

Formation of α -Iodine Pyruvic Esters from α -Chloroglycidic Esters Isomers in Diethyl Ether Solution: a DFT Study

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- ✓ Wiberg index.

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Abstract

We tried in this work to understand the ring opening mechanism of α -chloroglycidic esters in the presence of the Lewis acid MgI_2 , which leads experimentally to the formation of α -iodine pyruvic esters. Our theoretical study was done in the solvated phase using density functional theory at the B3LYP level with the atomic orbital basis set 6-31G(d) for C, H, O and Cl atoms. For the iodine atom we used the basis set of Dolg, which leads to more stable results than Huzinaga basis sets.

We studied two mechanisms: cationic mechanism and concerted mechanism. An analysis of the Wiberg binding index and the calculation of the percentage of bond breaking and forming evolution in transition states were realized in order to verify the reaction mechanism.

1. Introduction

The α -iodine pyruvic esters are intermediates involved in many biological processes [1] such as the transformation of glucidic (carbohydrate) groups into lipids [1]. These molecules (fig.1) are formed by the reaction between α -chloroglycidic esters and the Lewis acid MgI_2 [2] according to the reaction scheme in Figure 2.

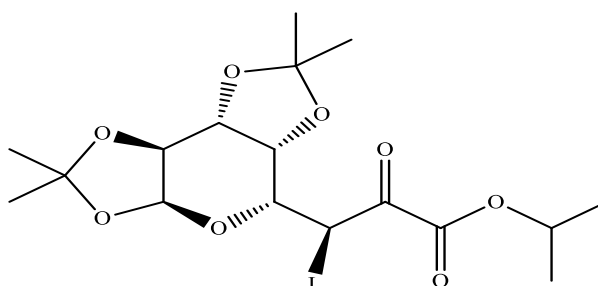


Figure 1: Structure of iodine pyruvic esters

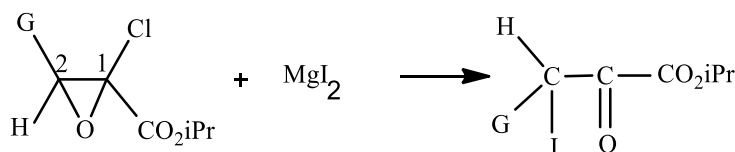


Figure 2: Reaction of an α -chloroglycidic ester with the Lewis acid MgI_2 (G denotes the glycidic group).

It was demonstrated experimentally that the reaction path of α -iodine pyruvic ester cannot pass through the α -chloropyruvic ester. The latter can be obtained from the reaction approach of the α -chloroglycidic ester and the Lewis acid $MgCl_2$ [2]. The experiments also demonstrated that the mechanism may be concerted or cationic whose one side is accessible and privileged [3, 4].

In the present work, we used the DFT [5] method to understand the mechanism of the epoxy ring opening reactions of the α -chloroglycidic esters in the presence of Lewis acid MgI_2 [2] (fig.2) leading to the α -iodine pyruvic esters [1].

2. Calculation methods

Density functional theory (DFT) [5] was found to be successful in providing theoretical insights into the chemical reactivity. In this context, our calculations were carried out with the program package Gaussian 09 [6], the results were visualized with GaussView 05 [7]. The geometries of the following stationary points were optimized; reactants, transition structures and products. We used DFT/B3LYP [8, 9] with the 6-31G(d) [10-13] basis set for carbon, hydrogen, oxygen and chlorine atoms. On the other hand for the iodine atom we used the basis set of Dolg [14] which gives the more stable results than the Huzinaga basis set [15]. The core electrons were modeled by a pseudopotential [16]. The optimized geometries of the reactants and the products were characterized by no imaginary frequency but the transition structures have only one. The IRC [17, 18] paths were traced in order to check the energy profiles connecting the transition structures (TS) with the two associated minima of the proposed mechanism.

The electronic structures of stationary points were analyzed by the natural bond orbital (NBO) method [19]. The solvent effect was taken into account by a self-consistent reaction field (SCRF) [20, 21] based on the polarizable continuum model (PCM) of Tomasi et al. [22-24]. The structures of the reactants, the transition state and the products were studied using diethyl ether as solvent at the experimental temperature 298K [2]. A full optimization of the geometries [25-28] was done.

To describe the epoxy ring opening reactions of the α -chloroglycidic ester in the presence of the Lewis acid MgI_2 , we did a full optimization of the stationary points on the reaction path. This optimization was followed by a vibrational frequency calculation in order to decide if the geometry of stationary points is a minimum [26, 28] on the potential energy surface or a transition state [27, 28].

3. Results and Discussion

3.1. Mechanistic study of the reaction approach between α -chloroglycidic ester and the Lewis acid MgI_2

3.1.1. Optimal geometry and energetic aspect of the reactants

Experimentally, it was demonstrated [2] that the α -chloroglycidic ester gives four diastereoisomers (2R,1S); (2S,1R); (2S,1S) and (2R,1R) [1]. The two cis diastereoisomers (2S,1S and 2R,1R) are more stable than the trans ones. The four diastereoisomers are presented in Figure 3.

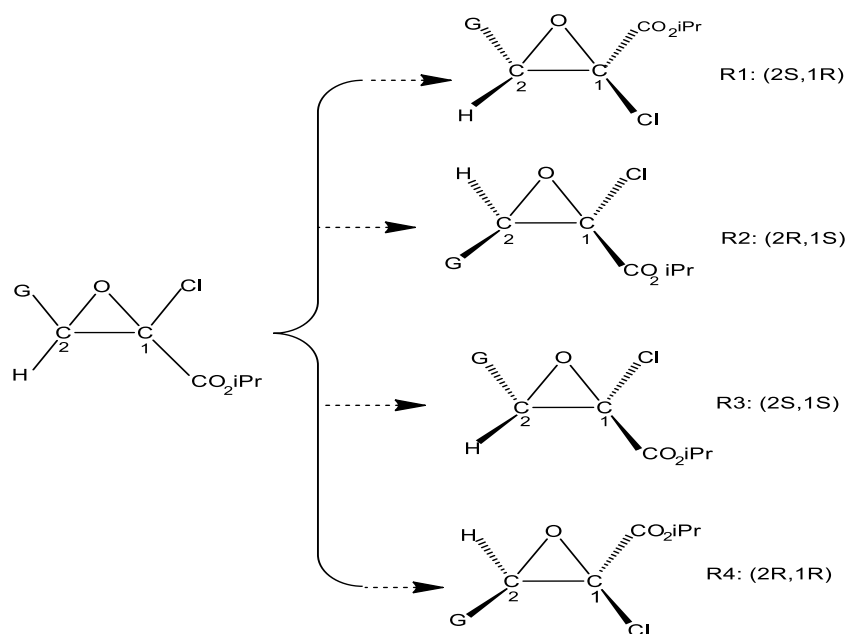


Figure 3: Four diastereoisomers of the α -chloroglycidic ester

To determine the optimal geometry of α -chloroglycidic ester, we calculated the energetic aspect and the thermodynamic parameters of the different diastereoisomers R1(2S,1R), R2(2R,1S), R3(2S,1S) and R4 (2R,1R). The results are reported in Table 1. The optimized structures of the product are represented in the Figure 4.

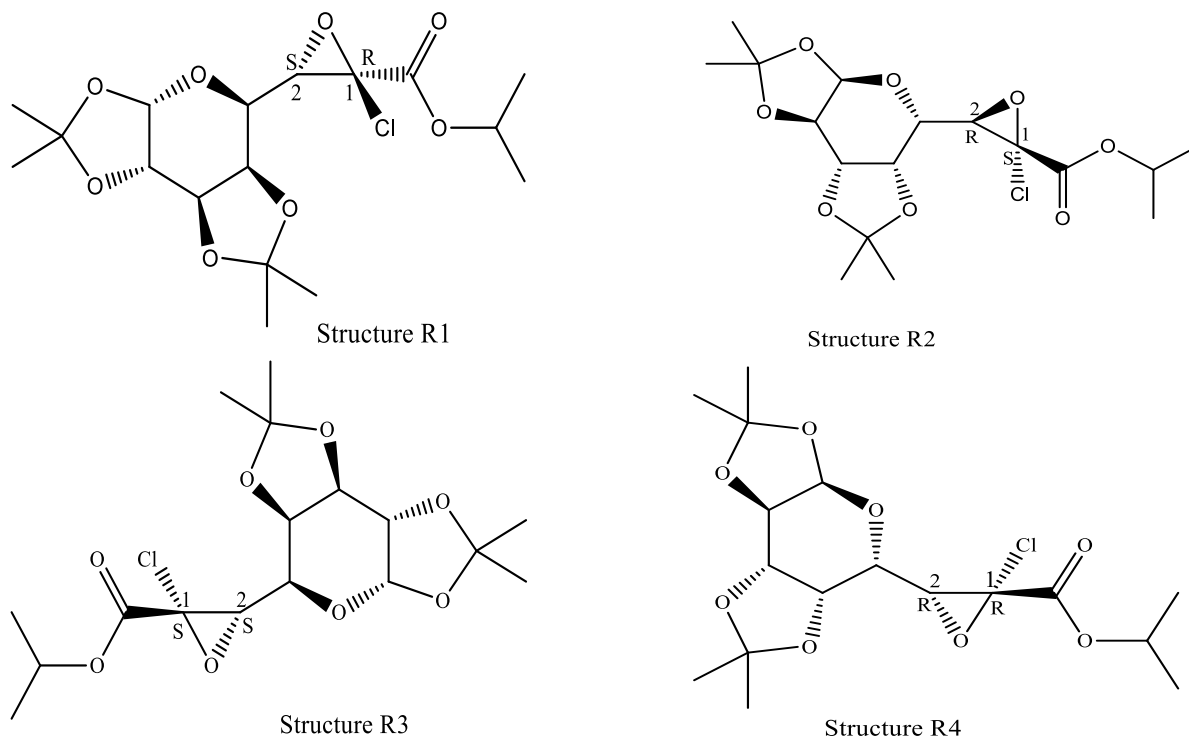


Figure 4: Optimized structures in the solution for α -chloroglycidic ester

Table 1: Energetic values and thermodynamic parameters of different diastereoisomers of chloroglycidic ester in diethyl ether solution.

α -chloroglycidic ester	E(a.u.)	G(a.u.)	H(a.u.)
(2S,1R)	-1724.822834	-1724.464177	-1724.377422
(2R,1S)	-1724.822834	-1724.464178	-1724.377422
(2S,1S)	-1724.823628	-1724.464294	-1724.378219
(2R,1R)	-1724.823534	-1724.464381	-1724.378177

Table 1, shows that the isomers Z "cis diastereoisomers" (2S,1S) and (2R,1R) are more favored thermodynamically than the isomers E "trans diastereoisomers" (2S,1R) and (2R,1S). We conclude that our theoretical studies are in agreement with the experiment [3] and with the previous study [28] carried in the THF solution at the temperature 323K. The optimized geometry of the α -chloroglycidic ester R3 is shown in Figure 5. The geometrical parameters in the two solvent diethyl ether and THF [29] are listed in Table 2. The numbering of atoms is imposed by the program package of Gaussian 09 [6].

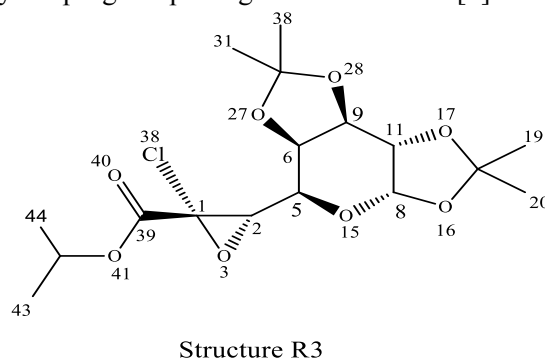


Figure 5: Structure of the α -chloroglycidic ester optimized in diethyl ether at B3LYP level.

Table 2: Structural parameters of the α -chloroglycidic ester in diethyl ether and in THF. Bond lengths are in Angstroms, bond angles and dihedral angles are in degrees.

Parameters (2S,1S)	Diethyl ether	THF
d(C ₁ -Cl ₃₈)	1.794	1.793
d(C ₁ -O ₃)	1.398	1.398
d(C ₂ -O ₃)	1.447	1.447
d(C ₂ -C ₅)	1.509	1.509
d(C ₅ -O ₁₅)	1.432	1.432
d(C ₆ -O ₂₇)	1.427	1.427
A(C ₂ -C ₅ -C ₆)	112.20	112.20
A(C ₂ -C ₁ -Cl ₃₈)	120.58	120.61
A(C ₂ -C ₅ -O ₁₅)	105.72	105.69
A(C ₂ -C ₁ -C ₃₉)	118.02	118.02
A(C ₅ -C ₆ -O ₂₇)	110.33	110.27
A(C ₁ -C ₃₉ -O ₄₁)	113.33	113.27
A(O ₃ -C ₂ -C ₅)	117.30	117.28
D(O ₃ -C ₂ -C ₅ -C ₆)	155.75	156.62
D(O ₃ -C ₁ -C ₃₉ -O ₄₀)	31.16	37.35
D(C ₁ -C ₂ -C ₅ -C ₆)	88.82	89.69
D(C ₂ -C ₅ -C ₆ -C ₉)	157.77	157.77

We conclude that the two solvents do not differ in their effect on the parameters of the optimal geometries. This is due to the fact that THF and diethyl ether both are polar solvents and belong to the same category of solvents. The temperature, these are the temperatures in which the reaction of opening of the epoxy cycle occurs.

3.1.2. Optimal geometries and energetic aspect of the products

The approach of Lewis acid MgI₂ was realized on both sides of the epoxide ring of the structure (2S,1S). This leads to the formation of two iodine pyruvic esters P1 and P2 [3]. The configuration of the asymmetric carbon atom C₁₇ is "S" and "R" respectively is schematized in Figure 6 and the energy results are reported in Table 3.

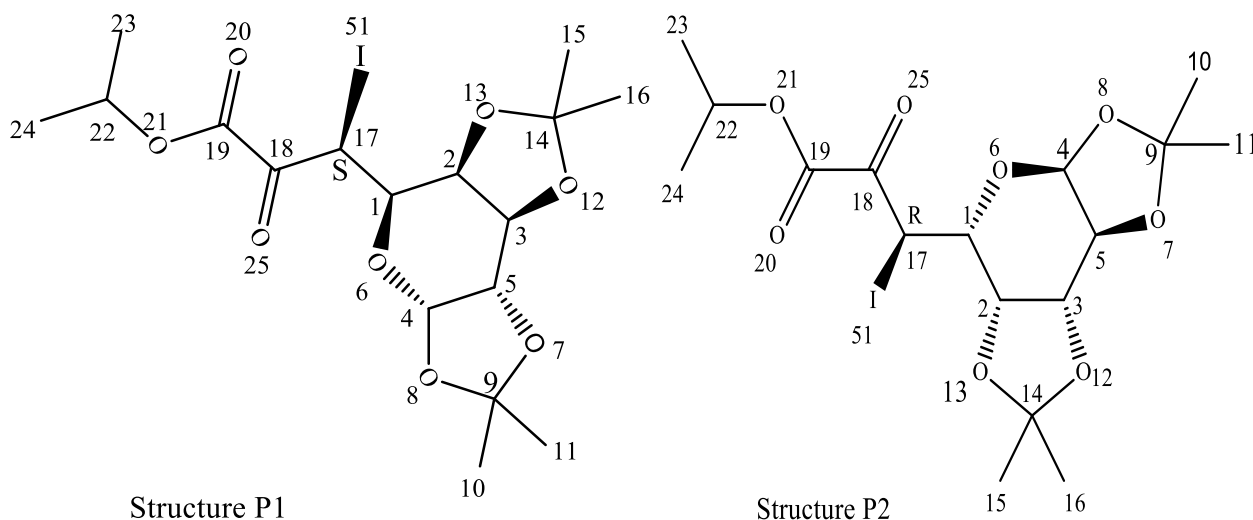


Figure 6: Optimized structures of the iodine pyruvic ester

Table 3: Energetic values and thermodynamic parameters of the structure P1 and P2 of iodine pyruvic esters.

iodine pyruvic esters	E(a.u.)	G(a.u.)	H(a.u.)
P1	-1276.056709	-1275.700184	-1275.611128
P2	-1276.048829	-1275.692853	-1275.603485

These results show that the iodine pyruvic ester P1 with configuration "S" is more stable than the iodine pyruvic ester P2 with configuration "R". This is in agreement with the experiments [3] and with previous theoretical studies [28] concerning the chloropyruvic ester. We report in Table 4 some parameters values of the optimal geometry (P1) obtained.

Table 4: Structural parameters of the optimal geometry (P1) of iodine pyruvic ester.

Bond length(Å)		Valence angle (degrees)		Dihedral angle (degrees)	
C ₁₇ -I	2.25	I-C ₁₇ -C ₁	111.34	O ₆ -C ₁ -C ₁₇ -I	-62.67
C ₁₈ -O ₂₅	1.21	I-C ₁₇ -C ₁₈	103.94	O ₆ -C ₁ -C ₁₇ -C ₁₈	179.65
C ₁₇ -C ₁	1.52	C ₁₇ -C ₁₈ -O ₂₅	123.64	I-C ₁₇ -C ₁ -C ₂	177.41
C ₁ -O ₆	1.43	C ₁₇ -C ₁ -O ₆	107.16	C ₂ -C ₁ -C ₁₇ -C ₁₈	59.73

3.1.3. Optimal geometry and energetic aspect of the transition structure

The reaction mechanisms of the isomerization of the α -chloroglycidic ester in the presence of Lewis acid MgI₂ are presented in this section. Theoretically several mechanisms are plausible:

1- Passing through the formation of the α -chloropyruvic as an intermediate, which is forming from the α -chloroglycidic ester.

2- Concerted mechanism in which the iodine atom of the Lewis acid MgI₂ attacks the carbon C₂. This leads to the opening of the epoxy (epoxide) ring, the formation of a ketone bond and the breaking of the bond between the chlorine atom and the carbon atom C₁.

3- Cationic mechanism, which is very similar to the concerted mechanism. However, here the atom C₂ attacked by the iodine ion is a carbocation instead of an uncharged atom.

Experimental studies indicated [2, 3] that the reaction path of α -iodine pyruvic ester cannot pass through the α -chloropyruvic ester as an intermediate [2, 3]. Experiment also found that the mechanism is concerted [3, 4].

All these results were verified by our calculations.

3.1.3.1. Structure and energetic aspect of the chloro pyruvic ester as an intermediate

The optimal geometry of the α -chloropyruvic ester was determined. The optimal geometry is schematized in Figure 7. Some parameter values are given in Table 5.

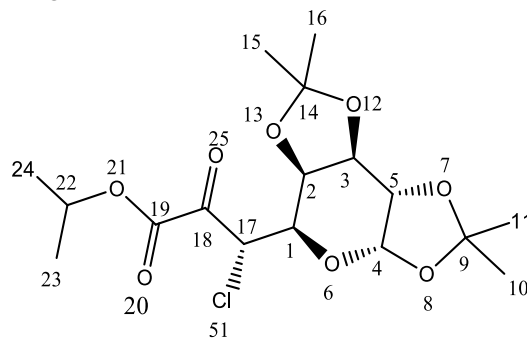


Figure 7: Optimized structure of chloropyruvic ester

Table 5: Structural parameters of the optimal geometry of chloropyruvic ester.

Bond length(Å)		Valence angle (degrees)		Dihedral angle (degrees)	
C ₁₇ -Cl	1.83	Cl ₅₁ -C ₁₇ -C ₁	111.07	O ₆ -C ₁ -C ₁₇ -Cl ₅₁	-62.51
C ₁₈ -O ₂₅	1.21	Cl ₅₁ -C ₁₇ -C ₁₈	104.41	O ₆ -C ₁ -C ₁₇ -C ₁₈	179.97
C ₁₇ -C ₁	1.52	C ₁₇ -C ₁₈ -O ₂₅	123.49	Cl ₅₁ -C ₁₇ -C ₁ -C ₂	177.33
C ₁ -O ₆	1.42	C ₁₇ -C ₁ -O ₆	106.47	C ₂ -C ₁ -C ₁₇ -C ₁₈	59.81

The energetic and thermodynamic properties of the reactants, the products, and the chloropyruvic ester as an intermediate are regrouped in Table 6.

Table 6: Energetic values and thermodynamic parameters of reactants, products and of the intermediate state.

		E(a.u.)	G(a.u.)	H(a.u.)
Isolated Species	Chloroglycidic ester	-1724.823628	-1724.454294	-1724.378219
	MgI₂	-223.110409	-223.137262	-223.102948
	Chloropyruvic ester	-1724.856808	-1724.497730	-1724.410750
	Iodine pyruvic ester	-1276.056709	-1275.700184	-1275.611128
	Cl-Mg-I	-671.888948	-671.914622	-671.881318
Reactants	Chloroglycidic ester + MgI₂	-1947.934037	-1947.601556	-1947.481167
Intermediate Reactionnal	Chloropyruvic ester + MgI₂	-1947.967217	-1947.634992	-1947.513698
Products	Iodine pyruvic ester+ Cl-Mg-I	-1947.945657	-1947.614806	-1947.433495

We evaluated thermodynamic properties characterizing the formation reaction of the iodine pyruvic ester from the chloropyruvic ester. The results show a positive enthalpy and a positive Gibbs free energy which are 50.32 kcal/mol and 12.67 kcal/mol, respectively. We can conclude that the formation reaction of iodine pyruvic ester from the chloropyruvic ester is endothermic and thermodynamically impossible. These findings are in good agreement with the experiment [2] which reveals that the reaction path cannot pass through the α -chloropyruvic ester.

3.1.3.2. Energies of the transition state

The experimental studies [2, 3] indicated that the mechanism of the epoxy ring opening reaction of the α -chloroglycidic ester (Fig. 2), is cationic with presence of a pair of intimate ions (TS1) [2], or concerted (TS2) [3, 4]. The different optimized structures are illustrated in Figure 8. The total energies of all stationary points (reactants, transition structures and products) and relative energies of the transition states are summarized in Table 7.

According to the relative energies, the activation barriers in the cationic and the concerted mechanism are 31.09 kcal/mol for TS1 and 28.23 kcal/mol for TS2, respectively. These values are very close. Their relative energy difference is about 2.8 kcal/mol. This proves that the both mechanisms are possible. This argument will be verified later by calculating the variation of binding order [29, 30] along the reaction process. This make it possible to calculate the synchronicity index (S_y) given by the formula of Moyano et al. [31] (see Table 8).

Table 7: Energies of different stationary points and relative energies of reactants, transition states and products in solution.

Stationary Points	E(a.u)	E _R (kcal/mol)
Chloroglycidic ester	-1724.823628	---
MgI ₂	-223.110409	---
E _{Reactants}	-1947.934037	---
TS1	-1947.884497	31.09
TS2	-1947.889044	28.23
Iodine pyruvic	-1276.056709	---
Cl-Mg-I	-671.888948	---
E _{Products}	-1947.945657	-7.29

3.1.1.3. Geometries of the transition structures

One of the focuses of our study was the understanding of the mechanism of the epoxy ring opening reactions of the α -chloroglycidic ester (fig.2). For this, we were interested in the determination of the transition structures TS1 and TS2. Where TS1 is a pair of intimate ions with a nucleophilic carbocation attack by Iodine on the same side as the leaving group. TS2 is the transition state of the concerted mechanism. In TS1 and TS2, the atom C₂ keeps its configuration "S" like in the cis diastereoisomers of chloroglycidic esters, which allows to leads to the most stable iodine pyruvic ester. These structures were determined through vibrational frequency analysis and were characterized by a single imaginary frequency. We found 132.7i and 209.3i cm⁻¹ for the cationic and the concerted mechanism respectively.

Figure 8 schematically shows the optimized geometries of the transition states in the two mechanisms.

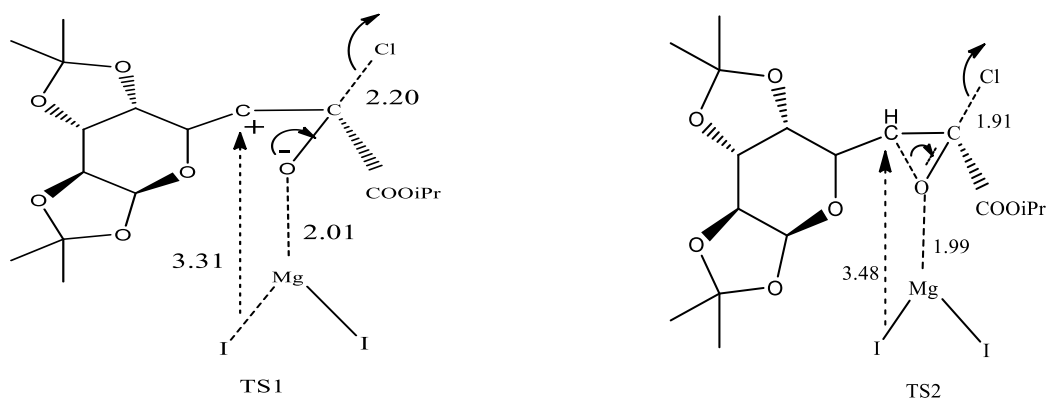


Figure 8: Structures of the transition states in the cationic (TS1) and in the concerted (TS2) mechanisms.

We noted that the length of the newly formed bond (C₂-I) and (C₁-O₃) and the breaking bond (C₂-O) and (C-Cl) are similar in the cationic and the concerted mechanism. In fact, the lengths of the bond C₂-I in the cationic and in the concerted mechanisms are equal to 3.31 and 3.48 Å, respectively, while the bond lengths of the C₁-Cl are equal to 2.20 and 1.91 Å, respectively. The potential energy profile corresponding to this reaction is reported in Figure 9.

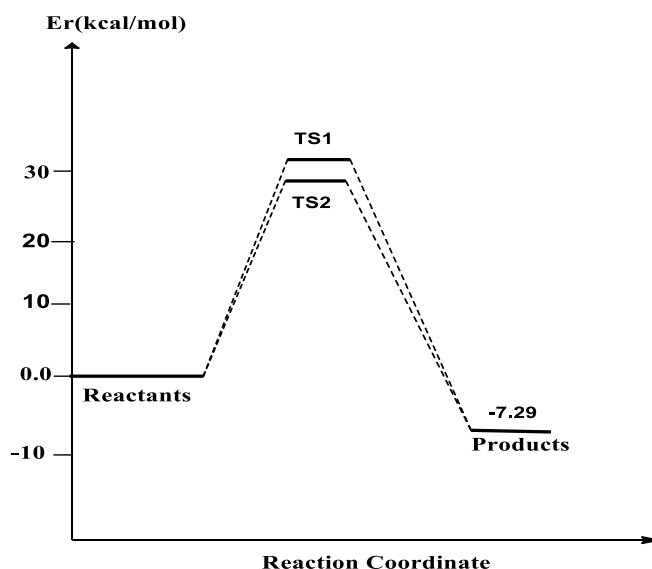


Figure 9: Energy profile of the reaction between α -chloroglycidic esters and the Lewis acid MgI_2 in diethyl ether solution.

3.2. Analysis of bond orders in the transition state

The bond order (BO) [29, 30] allows a more precise analysis of the ring opening evolution of the α -chloroglycidic esters. We also used this theoretical tool to study the molecular mechanism. Wiberg bond indices were computed by using NBO [29, 30] population analysis, the results are reported in Table 8.

The process of bond breaking and bond forming along the reaction path can be analyzed employing the synchronicity index (S_y) given by the formula of Moyano et al. [31] estimated by :

$$S_y = 1 - \frac{\sum_{i=1}^n |\delta B_i - \delta B_{av}|}{2n - 2}$$

where n is the number of bonds directly involved in the reaction and δB_i is the relative variation of the Wiberg bond index which is calculated as:

$$\delta B_i = \frac{B_i^{TS} - B_i^R}{B_i^P - B_i^R}$$

R, TS and P refer to reactants, transition states and products respectively. The average value δB_{av} is obtained from:

$$\delta B_{av} = n^{-1} \sum_{i=1}^n \delta B_i$$

The percentage of variation (% EV) [33] of the bond order is calculated as: %EV= $100\delta B_i$. Thus, (S_y) is unity for a fully synchronous process and zero for a fully asynchronous process.

The percentage values of the variation of the new bond (C₂-I and C₁-O₃) were calculated using the formula of Moyano [31]. They are (66% and 52%), in the cationic mechanism but (30% and 29%) in the concerted mechanism. However, the percentages of variation of the breaking bond C₂-O₃ and C-Cl are (96% and 61%), in the cationic mechanism and (68% and 29%) in the concerted mechanism. An analysis of these values reveal that the variation of the breaking bond and the forming bond takes place in the same way for the two mechanisms.

To determine the evolution process of the bonds along the reaction path, we calculated the synchronicity index (S_y) [31]. The DFT calculations give similar values for TS1 and TS2. In fact, we found 0.85 and 0.90 in the cationic and the concerted mechanisms, respectively.

All this proves that the ring opening mechanism of α -chloroglycidic esters in the presence of the Lewis acid MgI₂ can be considered cationic with a pair of intimate ions or concerted. We conclude that our theoretical results are in good agreement with the experiment [3, 4].

Table 8: Wiberg bond orders and evolution percentage of the bond breaking and forming in cationic and concerted mechanisms

	TS1					
	C ₂ -I	C ₁ -O ₃	Mg-I	Mg-O ₃	C ₂ -O ₃	C ₁ -Cl
B_i^R	0.	0.95	----	0.00	0.95	0.99
B_i^{TS}	0.60	1.47	----	0.37	0.04	0.39
B_i^P	0.91	1.95	----	0.00	0.00	0.00
%EV	66	52	----	----	96	61
S_y	0.85					
	TS2					
	C ₂ -I	C ₁ -O ₃	Mg-I	Mg-O ₃	C ₂ -O ₃	C ₁ -Cl
B_i^R	0.00	0.95	0.00	0.00	0.95	0.99
B_i^{TS}	0.27	1.24	0.35	0.29	0.30	0.70
B_i^P	0.90	1.95	0.00	0.00	0.00	0.00
%EV	30	29	----	----	68	29
S_y	0.90					

Conclusion

The DFT study of the chloroglycidic ester ring opening in the presence of the Lewis acid MgI₂ shows that the cis diastereoisomers of chloroglycidic esters and the iodine pyruvic esters with configuration "S" are more stable than the trans diastereoisomers of chloroglycidic esters and the iodine pyruvic esters with configuration "R". These results are in agreement with the previous theoretical results and with the experiment.

The transition state was found in concerted and cationic mechanisms and was characterized by a single imaginary frequency in the Hessian matrix.

To confirm the appropriate mechanism, we analyzed the evolution of the bond order in the reaction process and the values of the synchronicity index. We show that the ring opening mechanism of α -chloroglycidic esters in the presence of the Lewis acid MgI₂ can be considered cationic or a concerted.

The relative energy difference of the transition states obtained in the two mechanisms is low. We can explain this by the fact that the attack of the iodine atom on the carbon C₂ followed by opening of the epoxy ring and the departure of chlorine atom is rapid, so the intermediate cannot be formed.

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