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Mechanism of Cyclopropane–Propene Isomerization

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A SINDO method was used to investigate the sequence of rearrangements in the cyclopropane–propene isomerization. Geometries of reactant and product were optimized for a complete set of 21 independent internal coordinates. Then the bond angle of the migrating H atom was chosen as reaction coordinate and all other geometrical parameters were energy minimized along this reaction coordinate. In the neighborhood of the transition state a Newton type iteration process is initiated to locate the transition state. The latter is characterized by a CCC bond angle close to 90° and an almost finished migration of the H atom. The activation energy was found about 25% lower than the experimental value of 65 kcal/mole. A sequence of rearrangements was established, suggesting the initiation of the reaction by a combination of two normal modes: a torsional vibration of the methylene groups together with an asymmetric stretch of the carbon framework. Our calculations classify the reaction as concerted.

Key words: Cyclopropane–propene isomerization

1. Introduction

The cyclopropane–propene isomerization has been the subject of numerous experimental investigations [1]. Although all agree in the fact that the activation energy is rather high, which would place it in the category of “forbidden” reaction in the Woodward-Hoffmann terminology [2], surprisingly little is known about its mechanism. This was an incentive for us to attack the following catalogue of questions: 1) Is the reaction concerted or non-concerted, 2) are the rearrangements simultaneous or sequential, 3) what is the sequence of rearrangements? The detailed information in the last question involves ring opening and CC bond breaking, CH_2 group rotation and migration of an H atom. Among the possibilities for a sequential order two alternatives are particularly noteworthy: Does the CC bond breaking occur completely before the CH_2 rotation sets in freely or does the CC bond only loosen so that free rotation of the CH_2 is hindered?

We try to provide answers to these questions by means of semiempirical molecular orbital theory. The approach used for the calculations will be described in the next section.

2. Method

Recently we developed a scheme for semiempirical extended Hartree-Fock theory based on symmetrically orthogonalized atomic orbitals [3]. The various levels we label in the following manner, SCNDO, SINDO etc., where the S indicates the symmetrical orthogonalization. The essential difference to Pople's methods [4] occurs in the bonding parameter β. The approximate form of this parameter was derived via commutator equations. The parametrization was implemented on the SINDO level [5]. The consistency of the derivation avoids the pitfalls of the original ZDO methods by Pople as was demonstrated in test calculations for bonding energies of a large number of diatomics [5].

Since then various chemical reactions [6, 7] were investigated successfully. Some of the technical problems encountered in these investigations were based on the inefficiency in handling large amounts of input data to proceed in various directions on the multidimensional potential surface and the difficulty in locating transition states. In the meantime we have developed a Newton-type iteration procedure which makes use of the first and second derivates of the energy at each point of the surface. The method calculates the wavefunction at reference points and uses the results of the initial run as input for neighbor points given by small increments in all possible directions of energy hypersurface. The magnitude of these increments was determined to be practical for bond lengths in the order of 0.0001 Å and bond angles in the order of 0.01°. It is to be emphasized that the accuracy of the SCF iteration for arbitrary points on the surface has, in general, to be much higher than for equilibrium calculations. The energy has to be consistently iterated up to 10^{-9} to 10^{-10} a.u. The reason is that this difference scheme needs the accuracy for the second derivative which in turn determines the curvature and locates the transition state by diagonalization of the force constant matrix. After much of the method had been implemented we discovered that the basic idea has been developed a decade ago in a different context by mathematicians [8] and that McIver and Kormonicki [9] and Dewar and collaborators [10] have applied such schemes along similar lines. We differ from Dewar in that we vary in the calculation of the derivatives the density matrix, too. The second derivative is quite susceptible to changes in the density matrix, whereas the first-order derivative, according to the Hellmann-Feynman theorem, should not be. In the following section details of the calculation and a discussion will be presented.

3. Results and Discussion

First the geometries of cyclopropane and propene were optimized (Fig. 1). The bond lengths are too long by 10%, which is to be expected for semiempirical methods on this level [5]. On the SCF level cyclopropane was found more stable than propene by 5.2 kcal/mole whereas the experimental data stabilize propene by 7.8 kcal/mole. A subsequent limited CI calculation for reactant and product resulted in the correct ordering with propene more stable by 3.5 kcal/mole. The dipole moment of propene was at 0.17D, close to the experimental value of 0.35D. Since we do not expect any qualitative changes in the various results to be reported and for the sake of computer time saving, we kept the calculations on the SCF level. CI was used only to determine whether there would be diradical character at the transition state.

We then selected from the total of 21 independent internal coordinates, consisting of 8 bond lengths, 7 bond angles and 6 dihedral angles, a reaction coordinate. The energy was minimized for all other 20 coordinates along this pathway. First we tried the bond angle ϑ_1 describing the ring opening (Fig. 2A). But with this coordinate it was impossible to convert cyclopropane to propene or vice versa. The difficulty was in the fact that the H atom, which was supposed to migrate, stayed at the H atom where it was initially placed. In order

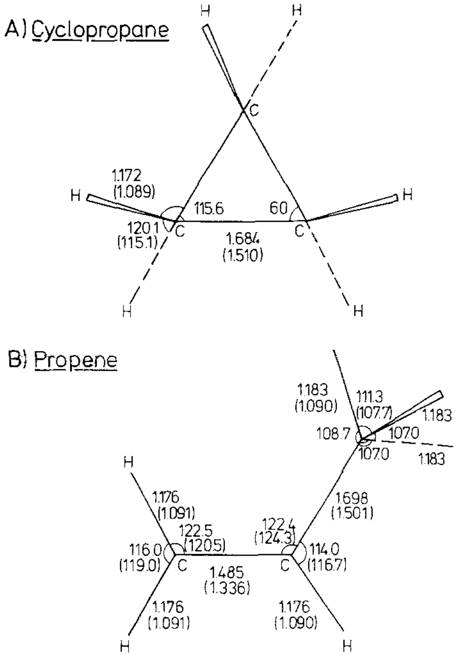

Fig. 1. Equilibrium geometries of cyclopropane (A) and propene (B) with bond lengths in Angstrom and bond angles in degrees; experimental values in parentheses

to correct this deficiency and to enforce the reaction we chose the bond angle ϑ_5 of one of the H atoms opposite the CC bond which was to be broken as the reaction coordinate. We then minimized the energy with respect to all other coordinates. This resulted in two regions, one in which the distorted cyclopropane was more stable and another in which the distorted propene was more stable. So we were again left with the problem of how to convert cyclopropane to propene. To achieve this we checked the cyclopropane path for a negative eigenvalue of the second-order derivatives of the energy with respect to the coordinates. After locating such a point, we then searched with a Newton-type iteration for the transition state by following the path of minimal curvature. We found the transition state as a saddle point on the potential surface. The direction which leads to the maximum is attributed primarily to bond angle ϑ_1 describing the ring opening with some admixture of dihedral angle, φ_1 describing the rotation of $C_1H_4H_5$, and dihedral angle φ_3 describing the rotation of C_2H_6. The geometry of the transition state is given in Fig. 2B. It is characterized by a ring opening angle of 86° and an advanced migration of the H atom. The set of parameters is given in Table 1.

The energy profile of the reaction is illustrated in Fig. 3. We find an activation energy of 48 kcal/mole compared to 65 kcal/mole experimentally [11]. A limited CI calculation did not lower the barrier appreciably (2 kcal). The dashed lines characterize the minimal pathway starting from reactant or product. It is obvious that these lead to dead-end streets on the reaction surface. This again draws attention to the two-valley structure of forbidden reactions advocated by Dewar [12]. To get from one valley to the other the pathway of minimal energy has to be given up in favor of the pathway of minimal curvature.

The motion of methylene groups can be traced from Fig. 4. The dihedral angles φ_1, φ_2 describe the behavior of the outer methylene group belonging to the double bond in propene, φ_3, φ_4 describe the second, φ_5, φ_6 the third methylene group. The absolute change of φ_1 and $-\varphi_2$ indicates the extent of bending, whereas the relative change of φ_1,

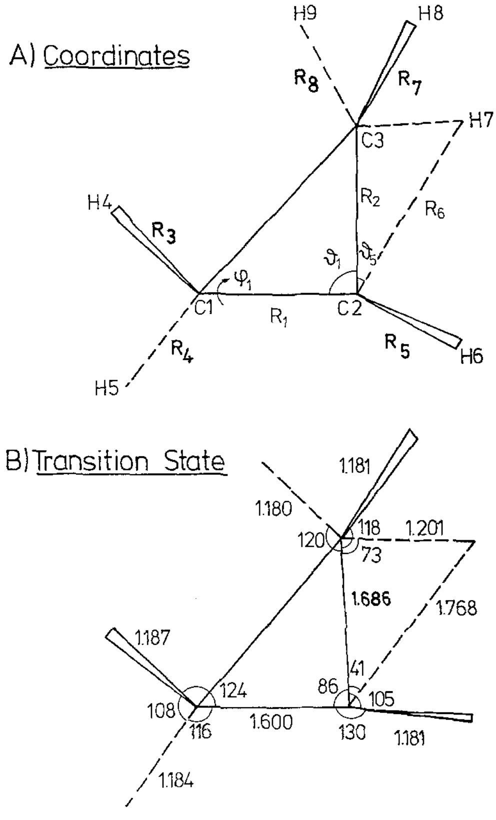

Fig. 2. Labelling of atoms and coordinates (R bond lengths, ϑ bond angles, φ dihedral angles) (A) and geometry of transition state (B)

$-\varphi_2$ indicates the extent of rotation. The same holds for the other two pairs of dihedral angles. Slight bending of the three groups is followed by a rotation of the outer two methylene groups starting between 60°-70° of the reaction coordinate ϑ_5. At the transition state T most of the rotation of these two groups has taken place, whereas the bending of the middle methylene group continues. The rotation of this latter methylene group sets in shortly after the transition state. The orbital energy diagram (Fig. 5) shows a maximum for the highest occupied MO and a minimum for the lowest unoccupied MO. This indicates that the reaction is forbidden, whereas a crossing of these levels is prevented by the lack of symmetry.

All these considerations still give no clue with respect to the question of concertedness of the reaction. To answer this question we have investigated the possibility of the diradical character of the transition state. A diradical character would imply the degeneracy of singlet and triplet [13] or, more popularly, one bond is broken before the other

Table 1. Internal coordinates of the transition state

Coordinate	1	2	3	4	5	6	7	8
R(Å)	1.600	1.686	1.187	1.184	1.181	1.768	1.181	1.180
ϑ^a	85.7	123.9	116.2	105.0	40.6	118.3	119.9	
φ^a	33.0	−105.0	130.1	−138.8	−110.0	35.9		

[a] For definition of R, ϑ, φ see Fig. 2.

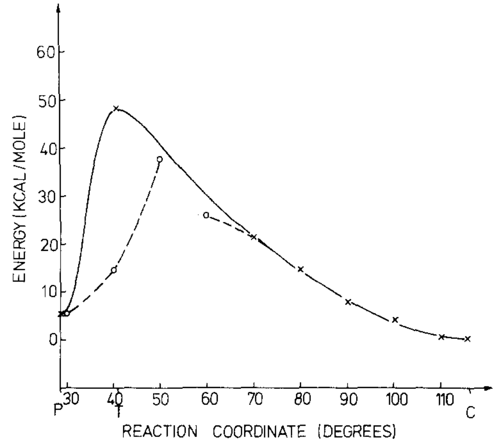

Fig. 3. Total energy in dependence of reaction coordinate ϑ_5; minimum energy pathways in dashed lines; C cyclopropane, P propene, T transition state

one is formed [14]. We have looked at the problem both ways. The CI wavefunction has less than 10% open shell (diradical) character which in consequence gives very little lowering of the barrier. There is also no indication that the geometry of the transition state will be much different on the CI level. So the answer is: the reaction is concerted because there is no degeneracy of singlet and triplet at the transition state. Also the breaking and forming of bonds is gradual. To support this latter claim we have developed a new definition of bond order whose details will be given elsewhere [15]. It can be briefly characterized as a principle of maximum bond order. The latter is set up as a sum of pairs of orbitals on two different centers coupled by the density operator. Fig. 6 shows application to this case. The carbon framework is labelled 1, 2, 3 and the migrating H atom is labelled 7. It is apparent from this figure that the breaking (P_{27}) and forming (P_{37}) of the CH bonds is simultaneous and most of it occurs before the transition state is reached. The ring opening occurs somewhat later with the related CC bond loosening (P_{13}) but no increase in the double bond character (P_{12}) of the adjacent CC bond until the transition state is reached from the cyclopropane side. The final breaking of the C_1C_3 bond and C_2H_7 bond as well as the increase in the double bond character of the C_1C_2 bond occur only after the transition state.

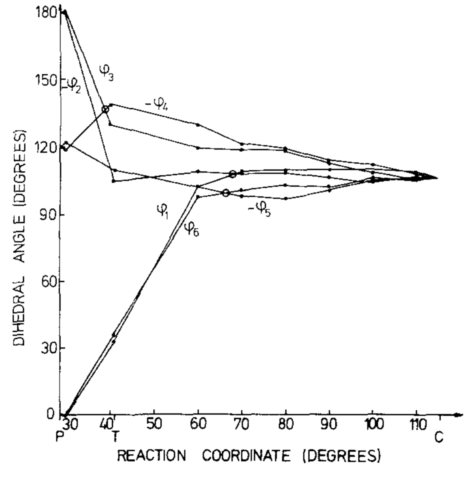

Fig. 4. Dihedral angles in dependence of reaction coordinate ϑ_5

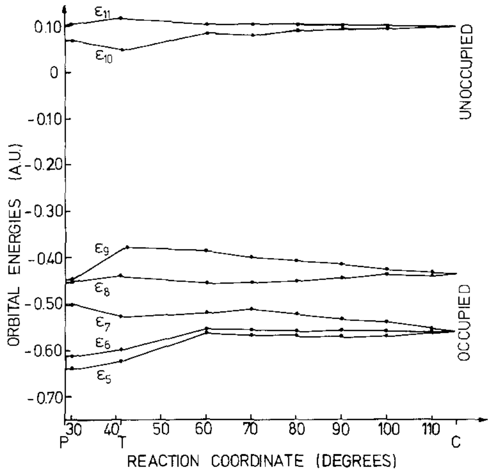

Fig. 5. Orbital energies in dependence of reaction coordinate ϑ_5

To understand the initial steps of this reaction better, we have looked at the normal vibrations of cyclopropane in a simplified way. Fig. 7 describes how a combination of a torsional vibration (a) and an asymmetric stretch (b) [16] can be combined to give a qualitative idea of the rearrangement along the minimal energy path followed for ϑ_5 between 115.6° to 60°. This region is the cyclopropane "valley" [12]. We have collected the results of this work in Table 2.

In this work we have not emphasized that there is a degeneracy in the cyclopropane which would lead to a statistical distribution of six possibilities for the migration of the H atom.

4. Conclusion

We found the cyclopropane-propene reaction concerted. We suggest that this reaction can be initiated by transfer of collision energy to a combination of torsional vibration of the methylene groups and an antisymmetric stretch of the carbon framework. To transcend from the cyclopropane valley over the transition state to the propene valley the migration of an

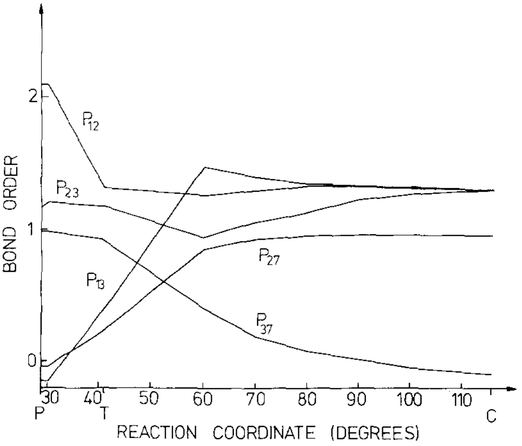

Fig. 6. Bond orders in dependence of reaction coordinate ϑ_5

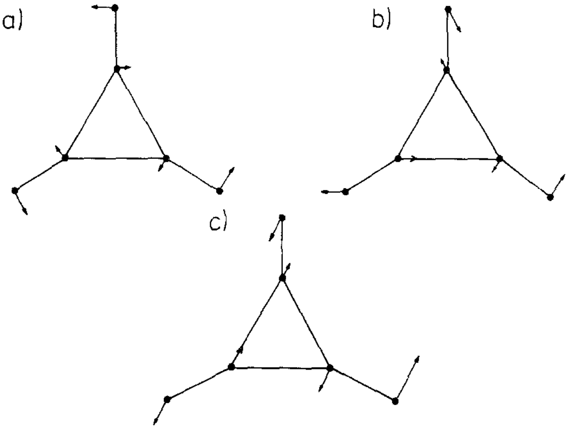

Fig. 7. Superposition of torsional vibration ν_3 (a) and asymmetric stretch ν_{6b} (b) yields cyclopropane pathway of minimal energy (c)

Table 2. Simplest sequence of rearrangements of cyclopropane–propene reaction

Region	Type
C	Bending of the three methylene groups
	Asymmetric stretch of carbon framework
	Rotation of outer methylene groups
T	Migration of H atom
	Ring opening
	Loosening of middle CC bond
P	Rotation of middle methylene group
	Breaking of middle CC bond
	Forming of double bond character

H atom has to be accompanied by a rotation of the outer methylene groups and a loosening of a CC bond. In the propene valley the final breaking of the CC bond and forming of double bond character of the adjacent CC bond occurs together with the final breaking of the CH bond and rotation of the middle methylene group.

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References

1. Willcott, M. R., Cargill, R. L., Sears, A. B.,: Progr. Phys. Org. Chem. 9, 25 (1972)
2. Woodward, R. B., Hoffmann, R.: The conservation of orbital symmetry. Weinheim: 1971 Verlag Chemie–Academic Press
3. Jug, K.: Theoret. Chim. Acta (Berl.) **30**, 231 (1973)
4. Pople, J. A., Beveridge, D. L.: Approximate molecular orbital theory. New York: McGraw-Hill 1970
5. Coffey, P., Jug, K.: J. Am. Chem. Soc. **95**, 7575 (1973)
6. Coffey, P., Jug, K.: Theoret. Chim. Acta (Berl.) **34**, 213 (1974)
7. Jug, K., Chickos, J.: Theoret. Chim. Acta (Berl.) **40**, 207 (1975)
8. Himmelblau, D. M.: Applied nonlinear programming. New York: McGraw-Hill 1972
9. McIver, J. W., Kormonicki, A.: J. Am. Chem. Soc. **94**, 2625 (1972)

10. Dewar, M. J. S., Kirschner, S.: J. Am. Chem. Soc. **96**, 4262 (1974)
11. Schlag, E. W., Rabinovitch, B. S.: J. Am. Chem. Soc. **82**, 5996 (1960)
12. Dewar, M. J. S., Kirschner, S.: J. Am. Chem. Soc. **93**, 4292 (1971)
13. Salem, L., Rowland, C.: Angew. Chem. **84**, 86 (1972)
14. Berson, J. A., Dervan, P. B.: J. Am. Chem. Soc. **95**, 267 (1973)
15. Jug, K.: J. Am. Chem. Soc. submitted
16. Herzberg, G.: Molecular spectra and molecular structure, II. Infrared and Raman spectra of polyatomic molecules, p. 91. Princeton: Van Nostrand 1968

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