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Cycloreversion of Cyclobutanes

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Semiempirical MO calculations with the method SINDO1 were performed to study the potential energy surface of cyclobutane and several substituted cyclobutanes with substituents F, OCH_3 and CN. The reaction pathway with the lowest activation energy leading to two ethylenic fragments is nonconcerted. One carbon bond is broken after symmetric opening of two adjacent bond angles and twisting of the carbon framework. The first transition state is asymmetric and diradicaloid. The reaction proceeds to a diradicaloid, non-zwitterionic intermediate. The second transition state is characterized by bond breaking of the inner carbon-carbon bond. For the unsubstituted case, the barrier for free rotation of the outer methylenic groups was also calculated. In comparison, the unsubstituted reaction is characterized by transition states of almost equal energy, whereas in the substituted reactions the barriers for the second bond breaking are much higher than for the first bond breaking step.

Key words: Cycloreversion of Cyclobutanes.

1. Introduction

The cycloreversion of cyclobutane has been the subject of theoretical and experimental interest for some time. The question has been whether the fragmentation follows a concerted or a two-step mechanism and whether the transition state is planar or twisted. In the framework of the Woodward–Hoffmann rules [1], the concerted process $[2_s + 2_s]$ is thermally forbidden by orbital symmetry. The pathway $[2_s + 2_a]$ requires a highly twisted transition state and was suggested to be limited to rare cases; the pyrolysis of cyclobutanes was regarded as nonconcerted [2]. The recipe of the Woodward–Hoffmann rules for the construction of correlation diagrams is a reduction of a reaction to its highest inherent symmetry. The rules predict that there is no substantial difference between the reaction of a substituted and the unsubstituted compound.

On the basis of his LCFC (Linear Combination of Fragment Configurations) method Epiotis [3] distinguishes between nonpolar and polar $2\pi + 2\pi$ cycloadditions. He compares the *supra-supra*, *supra-antara* and a *transoid* biradicaloid pathway for the cycloaddition of two unsubstituted ethylenes and concludes that the *supra-antara* pathway will produce the lowest barrier. In contrast to this nonionic reaction the result of increased polarity in this reaction, e.g. by substitution of the hydrogen atoms by proper substituents, should be the formation of an intermediate as a minimum on the potential energy surface. He expects this in both the *supra-supra* and the *supra-antara* pathways, as well as in the *transoid* diradicaloid pathway. He quotes experimental data in support of a stereoselective *supra-supra* reaction.

Huisgen [4] has studied the cycloaddition of donor and acceptor olefines, e.g. enol ethers and tetracyanoethylene, and finds all mechanistic criteria in favor of a zwitterionic intermediate in which one of the new σ-bonds is established. These cycloadditions are reversible; the same mechanistic conclusions pertain to the cycloreversion. The lack of stereospecificity in the above-mentioned cycloaddition as well as the stereochemistry of the interception by alcohols points to a *cisoid* or *gauche* conformation of the intermediate [5].

Until now most theoretical work was restricted to the unsubstituted case. Segal [6] found that the pyrolysis of cyclobutane proceeds through a nonconcerted pathway. His calculations result in a diradical which is a thermodynamically stable species. The *gauche* minimum presents a barrier of 3.6 kcal/mol to dissociation and 2 kcal/mol to reclosure of the ring. There is also the *transoid* diradicaloid as minimum on the potential energy surface. Segal's calculations were restricted to the major coordinates on the basis of STO-3G plus CI. The intermediates were found essentially on the two-dimensional surface spanned by a bond and a twist angle. Jug and Krüger [7] investigated the same potential energy surface with the semiempirical SCF method SINDO plus CI. All internal coordinates were varied. They found the transition state as a saddle point on the energy surface with appreciable diradical character. No intermediate was found.

In the present study we have repeated and extended the scope of cycloreversion of cyclobutanes. First, the semiempirical method SINDO1 [8] was used with an accuracy for equilibrium geometries and binding energies on the average better than MNDO. Second, various substituents were used to create polar and nonpolar complexes. Our results presented in the next sections suggest that intermediates are involved in the gas phase reactions of this type.

2. The Unsubstituted Reaction

Calculations had to be performed with SINDO1 to determine the geometry and energy of reactant, transition state and product. Energies calculated with SINDO1 represent binding energies which are enthalpies of formation at 0°K plus zero point vibration energies. The geometries and binding energies of cyclobutane and ethylene are already published in the applications [9] of SINDO1. The geometry of cyclobutane is obtained as a planar ring with $r_{CC} = 1.561$ Å (1.548 Å), $r_{CH} = 1.087$ Å (1.133 Å), $\theta_{HCH} = 108.4°$ (108.1°); and of ethylene with $r_{CC} = 1.324$ Å (1.337 Å), $r_{CH} = 1.076$ Å (1.086 Å) and $\theta_{CCH} = 122.2°$ (121.2°). Experimental values are in parentheses. Cyclobutane is too stable by 9.4 kcal/mol whereas the stability of ethylene is underestimated by 1.1 kcal/mol. So the thermodynamic stability of cyclobutane versus two ethylenes is calculated to be 27.9 kcal/mol versus 16.3 kcal/mol experimentally. We do not consider the planar arrangement of cyclobutane a problem since the twisted form with a dihedral angle of 15° increases the energy by less than 3 kcal/mol. Experimentally a decrease by about 1 kcal/mol is found.

We searched the hypersurface by varying all internal coordinates in a 4×4 CI calculation. This includes the ground state and the lowest doubly excited configuration and the two lowest singly excited configurations. Three singlet states and one triplet state are obtained. Following Salem and Rowland [10] we define a diradical as a situation in which singlet and triplet states are degenerate. A zwitterion would appear when the ionic part of the wavefunction is dominating through the singly excited configurations. A transition state is a saddle point on the potential energy surface with one negative root of the force constant matrix. An intermediate is a local minimum.

The pertinent results for this reaction are shown in Fig. 1. The experimental activation energy for fragmentation of cyclobutane is 62.5 kcal/mol. We find that the breaking of one carbon bond and forming of a planar *cisoid* carbon framework requires 57.7 kcal/mol. Subsequent rotation of one outer CH_2 group into the carbon plane requires an additional 8.6 kcal/mol. This barrier is reduced to 7.2 kcal/mol for a twist angle of 20°. So the barrier for geometrical isomerization, i.e. ring opening, rotation and reclosure, is calculated to be 64.9 kcal/mol. The geometry of the transition state for this process is in T_1 of Fig. 1. The bond angles are almost equal with 115.1° and 115.3°. Compared to the ring the central remaining CC bond and the inner CH bonds are almost unchanged whereas the outer CC and CH bonds are appreciably shortened. The triplet is 0.4 kcal/mol below the singlet. So this transition state is a diradicaloid. For bond angles θ_{CCC} at 115° and dihedral angle ϕ_{CCCC} between 0° and 20° the energy stays relatively constant between 57 and 58 kcal/mol above the cyclobutane energy.

The first transition state T_2 for fragmentation is at $\phi_{CCCC} = 30°$ with an activation energy of 70.1 kcal/mol. Except for the dihedral angle, the carbon framework has a geometry close to T_1. The triplet energy is 0.8 kcal/mol below the singlet energy. So this transition state T_2 is still in the diradicaloid region. At a dihedral angle of 35° the triplet is still 0.6 kcal/mol below the singlet, but at 40° the stability changes to favor the singlet by 0.1 kcal/mol. Further increase of the dihedral angle leads to an intermediate I at $\phi_{CCCC} = 70.6°$ with a barrier to ring closure of 3.9 kcal/mol. The inner CC bond is slightly contracted compared to T_2. The singlet is more stable than the triplet by 1.4 kcal/mol. From this intermediate a

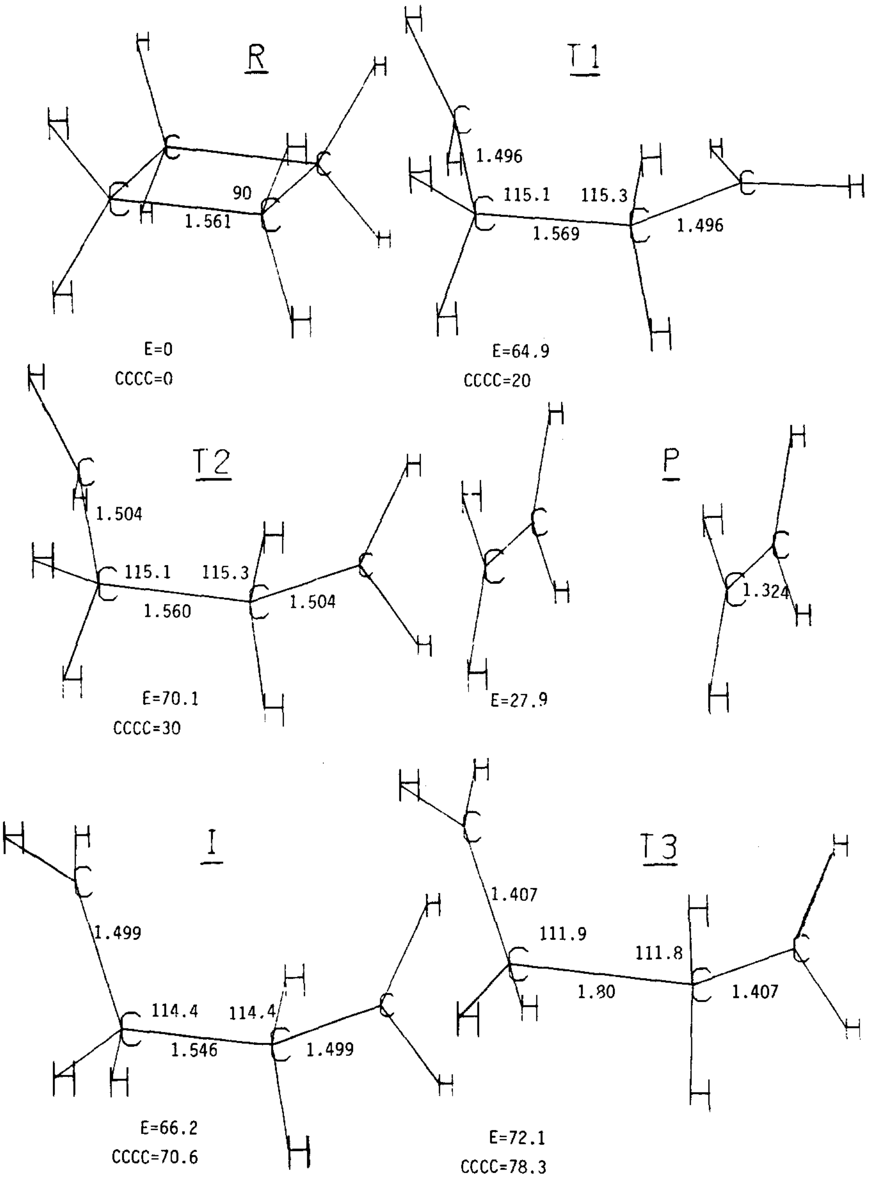

Fig. 1. Energies (kcal/mol) and geometries (Å, degrees) of cyclobutane fragmentation

barrier of 5.9 kcal/mol has to be overcome to fracture the inner carbon bond and to relax the system to the product *P* of two ethylenes. The geometry of transition state T_3 shows a weakened inner CC bond at 1.80 Å with the adjacent CC bond at 1.40 Å having appreciable double bond character. The dihedral angle has increased only by a few degrees compared with the intermediate. From these results we conclude that the planar transition state of Jug and Krüger [7] was not an essential saddle point for dissociation.

Qualitatively these results are in agreement with Segal's [6]. The agreement goes even further. Increasing the dihedral angle ϕ_{CCCC} beyond of 70.6° for the *gauche* intermediate leads to another channel for fragmentation. At 131° there is another transition state with a barrier of 4.0 kcal/mol leading to a *transoid* intermediate. This intermediate is 2.0 kcal/mol above the *gauche* intermediate. It is not a diradical because the singlet state is 2.4 kcal/mol below the triplet state. We find that a fragmentation of the remaining inner CC bond is favorable also at $\phi_{CCCC} = 180°$ leading to a barrier of 4.3 kcal/mol. If the dihedral angle is reduced to 150° the barrier is only 1.2 kcal/mol above that of T_3. To complement the study, we have determined that the barrier to fragmentation at $\phi_{CCCC} = 20°$ is about 10 kcal/mol higher than that of T_3. This means that fragmentation of cyclobutane without twisting is less likely than via *gauche* or *trans* twisting. These two channels of fragmentation are equally likely. The early EH calculation by Hoffmann et al. [2] revealed a portion of the flat part of the hypersurface, but was inconclusive with respect to the intermediates.

3. The Substituted Reaction

We investigated the fragmentation of 1,1-dicyano-2-methoxycyclobutane to methylvinylether and 1,1-dicyanoethylene. This is a case of polar character discussed by Huisgen and Epiotis. The question was whether this polarity would appreciably deepen the potential well of the intermediates so that the latter could be intercepted. Again the energy of reactant and product was determined and the scheme of possible pathways described in the previous section investigated.

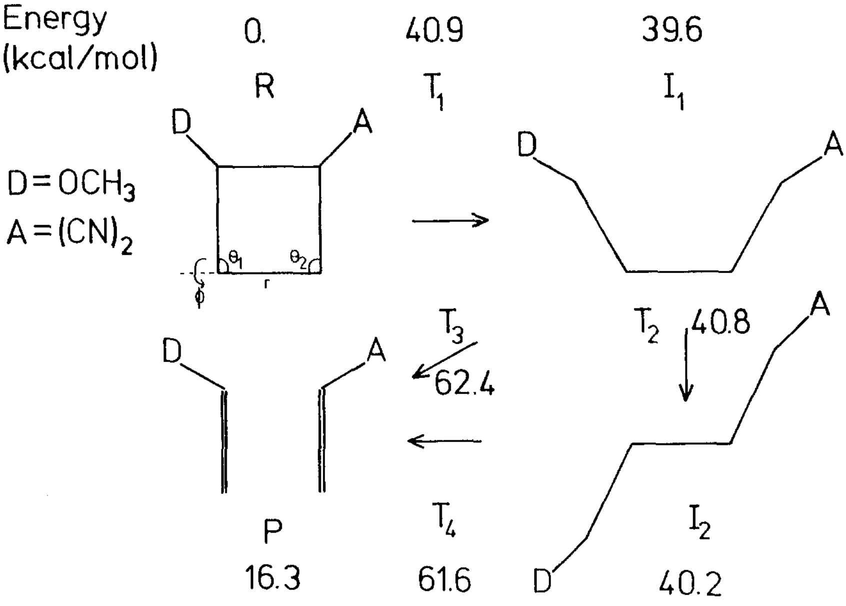

Fig. 2. Energies (kcal/mol) of 1,1-dicyano-2-methoxycyclobutane fragmentation

Table 1. Bond lengths (Å) and angles (degrees) of essential internal coordinates in the 1,1-dicyano-2-methoxycyclobutane fragmentation

	Coordinates[a]			
State	r	θ_1	θ_2	ϕ
R	1.558	90.0	90.0	0.0
T_1	1.541	112.5	113.0	69.0
I_1	1.532	113.9	114.1	74.6
T_2	1.534	112.8	113.3	128.3
I_2	1.534	113.5	114.3	169.0
T_3	1.920	113.0	109.8	85.0
T_4	1.920	112.0	107.5	170.0
P	∞			

[a] See Fig. 2.

All internal coordinates were varied to determine all transition states (T) and intermediates (I) pertinent for the fragmentation.

The relative energies between reactant and the other states are given in Fig. 2 and the essential coordinates in Table 1. The main results compared to the unsubstituted case are: (1) The number of transition states (four) and intermediates (two) remains the same. (2) The barrier for fragmentation of the first bond is appreciably lowered. (3) The potential well for reclosure of the ring has decreased and the twist angle of T_1 is much closer to that of I_1. (4) The barrier for breaking of the second bond is equally lowered for *gauche* and *trans*, but it is much higher than that of T_1. Whereas result 2 is very much like the prediction of Huisgen and Epiotis, results 3 and 4 are different from their expectation. On the basis of our results we would find it difficult, if not impossible to intercept the reaction intermediates in the gas phase. Appreciable further stabilization by polar solvents must intervene to get experimental evidence of reaction intermediates in this case. With respect to the question of *cis* or *trans* intermediates as disputed by Huisgen and Epiotis, we find that their energy difference is not high enough to warrant model arguments in favor of one or the other.

The next question which we found interesting to discuss was the existence of diradicals versus zwitterions. Some guidelines are given in Table 2. If we measure in the spirit of Salem and Rowland [10] the diradical character by the amount of admixture of the doubly excited configuration to the SCF ground state configuration and the zwitterionic character by the amount of the singly excited configuration in the CI wavefunction, it is clear that the reaction passes through a region which is dominantly diradical with a small portion of zwitterion. The region includes T_1, I_1, T_2 and I_2. The same answer yields the singlet triplet splitting energy which shows almost degeneracy of these states between T_1 and I_2. At T_3 the singlet is already appreciably lower than the triplet. The consideration of dipole moments shows an increase by a factor of two compared to reactant or product during the reaction. This increase is mainly due to charge transfer and

Table 2. Coefficients C_0 (SCF), C_2 (doubly excited), C_1 (singly excited singlet) of CI wavefunction, singlet-triplet splitting ΔE (kcal/mol), dipole moments D (Debye) and charge transfer ΔQ in the 1,1-dicyano-2-methoxycyclobutane fragmentation

State	C_0	C_2	C_1	ΔE	D	ΔQ
R	1.0				3.37	0.11
T_1	0.699	−0.667	0.181	0.4	7.87	0.20
I_1	0.705	−0.644	0.178	0.3	8.04	0.20
T_2	0.722	−0.655	0.157	−0.0	8.03	0.18
I_2	0.711	−0.654	0.184	0.1	8.63	0.20
T_3	0.944	−0.316	−0.070	−24.9	6.77	0.13
T_4	0.943	−0.319	−0.068	−25.5	7.37	0.12
$P_{r=2.15}$	0.988	−0.156	−0.003	−62.3	4.94	0.06

only to a small extent to changes in the hybrid moments of the atoms. However, the charge transfer ΔQ from the methoxy part to the dicyano part of the molecule is much less than one would expect for a zwitterionic transition state or intermediate. In this sense the increase of dipole moment cannot help to distinguish diradicals and zwitterions. Experimental data [3, 11] for zwitterionic intermediates of tetracyanoethylene in solution yield dipole moments of 15–17 D compared to our calculated 8.6 D in the gas phase.

To complement the study we have investigated the nonpolar case of fragmentation of 1,1-2,2-tetrafluorocyclobutane to two 1,1-difluoroethylenes. The *gauche* transition state T_1 and intermediate I_1 have disappeared. The transition state T_2 is at a dihedral angle $\phi_{CCCC} = 131.8°$. It presents a barrier of 34.3 kcal/mol to the ring. It is followed by a *trans* intermediate at $\phi_{CCCC} = 180°$ with a well of 3.8 kcal/mol. Fragmentation of the second CC bond needs an additional 43.1 kcal/mol from the intermediate so that the overall barrier from the ring is 73.6 kcal/mol. This barrier is substantially higher than the barrier of the dicyanomethoxy ring. In both cases, the last transition state is by far the highest and thus essential for fragmentation. This situation is different in the unsubstituted case where the first and the last transition state had almost equal energies. Finally, in the fluorine substituted cyclobutane the first transition state and the intermediate have diradicaloid, non-zwitterionic character.

4. Conclusion

CI calculations with four configurations using the semiempirical MO method SINDO1 to study the fragmentation of cyclobutane rings showed intermediates during the reaction both in the unsubstituted and substituted polar and unpolar cases. However, the energy wells are so small, i.e. a few kcal/mol only, that their existence should have little impact on the reaction. In this sense our investigation demonstrates that the Woodward–Hoffmann rules might be applied even in non-concerted reactions, if the intermediates have no substantial lifetimes to interfere with the process of the overall reaction.

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