

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In this article we describe the investigation of 1,2-dimethylcyclobutane. Our incentive stems from experimental work of Chickos and Wang [4] on the thermolysis of this compound. These authors determined rate constants in deuterated compounds. Our calculations are not directly comparable since they cannot account for deuteration. So our comparison is taken with the early work of Gerberich and Walters [5], who determined rate constants and activation energies for fragmentation and isomerization of 1,2-dimethylcyclobutane. In this case the reduced symmetry of the cyclobutane ring gives rise to a large number of transition states. Chickos and Wang also conclude the presence of intermediates of diradical nature for the various fragmentation possibilities. In the next section, we present semiempirical MO studies which are basically in agreement with the experimental findings of Chickos and Wang. In particular we substantiate the conclusion that the fragmentation reaction is non-concerted and takes place most likely via breaking of the CC bond between the methyl substituted C atoms.

2. Results and Discussion

We first calculated binding energy and geometry of reactants cis-1,2-dimethylcyclobutane (0 kcal/mol) and *trans*-1,2-dimethylcyclobutane (3.4 kcal/mol) with SINDO1. The relevant lengths and angles are defined in Fig. 1. Breaking of the bonds related to r_4 and r_2 leads to two propene molecules which are 9.5 kcal/mol higher in energy than *cis*-1,2-dimethylcyclobutane. We call this the symmetric fragmentation. Alternatively, bonds related to r_1 and r_3 lead to the asymmetric fragmentation into *cis*-butene and ethylene (11.5 kcal/mol) or *trans*-butene and ethylene (10.7 kcal/mol). So the thermodynamic control of fragmentation would favor the symmetric process leading to two propenes. This way of fragmentation

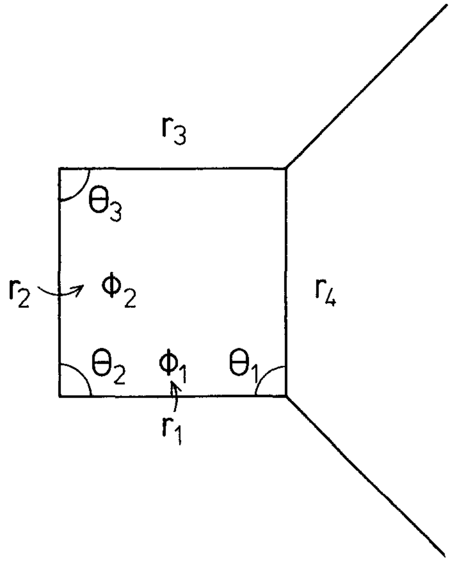

Fig. 1. Labeling of lengths and angles of 1,2-dimethylcyclobutane

is also favored by consideration of a static index like the bond orders of the four CC bonds of 1,2-dimethylcyclobutane in the ground state. Bond orders are calculated with our maximum bond order principle [6] under consideration of the projection criterion for bonding and antibonding [7]. The bond order of r_4 is 1.07–1.08 and smaller than either r_2 with 1.14–1.15 or r_1 and r_3 which are both 1.11. The comparison of bond orders would suggest an initial breaking of the bond between the methyl substituted C atoms. It is essential now to realize that the thermodynamic control is only part of the process of fragmentation. The kinetic control is given by the various activation energies. Thus, in general, consideration of the bond orders of ground state is insufficient. We therefore determined in 4×4 CI calculations including the lowest doubly and the two lowest singly excited configuration the energies of transition states leading towards fragmentation under optimization of all internal coordinates. A collection of the various possibilities is shown in Fig. 2. We find that the fragmentation process is a two-step reaction in all four directions. The initial transition states T_1 and T_2 from *cis*- and *trans*-dimethylcyclobutane favor both the opening of the bond between the methyl substituted C atoms. The lowest barrier of 41 kcal/mol is from the *cis*-compound. Initial breaking of an adjacent CC bond leads to transition states T_5 and T_6 which are higher in energy by more than 20 kcal/mol than either T_1 or T_2. All these transition states can be stabilized to intermediates I_1, I_2, I_3, I_4. However, we find the well depth of these minima between 0.3 and 1.4 kcal/mol, too small to be proved or disproved by present experimental techniques. In the symmetric fragmentation case an additional

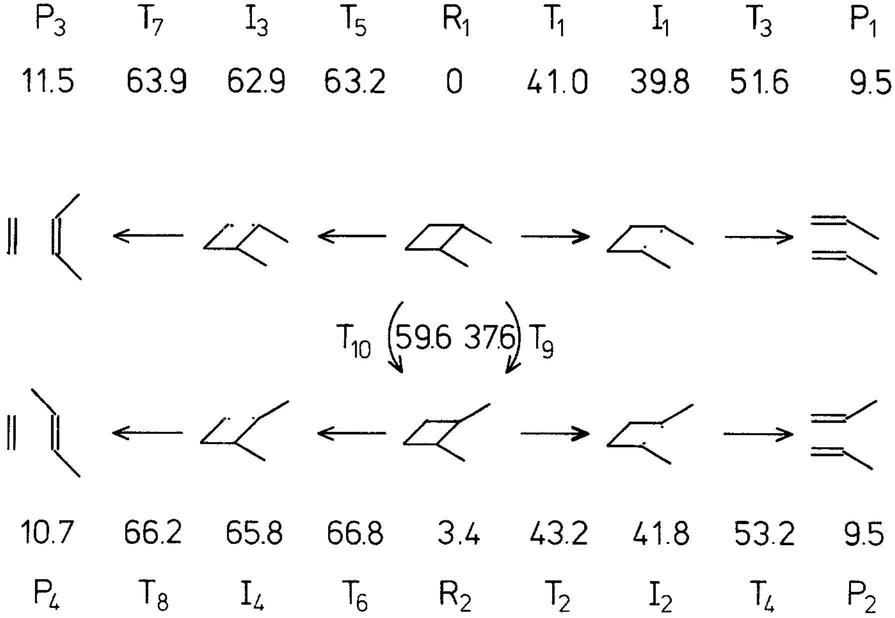

Fig. 2. Relative energies (kcal/mol) of 1,2-dimethylcyclobutane and its transition states and intermediates for fragmentation and isomerization

10 kcal/mol has to be overcome to fracture the second CC bond given by r_2. T_3 has the lowest barrier of 51.6 kcal/mol for this process which is again obtained from the *cis*-compound compared to 53.2 kcal/mol of T_4 from the *trans*-compound. The asymmetric fragmentation proceeds from I_3 and I_4 with practically no further barrier. This surprising result implies that fragmentation of one stronger ring bond, e.g. that one related to r_3, weakens the opposite bond substantially. Calculated bond orders support this. The bond order for the remaining CC bond in T_1 (1.01) and T_2 (1.04) is much higher than corresponding bond order in T_5 (0.93) and T_6 (0.92). The overall reaction shows that the symmetric fragmentation is about 12 kcal/mol lower than the asymmetric fragmentation. This result is qualitatively in agreement with the findings of Chickos and Wang [4].

There is, however, a difference in concept from the above authors as far as the isomerization is concerned. Chickos and Wang describe the isomerization as occurring between intermediates I_1 and I_2 or I_3 and I_4. We feel that this concept is rather arbitrary. Isomerization from cis to trans can take place by breaking a bond described by r_4 or r_3. We call the former transition state T_9 and the latter T_{10}. A synchronous or sequential rotation of the CH_2 groups must be involved. The two transition states show an activation energy of 37.6 kcal/mol and 59.6 kcal/mol which is lower than the corresponding intermediates for fragmentation. Transition states between I_1 and I_2 or I_3 and I_4 must have an energy which is higher than the higher one of each pair. This means that isomerization takes place more likely without recourse to intermediates. Gerberich and Walters [5] studied the thermal decomposition of *cis*-1,2-dimethylcyclobutane in the pressure region 5.8–393 mm at 420°C and over the temperature range 380–430°C for pressures near 15 mm. For *trans*-1,2-dimethylcyclobutane the pressure was varied from 13–375 mm at 430°C and the temperature from 390°–440°C at 15–19 mm pressure. They find activation energies of 60.4 kcal/mol for the symmetric cleavage of the *cis*-compound and 61.6 kcal/mol of the *trans*-compound. The asymmetric cleavage of the *cis*-compound has an activation energy of 63.0 kcal/mol compared to 63.4 kcal/mol for the *trans*-compound. The activation energy for *cis-trans* isomerization was found to be 60.1 kcal/mol versus 61.3 kcal/mol for the reverse reaction. The statistical errors are 0.5 and 0.9 kcal/mol for these reactions and could reverse the relative stability. The experimental differences between the various possibilities of reactions do not exceed 3.3 kcal/mol. Our agreement with these data is only qualitative – namely that asymmetric cleavage is less favorable than the symmetric cleavage.

Quantitatively we obtain a split of activation energies for the two different cleavages of 12.2 kcal/mol which is much higher than the experimental value of 2.6 kcal/mol. There is also qualitative agreement that the activation energy for *cis-trans* isomerization is lower than the activation energy for fragmentation. This is no contradiction to the fact that the rate of fragmentation is higher than the rate of isomerization [4, 5]. The entropy which determines the preexponential factor of the rate is larger for the fragmentation through its translational contribution, since a vibrational mode is converted to a translational mode when the second CC bond breaks. This implies a lowering of the free energy of the transition state for fragmentation compared to the transition state for isomerization.

A detailed collection of the important internal coordinates (Fig. 1) is given in Table 1. From these data we gather that all intermediates are obtained by twisting about r_2 or r_1. The dihedral angle for the transition states T_1, T_2, T_5, T_6 is between 130° and 120°. All intermediates I_1, I_2, I_3, I_4 have a dihedral angle of 180°. They are of *trans* type with respect to the remaining CC bond. In these reactions we were unable to find the *gauche* intermediate of the unsubstituted case [2]. Whereas the determination of dihedral angles ϕ_1 or ϕ_2 is rather easy for the early transition states T_1, T_2, T_5, T_6, the potential surface is rather flat in the region where the second CC bonds are broken. So the late transition states T_3, T_4, T_7, T_8 do not vary by more than 1 kcal/mol upon twisting from *trans* to *gauche*. The *gauche* alternative to the *trans* type transition state T_3, T_4, T_7, T_8 we have called T'_3, T'_4, T'_7, T'_8. Since the late transition states T_3, T_4, T_7, T_8 show the higher barriers compared to the early transition states T_1, T_2, T_5, T_6 we conclude that a distinction between *trans* and *gauche* forms has little consequences for the fragmentation.

Table 1. Relative total energies E (kcal/mol) and singlet-triplet splitting energies $E_T - E_S$ (kcal/mol) and internal coordinates (A, degrees) of reactants, transition-states, intermediates and products of 1,2-dimethylcyclobutane fragmentation and isomerization

State	E	E_T–E_S	r_1	r_2	r_3	θ_1	θ_2	θ_3	ϕ_1	ϕ_2
R_1	0	—	1.585	1.565	1.585	89.2	90.8	90.8	0	0
R_2	3.4	—	1.584	1.554	1.584	89.2	90.8	90.8	0	0
T_1	41.0	1.4	1.520	1.552	1.520	—	114.2	114.2	—	130
T_2	43.2	1.0	1.533	1.534	1.524	—	116.3	114.4	—	130
I_1	39.8	1.4	1.519	1.552	1.519	—	114.2	114.2	—	180
I_2	41.8	1.0	1.533	1.534	1.524	—	116.3	114.4	—	180
T_3	51.6	26.1	1.418	1.85	1.418	—	112.5	113.2	—	180
T'_3	52.0	23.7	1.418	1.85	1.418	—	112.5	113.2	—	68
T_4	53.2	22.5	1.428	1.85	1.427	—	114.3	112.2	—	180
T'_4	53.4	21.8	1.428	1.85	1.427	—	114.3	112.2	—	80
P_1	9.5	—	—	—	—	—	—	—	—	—
P_2	9.5	—	—	—	—	—	—	—	—	—
					r_4					
T_5	63.2	1.9	1.592	1.477	1.547	109.4	114.4	—	120	—
T_6	66.8	2.7	1.601	1.472	1.537	111.3	114.8	—	120	—
I_3	62.9	2.3	1.592	1.477	1.547	109.4	114.4	—	180	—
I_4	65.8	3.0	1.601	1.472	1.537	111.3	114.8	—	180	—
T_7	63.9	21.0	1.80	1.401	1.456	109.1	114.3	—	180	—
T'_7	64.9	21.5	1.80	1.401	1.456	109.1	114.3	—	70	—
T_8	66.2	22.9	1.80	1.394	1.445	109.5	113.8	—	180	—
T'_8	66.6	21.8	1.80	1.394	1.445	109.5	113.8	—	73	—
P_3	11.5	—	—	—	—	—	—	—	—	—
P_4	10.7	—	—	—	—	—	—	—	—	—
T_9	37.6	−0.1	1.524	1.545	1.536	—	121.6	116.8	19.5	—
T_{10}	59.6	0.4	1.554	1.501	1.552	112.4	114.4	—	50.0	—

We finally address ourselves to the question of diradical character during the reaction. In all cases included for fragmentation, the singlet state is lower than the triplet state by at least 1 kcal/mol. Early transition states and intermediates come close to quasi degeneracy of singlet and triplet, i.e. are close to diradicals. The late transition states have practically no diradical character. In contrast, the isomerization process passing through T_9 or T_{10} does involve diradicals. T_9 is the only case where the triplet is slightly lower (0.1 kcal/mol) than the singlet.

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