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A Comparative Semiempirical, Ab initio and DFT Study of Decarbonylation of Cyclic Ketones Part 1: Thermal Fragmentation of Cyclopropanone

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Abstract Calculations using different quantum mechanical methods including semiempirical (MNDO,AM1 and PM3), *ab initio* (RHF and MP2 calculations using the 6-311G and 6-311++G** basis sets), and density functional theory (LSDA, BP, MIXBP and B3LYP, i.e., B3LYP/6-311+G**// B3LYP/6-31G*) have been performed on the thermal fragmentation of cyclopropanone to ethylene and carbon monoxide. All RHF calculations predict a concerted single step mechanism for this conversion. The estimated activation energies vary from 34.4 to 54.6 kcal·mol^{-1}, mainly localized around 37 ± 2 kcal·mol^{-1}, depending on the method. Whereas the calculated RHF reaction energies also varied from 14.5 to -33.3 kcal·mol^{-1}, the B3LYP/6-311+G**//B3LYP/6-31G* method predicts the experimental value (-17.7 kcal·mol^{-1}) within experimental uncertainties. Remarkably, semiempirical AM1 and PM3 methods and simple DFT calculations, LSDA, predict comparable results to the more advanced methods. UHF *ab initio* calculations predict the same single step mechanism, whereas a multistep biradical mechanism with an unrealistically low activation energy is favored by the semiempirical methods. Structures of the activated complex of the single step mechanism, estimated by different methods, are very similar and consistent with a nonlinear cheletropic [$_2\pi_s + _2\omega_a$] reaction, as predicted by the orbital symmetry rules and earlier EHT calculations.

Keywords Semiempirical calculations, Ab initio calculations, DFT calculations, Reaction mechanisms, Cheletropic reactions, Decarbonylations, Cyclopropanone

Introduction

Thanks to the rapid developments in computer technologies and availability of user friendly program packages based on quantum and molecular mechanical methods, computational techniques are becoming a standard tool in chemical research and education [1]. Especially in the study of short lived spe-

cies, the contribution of the theoretical methods is essential. In this sense, the investigation of reaction mechanisms is a playground of theoretical calculations, although the quantitative results of calculations are often not reliable [2]. Pericyclic reactions are one of the most important and mechanistically best studied reactions of organic chemistry. These reactions have special interest for the theoretically oriented chemist since most of them are gas-phase reactions. They have cyclic transition states, are dependent on applied energy sources, thermal or photochemical, and show high
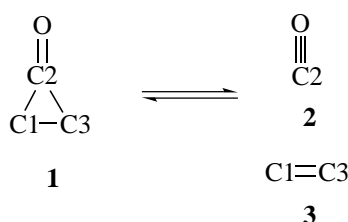

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stereospecificity. Theoretical explanations of these facts were given by Woodward and Hoffmann on the basis of the symmetry properties of the reacting molecular orbitals, about three decades ago [3].

From the mechanistic point of view, the situation is, however, still complicated since the same products may also be formed under certain circumstances stepwise *via* biradical mechanisms. Experimental distinction between all these mechanistic probabilities is not easy because of the difficulties in determining the stereochemistry of the products, or in the interpretation of the kinetic results. In spite of the enormous volume of experimental and theoretical work dealing with the mechanism of these reactions, it is still a subject of debate [4]. Controversy about the concertedness, stepwiseness and synchronicity of these reactions is still going on.

Houk et al. have reviewed the contributions of the theoretical approaches on this subject, regarding the results of *ab initio* and DFT calculations, performed on the sigmatropic and electrocyclic rearrangement and cycloaddition reactions [5,6]. Considering the energetic aspects, the results of *ab initio* calculations with electron correlation and DFT calculations using the hybrid method based on Becke's three parameter exchange correlation functional and the semiempirical AM1-method, all seem to fit the experimental activation energies of the discussed reactions quite well. Cheletropic reactions, another important class of pericyclic reactions, was not extensively included in the cited papers. In the Woodward-Hoffmann formalism cheletropic reactions are those in which two bonds are formed or broken, in one step, simultaneously to a single atom [7]. There are very few theoretical and mechanistic investigations on this subject, although it is a very interesting topic [8]. Prominent examples of these reactions are the addition of carbenes and nitrenes to olefins. Fragmentations of some cyclopropane derivatives or their higher homologues are given as further examples of the reverse cheletropic cycloaddition. In these cases the single atom components may be the CO, N_2, SO, or SO_2 groups [9]. Structural analysis of the single atom component is the most important problem in the experimental work. Recent progress on the analysis of the rotational energy distribution of the nascent products [10] or results obtained from femtosecond chemistry [11] make it possible to analyze the geometry of the single atom components.

As mentioned above, theoretical calculations on cheletropic reactions are rare and most of them are largely obsolete [8]. From this perspective, it seems worthwhile to study the energetic and stereochemical aspects of the cheletropic reactions by theoretical methods and test the predictive power of different approaches on this subject. In the present paper, decarbonylation of cyclopropanone, as a prototype model for cheletropic reactions, is comparatively studied to test the predictive power of different theoretical approaches at different levels.

Calculational methods

The calculations were carried out on a Pentium166-IBM compatible PC, using the MOPAC 7.0 [12] program for semiempirical MNDO, AM1 and PM3 calculations and PC-GAMESS 4.4 [13] for *ab initio* studies. In semiempirical calculations both the UHF and RHF formalism were employed in the searching potential energy surfaces. The initial geometries of the molecules were estimated from MM2 calculations [14]. All geometries are fully reoptimized in the semiempirical calculations, by minimization of the energy with respect to all structural parameters without using symmetry. Energy surfaces of the reactions were obtained using the C1C2 and C2C3 bond distances as independent parameters. Numbering of the heavy atoms in cyclopropanone **1**, and in the resulting products; carbon monoxide **2**, and ethylene **3** are shown in Scheme 1.

The grid calculations were repeated, taking the C1C2 bond and C1C2O bond angle and C1C2 bond and O4C2C3C1 torsional angles as independent parameters to study the effects of in plane and out of plane bending of the carbonyl group. The stationary points on the energy surface were defined by further refinement of the surfaces in the critical area, localized by the NLLSQ procedure, and then characterized by force constant calculation [15]. *Ab initio* quantum mechanical calculations were carried out at standard and extended levels, e.g. 6-311G, 6-31++G** at UHF and RHF/MP2. The calculated structures were completely reoptimized for each basis set, using analytical gradient based techniques. Analytical vibrational frequencies were calculated and all critical points were located and characterized as true minima or as saddle points. Initial geometries for the saddle point calculations were structures from the semiempirical calculations.

DFT calculations have been performed using local and non-local spin density functionals. In the LSDA, BP and MIXBP calculations, the LCGTO approximation coded by St-Amant [16] has been used. For the B3LYP calculations, the GAUSSIAN94 program has been used [17, 18]. The scaling factor 1.0 was used in ZPE calculations, for both *ab initio* and DFT methods.

Results and discussion

All the applied methods, consistent with the earlier calculations, predict a single step reaction path with similar transi-

O
‖
C2
/ \
C1—C3

1

$\longrightarrow\longleftarrow$

O
⫴
C2

2

C1=C3

3

Scheme 1 *Numbering of the heavy atoms in cyclopropanone* **1**, *and in the resulting products; carbon monoxide* **2**, *and ethylene* **3**.

Table 1 *Experimental and theoretical critical data of structures corresponding to stationary points characterized using semiempirical,* ab initio *and DTF calculations (r, in Å; ∠, in degree)*

|		EXPT. [20]	PM3	AM1	MNDO	MP2/ 6-311G	MP2/6- 311G**	LSDA	BP	MIXBP	DFT [a]
1	r (C1C2)	**1.475**	1.471	1.470	1.499	1.458	1.461	1.458	1.476	1.476	1.474
	r (C1C3)	**1.575**	1.525	1.524	1.548	1.559	1.561	1.554	1.575	1.581	1.571
	r (C1O)	**1.191**	1.194	1.209	1.203	1.201	1.172	1.203	1.212	1.214	1.202
	r (C1H)	**1.086**	1.096	1.105	1.096	1.072	1.076	1.096	1.093	1.097	1.088
	∠ (C2C3C1)	**57.42**	58.77	58.75	58.96	57.69	57.64	57.80	57.75	57.62	57.80
2	r (CO)	**1.128**	1.134	1.163	1.171	1.123	1.104	1.136	1.144	1.145	1.137
	r (CC)	**1.337**	1.321	1.325	1.334	1.320	1.316	1.325	1.335	1.340	1.330
3	r (CH)	**1.086**	1.085	1.098	1.088	1.072	1.076	1.095	1.092	1.096	1.087
	r (C1C2)		1.985	2.003	2.117	2.117	2.113	2.134	2.129	2.084	2.099
	r (C1C3)		1.428	1.436	1.426	1.438	1.437	1.442	1.474	1.475	1.457
	r (C2C3)		1.501	1.477	1.528	1.546	1.532	1.484	1.460	1.451	1.477
4	r (C1O)		1.164	1.186	1.175	1.159	1.139	1.146	1.182	1.185	1.176
	r (C1H)		1.08	1.08	1.10	1.08	1.07	1.08	1.09	1.09	1.082
	r (C2H)		1.10	1.11	1.10	1.10	1.08	1.10	1.11	1.10	1.09
	∠ (C2C3C1)		85.25	86.87	91.47	90.24	91.52	93.64	93.03	90.88	91.34

*[a] B3LYP/6-311+G**//B3LYP/6-31G**

tion state geometry, although the related energy values are different. Semiempirical methods were especially of interest in our study because of their availability and low computational cost and for our future work on similar but larger molecular systems. Hence, our discussions are mainly focused on the comparison of the results of the semiempirical calculations with more advanced *ab initio* and DFT calculations,

which were still manageable, thanks to the small size of the studied molecules, in reasonable time in our computer systems. The estimated critical structural data and related energy values are given in Tables 1 and 2 together with some available experimental values.

The MNDO, AM1 and PM3 calculations give qualitatively similar energy surfaces. The PM3-RHF and PM3-UHF energy surfaces of the reaction are obtained. The results from RHF and UHF calculations are obscure. Whereas the RHF formalism predicts a concerted single step mechanism with the transition state structure **4**, in the UHF formalism a two step mechanism involving the transition states **5** and **7** and the biradical intermediate **6**, is predicted (Scheme 2). Further searches on other possible stationary points on the energy surfaces have been undertaken using the bond angle and the dihedral angle as independent parameters. All attempts resulted in the stationary points mentioned above.

Reaction path calculations using the *ab initio* RHF and UHF formalisms result in a concerted single step reaction mechanism giving a similar transition state structure to that predicted by the RHF-PM3 calculations. Attempts using the UHF formalism to localize the transition states and intermediate corresponding to the structures **5**, **7** and **6**, resulted in either the starting compounds/ or products, or the transition state structure predicted by the RHF formalism.

DFT calculations, restricted only to the stationary points localization and characterization using the initial structures obtained from the calculations above, also verify the single step mechanism.
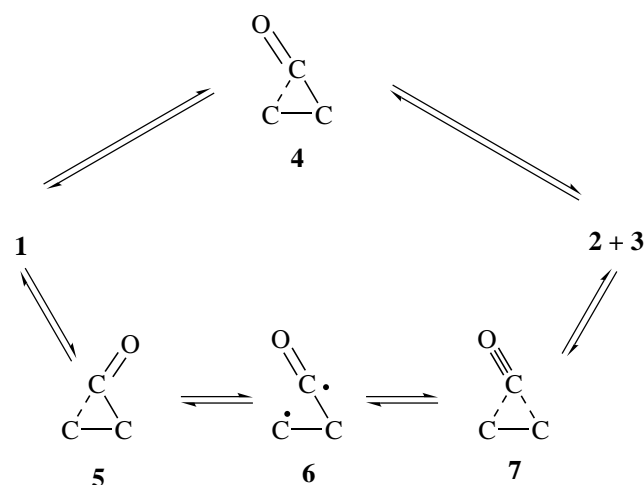
Scheme 2 *Transition state structures* **4** *(concerted single step mechanism, RHF);* **5** *and* **7** *(two step mechanism, UHF);* **6** *(biradical intermediate)*

Table 2 *Energetics of decarbonylation of cyclopropanone, in semiempirical,* ab initio *and DTF calculations (kcal·mol⁻¹)*

		1	2	3	4	$\Delta E^{\neq}$	ΔE_R
ΔH_f	PM3	-3.5	-19.7	16.6	34.1	**37.6**	**0.4**
	AM1	3.2	-5.7	16.4	40.9	**37.7**	**7.5**
	MNDO	-4.7	-5.5	15.3	38.1	**42.8**	**14.5**
	EXPT.	3.8[19]	-26.4[19]	12.5 [19]	-	**-**	**-17.7**
TOTAL	RHF/6-311G	-190.67886	-112.69949	-78.01944	-190.58784	**54.6**	**-28.1**
ENERGY [a]	MP2/6-311G	-191.09731	-112.92561	-78.20977	-191.02694	**41.6**	**-26.9**
	RHF/6-311++G**	-190.77835	-112.77136	-78.05613	-190.69887	**47.7**	**-33.3**
	MP2/6-311++G**	-191.40331	-113.08138	-78.34876	-191.33801	**38.8**	**-19.3**
	LSDA	-190.33596	-112.45848	-77.85289	-190.27266	**39.7**	**-15.4**
	BP	-191.96138	-113.35338	-78.61543	-191.90618	**34.6**	**-4.7**
	MIXBP	-191.95232	-113.34945	-78.61051	-191.89748	**34.4**	**-4.8**
	B3LYP/6-31G*	-191.88074	-113.30945	-78.58746	-191.81814	**37.5** **(39.3)** [b]	**-13.3** **(-10.1)** [b]
	B3LYP/6-311+G**// B3LYP/6-31G*	-191.94044	-113.34883	-78.61542	-191.88106	**35.4** **(37.3)** [b]	**-18.1** **(-14.9)** [b]
ZERO	6-311G	43.780	4.738	36.010	41.269		
POINT	6-311++G*	43.220	4.962	35.747	41.097		
ENERGY	B3LYP/6-31G	38.444	3.159	32.141	36.629		

[a] in Hartrees
[b] The values without zero point energies are given in parenthesis

Energetic of the reaction

Inspection of the Table 2 shows that the heats of formation and reaction energies are dependent on the applied method and strongly deviate from the experimental values. The high error in the estimated heats of formation of cyclopropanone **1**, and carbon monoxide **2**, is especially remarkable [19].

On the other side, *ab initio* calculations at the MP2/6-311++G** level and DFT calculations at the B3LYP/6-311+G**// B3LYP/6-31G*level with ZPE corrections fit the experimental reaction enthalpy very well (Table 2). Surprisingly, the reaction energy estimated by simple LSDA calculations is better than the values obtained from BLYP/6-31G*, BP and MIXBP, which include non-local gradient corrections.

Results of the activation energy calculations using the semiempirical methods are also confusing. The PM3 and AM1 calculations, in the RHF formalism, predict ca. 38 kcal·mol⁻¹ of activation energy for the concerted process, a higher barrier, ca. 43 kcal·mol⁻¹, is estimated by the MNDO method for the same process. Relative to the experimental observations, the estimated energy values seem to be very high; decarbonylation of the cyclopropanones is a smooth and stereospecific process [20]. Decarbonylation of the trans-2,3-di-tert-butylcyclopropanone, for example, takes place at about 150°C, resulting in stereospecific formation of E-di-tert-butylethylene [21].

The results from UHF calculations are even more perplexing, so much so that the predicted rate determining step of the multi-step reaction is controversial; while the first step was predicted as the rate determining step by the AM1 and PM3 methods in the UHF formalism, the second step is rate determining according to the MNDO calculations. Furthermore the calculated activation energies are unrealistically low, i.e., 32.6 to 27.3 kcal·mol⁻¹, for such a biradical process [22]. As < S2 > values deviate significantly from the expected values, restricted Open-shell Hartree Fock (ROHF) calculations were carried out to improve the UHF calculations. Better values are obtained for the reaction enthalpy, but the calculated activation energy barriers were still low for such a radical process.

Unlike the results of semiempirical calculations, the *ab initio* RHF and UHF calculations, both predict the concerted single step mechanism, which was also predicted by *ab initio* calculations at the MP2/6-311G level. Interestingly, the estimated activation energy by *ab initio* calculations at the MP2/6-311++G** level is rather close to the results of the semiempirical calculations using the PM3 and AM1 methods. Comparable activation energy values are also obtained at the MP4(SDTQ)+ZPE//MP2/6-31G* level [23]. On the other side RHF/6-311G* and RHF/6-311++G** calculations without electron correlation estimate much higher activation energy values.

Except MIXBP, and BP calculations, the activation energies obtained from LSDA and B3LYP calculations without ZPE correction are rather comparable to AM1 and PM3 calculations, although it has been claimed that the results for relative conformational energies calculations using the former two approaches are much better than results obtained using the LSDA approximation and comparable to the results of the MP2/TZP//MP2/6-31G* calculations [24]. After zero point

correction, the activation energy estimated from B3LYP/6-311+G**// B3LYP/6-31G* calculation lowered to 35.4 kcal·mol⁻¹.

Interpretation of the meaning of estimated different activation energy values is difficult due to the lack of the experimental values. It has been shown, however, that the results of the hybrid DFT methods based on Becke's three parameter exchange correlation functional, B3LYP, yield the most reliable results for the geometries and energies of major pericyclic reactions. Heats of reaction and activation energies of the electrocyclic ring opening of cyclobutene and Diels-Alder reaction butadiene and ethylene are predicted in a precision close to the experimental uncertainties [6a, 25]. The estimated activation energy (35.4 kcal·mol⁻¹) seems to be reasonable relative to the observed activation barrier for the allowed fragmentation of 3-cyclopentenone (51.3 ± 0.2 kcal·mol⁻¹, 46.4 ± 2.4 kcal·mol⁻¹) [25, 26]. Deviations of the calculated heat of reactions from the experimental value and the calculated activation energies from the B3LYP/6-311+G**// B3LYP/6-31G* +ZPE value are depicted in Figure 1. From the trend of both curves, it may be concluded that the deviation of the activation energies mainly results in the error of the estimated heat of formation of the starting compound.

Structural Aspects

As shown in Table 1, the estimated molecular geometries from the DFT, especially B3LYP/6-31G*, and the advanced *ab initio* calculations are in good agreement with experimental data for the starting compounds and products. Semiempirical methods underestimate the C1C3-bond in cyclopropanone, but overestimate the CO bond in carbon monoxide.
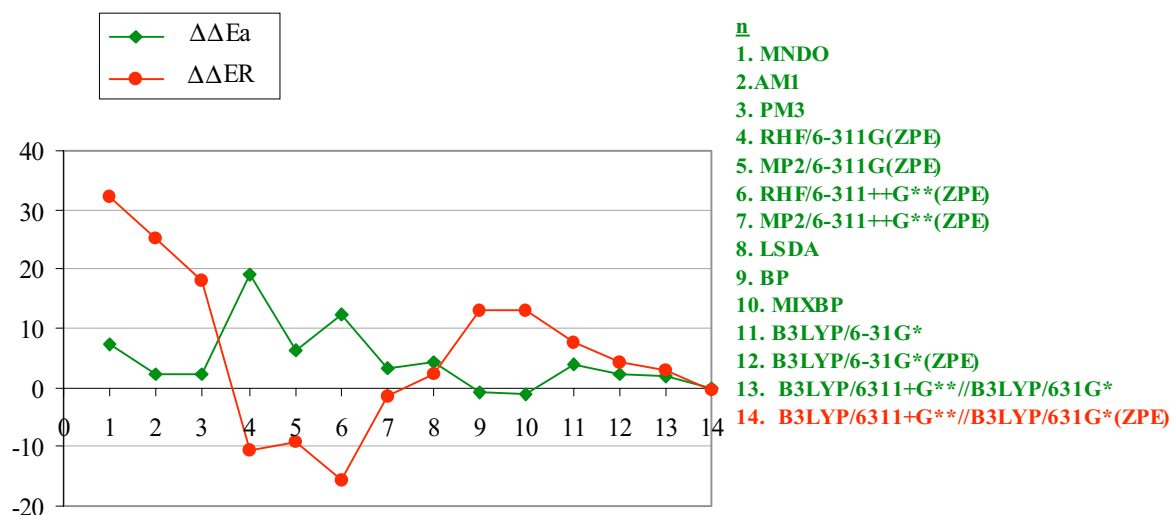
All applied methods predict a very similar transition state structure, which is also consistent with the experimental observations, and with the results of the Extended Hückel as well as *ab initio* calculations performed previously on the same system [8g-8h].

According to an orbital symmetry rule analysis, similar to addition of carbenes to olefins, two different geometrical approaches are expected for the reverse of the decarbonylation; a linear but thermally non-allowed ($_2\pi_s$ + $_2\omega_s$) process and a nonlinear thermally symmetry allowed ($_2\pi_s$ + $_2\omega_a$) process.

The estimated structure of **4**, corresponding to the transition state of the concerted, asynchronous mode of transformation, has a 'cisoid- structure' of C_s symmetry. The CO group, as expected for a nonlinear approach, is tilted at the transition state. Calculation indicates that the C_s symmetry is retained during the progress of the reaction. In the last stage of the reaction the dihedral angle, C1C2C3O4, is increased and the products are oriented in a distorted 'cisoid - structure' of C_1 symmetry. The semiempirical methods predict an early transition state at 1.99 Å, while the DFT and *ab initio* calculations each give a relatively late one at 2.10 Å and 2.13 Å, respectively.

A possible synchronous symmetrical cleavage of both bonds, corresponding to the linear non-allowed cheletropic decarbonylation, requires much higher energies and no stationary points on the corresponding diagonal of the energy surface, have been detected.

Concerning determination of the structure of the single atom component by novel experimental methods, it is interesting to note that very similar structures are predicted for the last stage of the concerted as well as for the estimated biradical reaction pathway predicted by the UHF calcula-

n
1. MNDO
2. AM1
3. PM3
4. RHF/6-311G(ZPE)
5. MP2/6-311G(ZPE)
6. RHF/6-311++G**(ZPE)
7. MP2/6-311++G**(ZPE)
8. LSDA
9. BP
10. MIXBP
11. B3LYP/6-31G*
12. B3LYP/6-31G*(ZPE)
13. B3LYP/6311+G**//B3LYP/631G*
14. B3LYP/6311+G**//B3LYP/631G*(ZPE)

Figure1 *The deviations of the calculated reaction heats from the experimental value and the calculated activation energies from the B3LYP/6-311+G**//B3LYP/6-31G*+ZPE value (kcal·mol⁻¹)*

tions. Apparently, the cisoid orientation of the nascent products of decarbonylation is not sufficient to ensure the concertedness of the process. Even a stereochemical analysis might be insufficient in this sense, since stereospecific product formation may also be expected by the two step mechanism if the rotation around the C1C3 bond is hindered in the intermediate **6**. Our calculations show that the rotational energy barrier of the C1C3- bond is much smaller than the necessary energy to cleave the C2C3- bond in intermediate **6**, i.e., 0.69 kcal·mol^{-1} and 3.4 kcal·mol^{-1} respectively. Hence, due to the easy bond rotation in intermediate **6**, nonstereospecific product formation should be expected for the biradical pathway.

It is remarkable that all the calculations indicate a considerable amount of bonding interaction between the non-bonded C1 and oxygen atoms in the transition state **4**, and in the late stages of the reaction. The results of the calculations, overall, seem to support the qualitative prediction of the Woodward -Hoffmann rules, and the decarbonylation of cyclopropanone may be described as an asynchronous ($_2\pi_s$ + $_2\omega_a$) concerted process. However, this interpretation cannot explain the remarkable bonding interaction between the non-bonded C1- and oxygen atoms. Furthermore an unusually large charge separation between C1 and C3 carbons in the transition state is found in all calculations, which is not expected for an regular pericyclic reaction. The same reaction was denoted as 'formally orbital symmetry allowed but effectively forbidden' using similar arguments and due to the lack of the expected energy of concert [23]. The nature of this peculiarity will be discussed in a separate paper, within the framework of bonding and MO interactions, as well as charge distribution analyses.

Conclusion

Among the theoretical methods investigated, the experimental heat of reaction of fragmentation of cyclopropanone was best estimated in order of decreasing accuracy, by the B3LYP/6-311+G**//B3LYP/6-31G*, MP2/6-311++G** and LSDA calculations. The results of semiempirical as well as *ab initio* calculations with smaller basis sets or without electron correlation are not satisfactory. It is interesting to note that the simplest DFT method, LSDA, gives better results than the non-local gradient corrected BP and perturbative MIXBP calculations.

A single step reaction mechanism was predicted by all the methods, except for semiempirical UHF calculations. Predicted activation energies are comparable, except the results from semiempirical MNDO and *ab initio* calculations without electron correlation.

Mechanistic studies of the larger systems with advanced methods are very time consuming, however; it may apparently be accelerated by using structures estimated by low cost semiempirical calculations, as starting point for more sophisticated studies.

Semiempirical UHF calculations predict a two step biradical mechanism with an unrealistically low activation energy, which is the result of a known defect of this method. Formation of similar biradical intermediates was not detected in *ab initio* UHF calculations.

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