



## THEORETICAL STUDY OF CHLORINATION REACTION OF NITROBENZENE FROM DFT CALCULATIONS

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### Abstract

The geometric parameters of stationary points on the potential surface energy of the chlorination reaction of nitrobenzene in the presence of Aluminium chloride as catalyst were investigated theoretically by hybrid DFT (Density Functional Theory) calculations in order to determine his general reaction mechanism in gas phase and in solution. The results obtained by DFT have been compared with CCSD(T) method which is the most powerful post-Hartree Fock method in terms of inclusion of dynamic correlation. Although the electrophilic substitution reaction is widely taught in most courses in organic chemistry, the mechanism has been very few studied theoretically. The results obtained in gas phase are consistent with the traditional description of these reactions: the orientation of this substitution in meta position depends on the stability of a reaction intermediate (Wheland said). Without taking in consideration the reactants and products, six stationary points are found on the potential surface energy of this reaction. The reaction has also been studied in the presence of solvent and we've noted that the influence of solvent decreases the electrostatic attraction on the Wheland complex, but the general reaction mechanism remains unchanged in solution.

### Keywords:

DFT; PCM; Nitrobenzene; Chlorination; Reaction Mechanism; Electrophilic substitution

**Academic Discipline And Sub-Disciplines:** Physical and Theoretical chemistry

**Subject classification:** Modelization of reaction mechanism with quantum chemical method

**Type (method/approach):** Theoretical and calculation with DFT (Density Functional Theory) method

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## 1. Introduction

Many researchers are very interested to study theoretically the reactivity or the geometry of molecules with quantum chemical methods. The concept of reaction mechanism plays a major role in organic chemistry for the comprehension of reaction processes. The description of reaction mechanism associated to a given reaction is based on the calculation of the geometries and the energies of stationary points from reactants to products via transition states and possible intermediates on the potential surface energy of Born Oppenheimer [1-5]. The mechanism of electrophilic substitution of non substituted benzene has been studied theoretically [6-11]. A relative recent paper has confirmed the presence of many intermediates in the case of chlorination reaction of non substituted benzene catalysed by  $\text{AlCl}_3$ : Two complexes  $\Pi$  and one  $\sigma$  have been characterized in this study [12]. Very recently, thermochemical parameters and IR spectra of chlorinated isomers of nitrobenzene have been calculated and showed that theoretical parameters are closed to experimental data [13]. The influence of nitrobenzene as a solvent in this reaction permits to obtain the activation barriers which are much closed to experimental values [14-16]. In the electrophilic substitution with benzene derivatives, the orientation of the second substitution depends on the nature of the first substituent and the stability of the intermediate  $\sigma$  called Wheland complex [17]. Experimental data have proved that these stable complexes  $\sigma$  exist and are responsible of the orientation of the substitution reaction [18-28].

In this work, we've propose to explore the potential surface energy of the chlorination reaction of nitrobenzene (which have an acceptor substituent of electron) in the presence of Aluminium chloride as catalyst in order to determine the geometry of all stationary points and his general reaction mechanism in gas phase and in solution before validate or invalidate the Wheland interpretation which said that the orientation of this reaction depends on the stability of a reaction intermediate.

## 2. Theoretical calculations

In the molecular orbital calculation, the chemical species participating in the chlorination reaction are assumed to be nitrobenzene ( $\text{C}_6\text{H}_5\text{-NO}_2$ ), molecular chlorine ( $\text{Cl}_2$ ) and Lewis acid, so that the reacting system is considered to be neutral at the starting point and to be more realistic in describing the overall reaction pathway. The aluminium chloride monomer  $\text{AlCl}_3$  is adopted as a Lewis acid catalyst in the present study. The overall reaction is formally written as follows:



The calculations have been carried out at the hybrid Hartree-Fock density functional method B3LYP level [29] and CCSD(T) level [30-33] with the basis 6-31G\*\* in Gaussian 03 software [34]. The vibrational analysis has been carried out at each optimized geometry with B3LYP level in order to confirm whether the obtained structure is located at energy minimum or Transition State; all positive for a minimum and one imaginary for a Transition State (TS).

## 3. Results and discussions

The relative energies obtained for the chlorination of nitrobenzene in the presence of Aluminium Chloride as catalyst in gas phase are in Table 1 below:

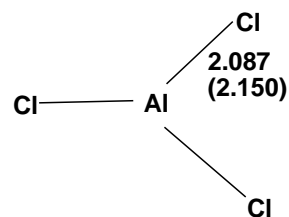
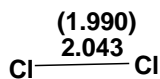
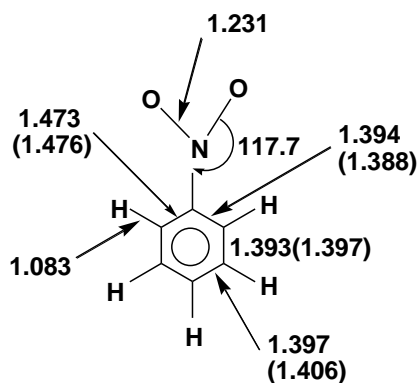
**Table1** Relative energies ( $\Delta E$ ) for chlorination reaction of nitrobenzene in gas phase; the reactants are taken as reference. The values of relative energies with CCSD(T) method are obtained from a single point calculation at the B3LYP optimized geometry.

	B3LYP/6-31G**			CCSD(T)/6-31G**		
	$\Delta E$ (Kcal/mol)			$\Delta E$ (Kcal/mol)		
	ortho	meta	para	Ortho	meta	para
Reactants	0.0	0.0	0.0	0.0	0.0	0.0
$\Pi_1$	-7.0	-7.0	-7.0	-6.0	-6.0	-6.0
$\text{TS}_1$	+0.2	-0.9	+2.2	+4.8	+0.8	+2.1
$\sigma_1$	-9.7	-11.7	-9.4	-22.5	-24.7	-22.9
$\sigma_2$	-11.0	-14.1	-10.2	-15.4	-17.8	-13.7
$\text{TS}_2$	-9.0	-9.1	-7.0	-13.4	-10.2	-11.3
$\Pi_2$	-28.8	-35.4	-35.5	-37.5	-43.0	-43.9
Products	-19.4	-26.6	-27.4	-25.5	-31.7	-32.1

### 3.1. Reactants and products

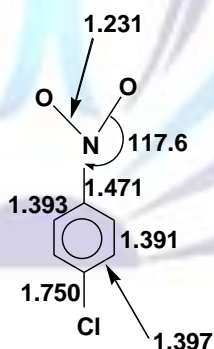
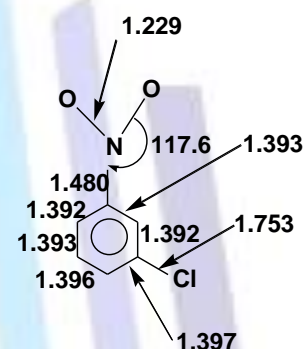
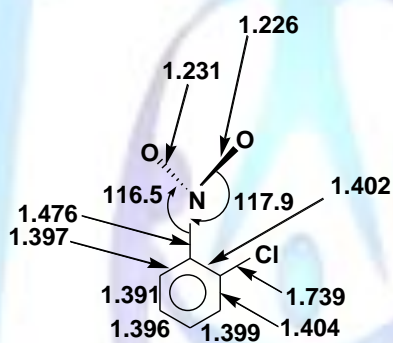


The geometric parameters of reactants are:



The optimized geometric parameters at B3LYP level obtained of reactants are in good agreements with the experimental values [35-40] in parentheses.

The optimized structures of products obtained with DFT are below (Units of bond lengths and bond angles of all parameters are Å and degrees (°), respectively.):



By comparing the three products of the chlorination reaction of nitrobenzene, the energy of ortho product is higher (-19.3 kcal/mol) than the meta and para products with the energies which are very closed (between -26.6 and 27.4 kcal/mol). It is the same situation with CCSD(T) calculation where the relative energies of products follows the same order of stability as in DFT calculations.

The three products have a differentiation on thermodynamic way. Geometrically, there is an important distortion towards NO<sub>2</sub> fragment in the ortho product than meta and para product. The two distances of N-O bonds are different in ortho product; but in meta and para products, these two N-O bonds have the same distance. The distance of C-Cl bond is too small in ortho product (1.739 Å) compared to the same bond in meta and para product (1.753 and 1.750 Å respectively).

### 3.2. Reactional intermediates

### 3.2.1. $\Pi_1$ complex

For the three attack ways, one unique  $\Pi_1$  complex has been localized corresponding for a fixation on meta position. The optimized structure of this complex is in Fig. 1 below (Units of bond lengths and bond angles of all parameters are Å and degrees (°), respectively):

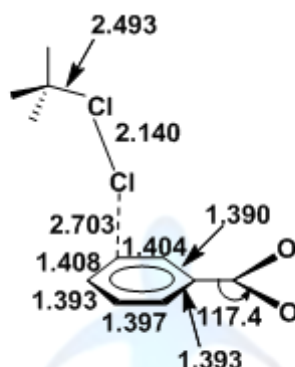


Fig. 1  $\Pi_1$  complex meta

Concerning the above-mentioned evidences, the complex formed by the interaction among nitrobenzene,  $\text{Cl}_2$  and  $\text{AlCl}_3$  may not be highly polarized species. Since the stabilization of the  $\Pi_1$  complex is mainly caused by van der Waals forces, there is no energy barrier to form such weakly bound  $\Pi$ -type complex in the initial stage of the reaction. This  $\pi_1$  complex is formed by weakness interaction between the reactants (nitrobenzene, dichlore and aluminium chloride). The optimized geometry show that the C-Cl bond increases from 2.043 Å in the reactant to 2.140 Å in the stabilized complex. It is the same situation for the Al-Cl bond which increases from 2.087 to 2.493 Å. The relative energy of stabilization of the  $\pi_1$  complex is -7 kcal/mol compared to isolated reactants. With CCSD (T) method, this stabilization energy becomes -6.0 kcal/mol.

### 3.2.2. Transition States $\text{TS}_1$

The three transition states which permit the formation of  $\sigma_1$  complexes localized for the three ways of attack are represented in Fig. 2 below (Units of bond lengths and bond angles of all parameters are Å and degrees (°) respectively):

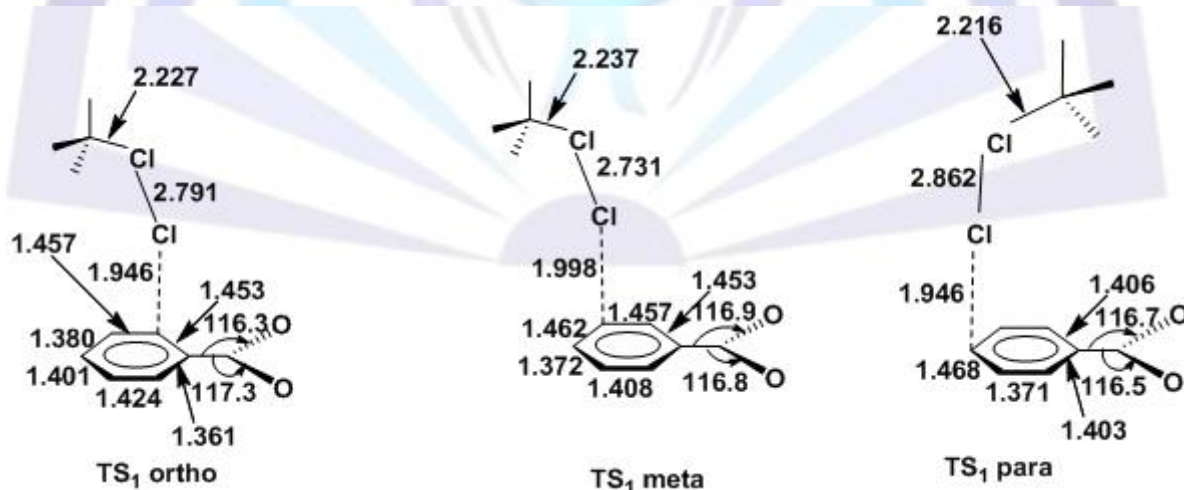


Fig 2. Transition States  $\text{TS}_1$  in the cases of ortho, meta and para position respectively

The relative energies obtained for  $\text{TS}_1$  in the case of meta approach is smaller (-0.9 kcal/mol) than the one obtained for ortho (+0.2 kcal/mol) and para (+2.2 kcal/mol). The energy barrier from  $\pi_1$  complex for ortho position is 7.2 kcal/mol, 6.1 kcal/mol for meta and 9.2 kcal/mol for para. From CCSD(T) calculations, we've obtained three  $\text{TS}_1$  with different order of stability with DFT calculations for ortho and para positions; the meta position remains the most stable of three of them: The relative energy obtained with CCSD(T) method on  $\text{TS}_1$  gives the values of +14.7 kcal/mol for ortho, +9.9 kcal/mol for meta position and +13.8 kcal/mol for para position.

### 3.2.3. Intermediates complexes $\sigma$ (sigma)

The system which we call  $\sigma$  complexes consists of two parts: cation being the traditional  $\sigma$ -complex  $\text{C}_6\text{H}_5\text{CINO}_2^+$  and the counter anion  $\text{AlCl}_4^-$  part. These two parts are mutually interacting with Coulombic forces. Since this species are purely

ionic, the Coulombic interaction between  $C_6H_5CINO_2^+$  and  $AlCl_4^-$  causes the large stabilization of the  $\sigma$ -complexes intermediate whose energies are much more stable than the energy of the  $\Pi_1$  complex.

But in this study, the intermediates  $\sigma_1$  (sigma) obtained for the chlorination reaction of nitrobenzene are elucidated in Fig. 3 below (Units of bond lengths and bond angles of all parameters are Å and degrees (°) respectively.):

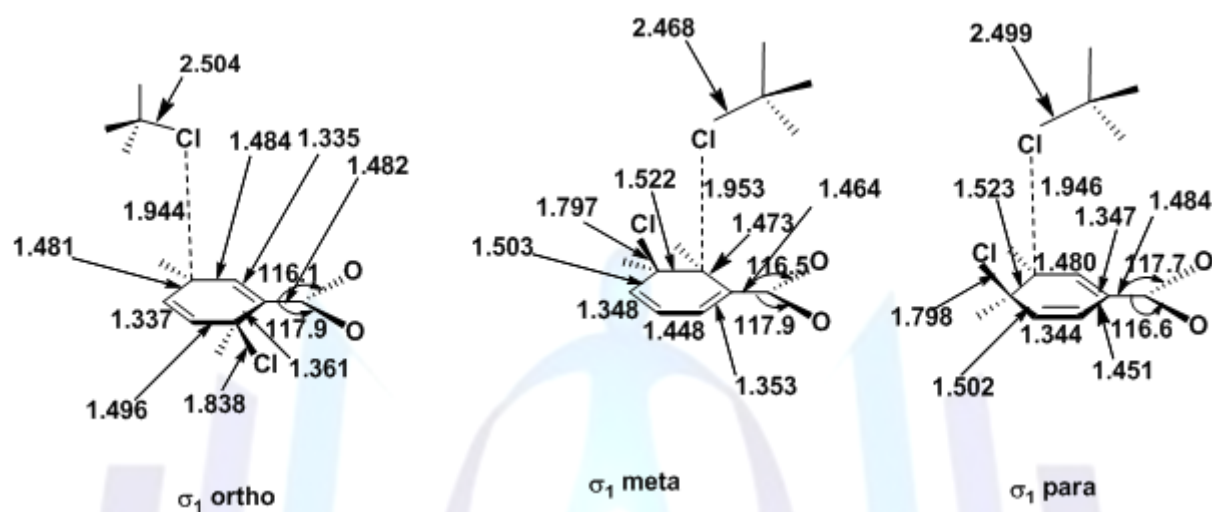


Fig 3.  $\sigma_1$  (sigma) complexes in the cases of ortho, meta and para position respectively

In these structures of  $\sigma_1$ , the counter ion  $AlCl_4^-$  creates a bond between one Cl atom and one C of the benzenic cycle. We've obtained then two C-Cl bonds in these complexes  $\sigma_1$ . These two C-Cl bond are in ortho positions each others for meta and para complexes and in para positions for ortho complex. In other hand, this second C-Cl bond formed with the C of the benzenic cycle is longer than the first one (see Fig. 2). The formation of this second C-Cl bond must be caused by the electrostatic attraction between the charged entities. The differences of relative energy between the charged entities in its cationic form and the  $AlCl_4^-$  anion for the different positions and correspondent  $\sigma_1$  complexes are in table 2 below:

**Table 2** Differences of relative energy at the B3LYP level between the charged entities in gas phase between the moieties listed, in its cationic form and the  $AlCl_4^-$  anion.

Position	Nitrobenzene (kcal/mol)	Aniline (kcal/mol)	Non substituted Benzene (kcal/mol)	Chlorobenze ne (kcal/mol)
ortho	-85.5	-74.9		-74.9
meta	-84.7	-74.2	-78.9	-76.7
para	-84.2	-76.1		-72.0

From this Table 2, we realize that in the case of non substituted benzene [12], the electrostatic attraction is -78.9 kcal/mol. In the case of aniline, we have the activation of benzenic cycle with group  $\pi$  donor which decreases the electrostatic attraction and increases the reactivity of benzenic cycle. The electrostatic attraction is important in the case of nitrobenzene with the group  $\pi$  acceptor which decreases the reactivity of benzenic cycle. In the case of chlorobenzene, we observe the values of electrostatic attraction (between -72.0 and -76.7 kcal/mol) very closed with the case of aniline. In the geometric consideration, the distance C-N is smaller in the  $\sigma_1$  complex meta (1.464 Å) than in the  $\sigma_1$  complex ortho (1.482 Å) and para (1.484 Å). It is the same situation for the distance Al-Cl which is smaller in meta complex (2.468 Å) than ortho complex (2.504 Å) and para (2.499 Å).

The formation of  $\sigma_1$  complex (between -9.4 kcal/mol and -11.7 kcal/mol) is less exothermic than the case of aniline; these values are smaller than the case of non substituted benzene (-20 kcal/mol). This stability is explained by the group  $\pi$  acceptor which is desactivant for the substitution. The relative energy of  $\sigma_1$  meta (-9.7 kcal/mol) and the  $\sigma_1$  para (-9.4 kcal/mol). With CCSD(T) method the para complex is a little more stable (-22.9 kcal/mol) than the ortho complex (-22.5 kcal/mol); meta complex remains the most stable (-24.7 kcal/mol) of three of them.

With the aim to proceed at the second step of the chlorination reaction of nitrobenzene, three  $\sigma_2$  complexes are been localized, see Fig. 4 below: (Units of bond lengths and bond angles of all parameters are Å and degrees (°) , respectively.):

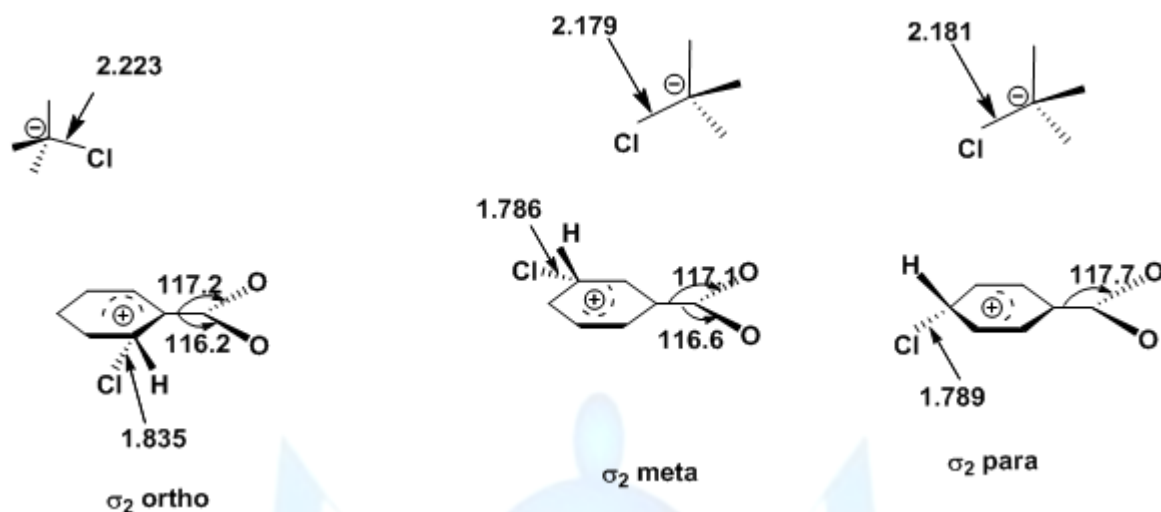


Fig 4.  $\sigma_2$  (sigma) complexes in the cases of ortho, meta and para position respectively

The structures of  $\sigma_2$  complexes are different of the ones of  $\sigma_1$ :  $\sigma_2$  complex presents one C-Cl bond as in the case of non substituted benzene [12]. These  $\sigma_2$  complexes are more stable than  $\sigma_1$ . The relative energies are -11.0 (ortho), -14.1 (meta) and -10.2 kcal/mol (para). The CCSD(T) calculations on the geometry of  $\sigma_2$  confirm this order of stability: the relative energies obtained with this method are -15.4 (ortho), of -17.8 (meta) and -13.7 (para) kcal/mol.

### 3.2.4. Transition States TS<sub>2</sub>

Three structures correspondent to the second transition states have been localized, see Fig. 5 (Units of bond lengths and bond angles of all parameters are Å and degrees (°), respectively.):

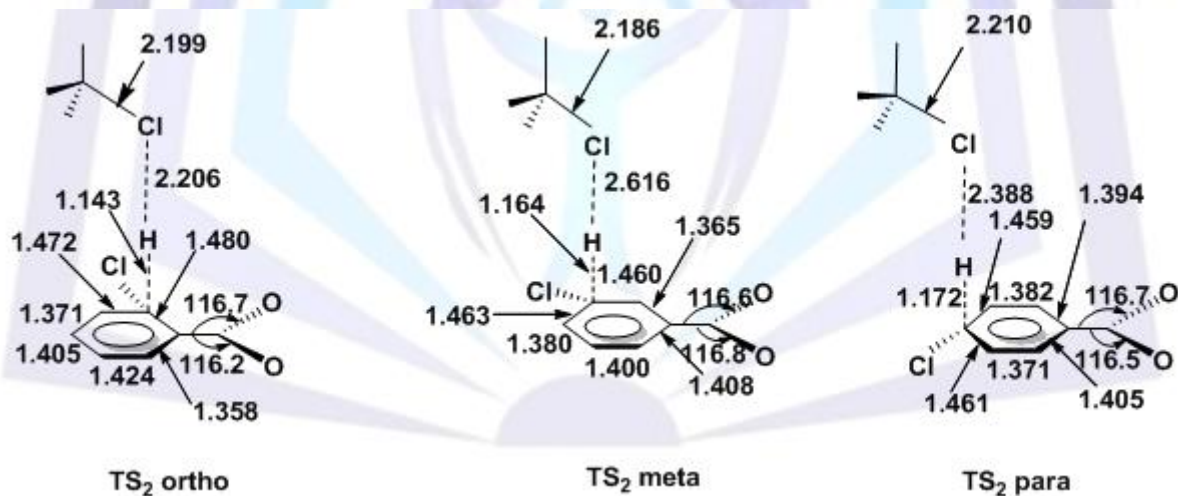


Fig 5. Transition States TS<sub>2</sub> in the cases of ortho, meta and para position respectively

The elimination process of hydrogen atom is done in concerted manner as in the case of non substituted benzene. The relative energies correspondent to transition states are equal to -9.0 kcal/mol for ortho approach, -9.1 kcal/mol for meta and -7.0 kcal/mol for para. The energy barrier obtained from  $\sigma_2$  for ortho position is -2 kcal/mol, 5 kcal/mol for meta and 3.2 kcal/mol for para.

### 3.2.5. $\Pi_2$ ( $\pi_2$ ) complexes

After passing through the second transition state TS<sub>2</sub>, the system would lead to the products. The optimized structures starting from TS<sub>2</sub> are shown in Fig. 6. These products complexes consists the donor-acceptor interaction between HCl and AlCl<sub>3</sub> and the  $\Pi$ -type hydrogen bonding between HCl and chloro nitro benzene. These structures can be called as the second  $\Pi$ -complex. Since one of the C-C  $\Pi$ -bonds of the nitrobenzene ring interacts with the hydrogen atom H of HCl which was originally a hydrogen atom of reactant nitrobenzene.  $\Pi_2$  complexes obtained for the chlorination reaction of nitrobenzene are illustrated in Fig. 6 below (Units of bond lengths and bond angles of all parameters are Å and degrees (°), respectively.):

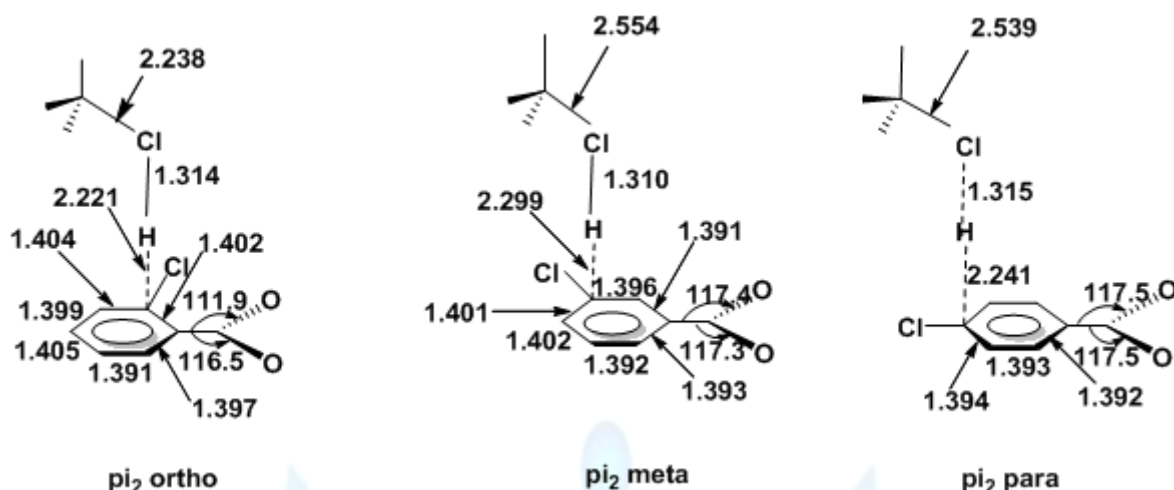


Fig 6.  $\pi_2$  complexes in the cases of ortho, meta and para position respectively

The complexes  $\pi_2$  meta and para have the same relative energy ( $\approx -35.5$  kcal/mol) which is lower than  $\pi_2$  complex ortho ( $-28$  kcal/mol). For the final products, we've obtained the same order of stability. These results are well confirmed by CCSD(T) single point calculations.

The global mechanism of chlorination reaction of nitrobenzene in the presence of aluminium chloride is summarized in Fig. 7 below:

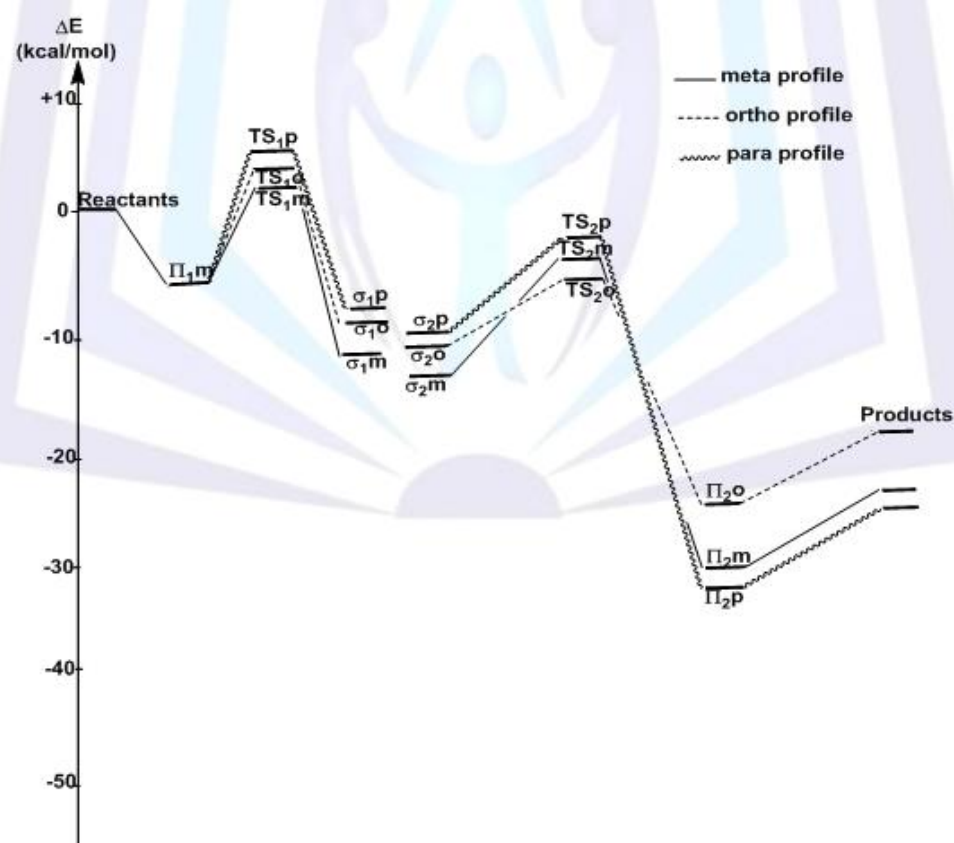


Fig 7. Mechanisms in gas phase at B3LYP level of electrophilic substitution of chlorination reaction of nitrobenzene in ortho, meta and para position respectively

In the three cases, the limitant reaction is the transformation of  $\pi_1$  to  $\sigma_1$  via transition state TS1. In this reaction, the final product formed easily is the one that  $\pi_1$  and intermediate is formed rapidly (reaction with kinetic control). The meta way is favoured compared to ortho and para ways. This permit us to validate the  $\pi_1$  and intermediate which said that the orientation of chlorination reaction of nitrobenzene is governed by the stability of  $\pi_1$  and complex ( $\sigma_1$  or  $\sigma_2$ ).

### 3.3. Solvent effect on the potential surface energy

The presence of acetonitrile as solvent in the chlorination reaction of nitrobenzene with the continuum model (PCM) [41-44] don't have an important difference on the reactants: the distance C-N in the nitrobenzene decreases from 1.473 Å in gas phase to 1.468 Å in solution, N-O bond from 1.231 Å in gas phase to 1.233 Å in solution. It is the same situation on products where we did not noted a significant difference and the energies of products follows the same order of stability in gas phase and in solution for the three reactions.

In the other hands the presence of acetonitrile as solvent bring an important modification on the structures of wheland complexes ( $\sigma_1$ ) where the second C-Cl bond that has been formed with the benzenic cycle has disappeared in solution (see Fig. 8) but the reaction mechanism remains unchanged in solution: we've obtained the same profiles as in gas phase for the three reactions.

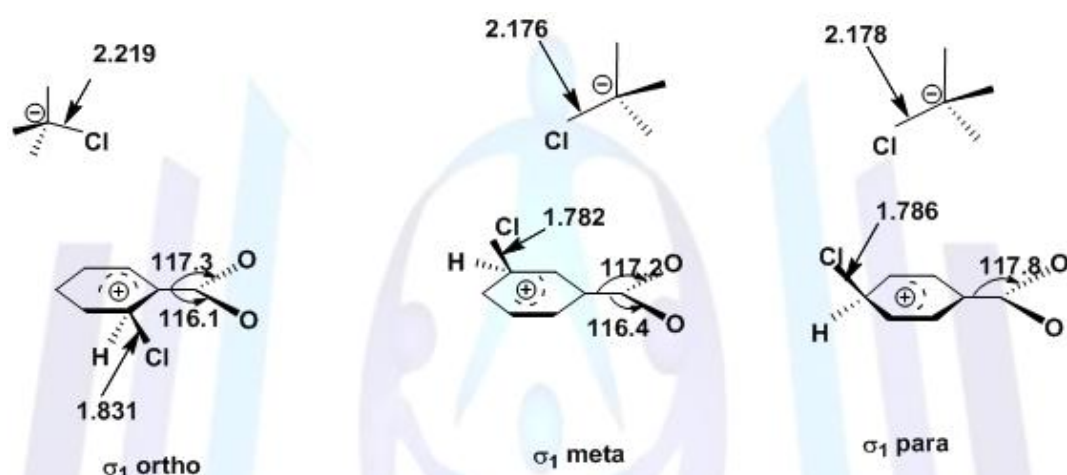


Fig 8.  $\sigma_1$  (sigma) complexes in solution in the cases of ortho, meta and para position respectively

With the influence of solvent, the differences of relative energy between the charged entities for the different positions and correspondent  $\sigma_1$  complexes are in Table 3 below:

**Table 3** Differences of relative energy at the B3LYP level between the charged entities in solution between the moieties listed, in its cationic form and the  $\text{AlCl}_4$  anion.

Position	Nitrobenzene (kcal/mol)	Aniline (kcal/mol)	Non substituted Benzene (kcal/mol)	Chlorobenzene (kcal/mol)
ortho	-4.0	-0.7		-1.4
meta	-5.1	-2.7	-1.5	-1.5
para	-4.0	-2.4		-0.2

This Table 3 shows that in the presence of solvent, the electrostatic attraction between the charged entities decreases considerably for the three reactions (see Tables 2 and 3). This diminution of electrostatic attraction explains the disappearance of the second bond C-Cl observed in Wheland complex  $\sigma_1$  in gas phase. This means that this second C-Cl bond was essentially an ionic bond. There is a diminution of activation barrier on the potential surface energy in solution on the second step of the reaction (between  $\sigma_2$  and  $\pi_2$ ) for the three positions: for ortho attack, this activation barrier decreases from 2.5 kcal/mol in gas phase to 1.7 kcal/mol in solution, for meta approach, it decreases from 3.6 to 2.4 kcal/mol and for para approach it decreases from 2.1 to 1.1 kcal/mol.

### 4. Conclusion

At the end of this study, we've obtained the general mechanism of chlorination reaction of nitrobenzene in the presence of aluminium chloride as a model of substituted benzene with  $\Pi$  group acceptor. In this reaction, the limitant step is the transformation of  $\pi_1$  to  $\sigma_1$  via transition state TS1. All stationary points are been localized and the results obtained in gas phase are consistent with the traditional description of these electrophilic substitution reactions: the orientation of these reactions in meta position depends on the stability of a reaction intermediate (Wheland said). The solvent plays a major role on this potential surface energy to decrease the electrostatic attraction on Wheland complex ( $\sigma_1$ ) and to lower the activation barrier of the second step of the reaction.





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