Study of the two nucleophilic attack modes $A_C$ and $A_{CI}$ the reaction between triethylphosphite and tetrachloromethane: DFT Analysis.

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abstract

The objective of our work was to theoretical study by the quantum method DFT/B3LYP/6-311G(d,p) of the reaction of tetrachloromethane ($CCl_4$) with triethylphosphite ($P(OEt)_3$). For the prediction of regioselectivity, several quantum approaches have been developed, namely molecular orbital frontier theory (MFO), Transition State Theory (TST), and reactivity descriptors derived from the conceptual DFT. The results obtained in this work show that triethylphosphite is defined as a nucleophile while tetrachloromethane behaves as an electrophile. The nucleophilic attack of the phosphorus atom of $P(OEt)_3$ is preferably on the chlorine of the tetrachloromethane instead of carbon and the reaction is polar and regioselective.

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1. INTRODUCTION

Phosphorus chemistry offers a wide range of scientific applications and has become a science in its own right. With its technology and scientific applications are many, varied and booming, especially in recent years. Generally speaking, biology and health are witnessing remarkable advances in phosphorus chemistry.

One category of phosphorus derivatives are organophosphorus compounds. These are organic compounds containing at least one phosphorus atom directly linked to a carbon. They have continued to develop in recent years and are increasingly present in modern organic chemistry because of their potential application in various fields such as the biological [1,2], therapeutic [3,4], agricultural as plant growth regulators [5] and biochemistry [6]. These derivatives are also of great interest in organic synthesis through their use as precursors [7,8]. However, biological activities have given organophosphorus compounds their most significant commercial developments, in particular as insecticides.

The reason for the interest of these applications is due to the diversity of the valency of phosphorus [9]. Several attempts have been made to demonstrate simple and effective methods for the formation of C-P bond and the synthesis of new organophosphorus compounds. An excellent book on the formation of carbon-phosphorus bonds has been published by Engel and Cohen [6]. In the classe of these derivatives, we particularly mention organophosphinates (A) and organophosphonates (B). The presence of a phosphonyl group in a molecule is often at the origin of specific applications which result either from the activation of the carbon bound to the phosphorus [10] or from the biological properties provided by the phosphorus group itself [11].

Phosphorus chemistry has developed considerably in the field of both synthesis and reactivity [12]. Indeed, the bibliographical study shows that the reaction of phosphorus derivatives trivalents [(RO)₃P, (RO)₂P-R′,…] with certain polyhaloalkanes (CCl₄, BrCCl₃, CCl₃PO(OE)₂…) leads to several products [13-18].

The aim of this work is to carry out a theoretical programme or study by the method DFT/B3LYP/6-311G(d,p) of the reactivity the CCl₄ with respect to triéthlphosphite P(OE)₃ (Figure 1).
In the course of this work, we studied from a kinetic and thermodynamic point view the feasibility and the regioselectivity of the reaction between tetrachloromethane and triethylphosphite.

2. CALCULATION DETAILS

This study was conducted using the GAUSSIAN 09 [19] program. The theoretical calculations of the energies of the corresponding optimized geometries for reagents, products and transition state structures were carried out using the DFT density functional theory method using the B3LYP [20, 21] combined with standard base 6-311G(d,p).

The optimization of stationary points, characterized by frequency calculations, was performed using the berny analytical gradient optimization method [22, 23]. IRC (Intrinsic Reaction Coordinate) calculations [24, 25] were performed to show whether the transition state (TS) is well related to the two minima (reagents and products). Enthalpy, entropy and free energy values were calculated using standard statistical thermodynamics.

3. RESULTS AND DISCUSSION

3.1 PREDICTING THE NATURE OF THE REACTION MECHANISM AND THE ELECTROPHILIC/NUCLEOPHILIC CHARACTER

3.1.1 Prediction of philicity by frontier orbital analysis

The frontier molecular orbital (FMO) study of the reaction between triethylphosphite \((\text{P(OEt)}_3)\) and tetrachloromethane \((\text{CCl}_4)\) was investigated theoretically using the B3LYP/DFT method. According to the analysis of the gap calculation \(\text{HOMO/LUMO}\), for the two possible combinations of the two reagents, the main interaction is between the \(\text{LUMO}\) of tetrachloromethane and the \(\text{HOMO}\) of \(\text{P(OEt)}_3\) (Figure 1). The gap
corresponding to the combination \(|E_{\text{HOMO}} - E_{\text{LUMO}}(\text{CCl}_4)|\) is more than that corresponding to the combination \(|E_{\text{HOMO}}(\text{CCl}_4) - E_{\text{LUMO}}|\). Therefore, \(\text{P(OEt)}_3\) behaves as a nucleophile while \(\text{CCl}_4\) acts as an electrophile.

![Figure 1](image-url)

Figure 1. Gaps \(\text{HOMO/LUMO}\), for the two possible combinations between the two reagents

From Figure 1, we can also note that the density of molecular orbital \(\text{HOMO}\) is well localized on the phosphorus atom indicating that it is rich in electrons whereas the \(\text{LUMO}\) is condensed at the chlorine atom. This indicates that the nucleophilic attack of the phosphorus atom is essentially on the chlorine atom.

3.1.2 Analysis based on global properties

The polar nature of donor-acceptor (DA) reactions can be obtained from the difference in the overall electrophilicity indices of two reagents. This difference has been used to determine the polarity of this type of reaction [26]. Indeed, recent studies of reactions (DA) have shown that reactivity indices derived from DFT (Density Functional Theory) are an efficient tool to establish the polar or non-polar character of reactions [27].

The calculated values of the global reactivity indices, i.e. electronic chemical potential \(\mu = \frac{E_{\text{HOMO}} + E_{\text{LUMO}}}{2}\), global hardness \(\eta = E_{\text{LUMO}} - E_{\text{HOMO}}\) [28, 29], global electrophilicity \(\omega = \mu^2 / 2\eta\) [30], the overall nucleophilicity \(N = E_{\text{HOMO}}(\text{Nd}) - E_{\text{HOMO}}(\text{tercycnmethyl})\) [31] as well as the overall maximum charge transfer \(\Delta n_{\text{max}} = -\mu / \eta\) [32] for both reagents are given in Table 1.
Table 1. Electronic chemical potential $\mu$, hardness $\eta$, electrophilicity global $\omega$, overall nucleophilicity $N$, charge transfer $\Delta n_{\text{max}}$, the overall electrophilicity deviation $\Delta \omega$ in (eV) of the reagents: CCl$_4$ and P(OEt)$_3$.

<table>
<thead>
<tr>
<th>reagents</th>
<th>$\mu$ (eV)</th>
<th>$\eta$ (eV)</th>
<th>$\omega$ (eV)</th>
<th>$N$ (eV)</th>
<th>$\Delta n_{\text{max}}$</th>
<th>$\Delta \omega$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl$_4$</td>
<td>-5.656</td>
<td>6.743</td>
<td>2.372</td>
<td>0.34</td>
<td>0.838</td>
<td>0.838</td>
</tr>
<tr>
<td>P(OEt)$_3$</td>
<td>-3.125</td>
<td>7.629</td>
<td>0.640</td>
<td>2.428</td>
<td>0.409</td>
<td>1.732</td>
</tr>
</tbody>
</table>

$E_{\text{HOMO}}$(tetracyanoethylene) = -9.368 (eV) calculated by DFT/B3LYP/6-311G (d, p).

In the case of the reaction between P(OEt)$_3$ with CCl$_4$, the electronic chemical potential of P(OEt)$_3$ ($\mu = -3.125$ (eV)) is higher than that of the reagent CCl$_4$ ($\mu = -5.656$ (eV)). This indicates that the electron transfer will take place from the triethylphosphite (electron donor) to the CCl$_4$. On the other hand, the overall electrophilicity index of P(OEt)$_3$ ($\omega = 0.640$ (eV)) is lower than that of the reagent CCl$_4$ ($\omega = 2.372$ (eV)) and therefore CCl$_4$ behaves as an electron acceptor (electrophile) while the P(OEt)$_3$ behaves as a nucleophile. Note that the overall nucleophilicity indices also show that polyhalogénométhane CCl$_4$ ($N = 0.34$ (eV)) is less nucleophilic than the phosphorus compound P(OEt)$_3$ ($N = 2.428$ (eV)). In addition, the maximum charge transfer $\Delta n_{\text{max}}$ is maximum for (CCl$_4$) (0.838) is minimum for P(OEt)$_3$ (0.409). In conclusion, in this reaction tetrachloromethane behaves like a strong electrophile ($\omega$(CCl$_4$) > 1.5 eV) [33, 34].

The difference of électrophilie $\Delta \omega > 1$ between (CCl$_4$) and P(OEt)$_3$ indicates an appreciable polarity of the NED character for these reactions.

4. KINETIC AND THERMODYNAMIC STUDY OF THE NUCLEOPHILIC ATTACK MODES $\text{Ac}$ AND $\text{AcI}$

4.1. THERMODYNAMIC STUDY

We studied from thermodynamic points of view the possibility and regioselectivity the reaction of CCl$_4$ and P(OEt)$_3$ (Figure 1). We determined under standard conditions of temperature and pressure (298.15 (K) and 1atm), using the calculation method DFT/B3LYP/6-311G(d,p), the variations in reaction energy $\Delta E_r$, the variations in reaction enthalpy $\Delta H_r$ and the variations in free enthalpy of reaction $\Delta G_r$ which correspond to the formation reactions of the products $P_C$ and $P_{CI}$ (Table 2).
**Table 2.** Calculated values (Kcal/mole) of $\Delta E_r$, $\Delta H_r$ and $\Delta G_r$ for the products $P_C$ and $P_{Cl}$.

<table>
<thead>
<tr>
<th>System</th>
<th>Products</th>
<th>$\Delta H_r$</th>
<th>$\Delta G_r$</th>
<th>$\Delta E_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P(OEt)_3 + CCl_4$</td>
<td>$P_C$</td>
<td>-22.987</td>
<td>-23.260</td>
<td>-23.696</td>
</tr>
<tr>
<td></td>
<td>$P_{Cl}$</td>
<td>-44.192</td>
<td>-44.567</td>
<td>-45.326</td>
</tr>
</tbody>
</table>

As shown in Table 2, the free enthalpy variations $\Delta G_r$ of the reactions are all negative. Therefore, these reactions are possible and thermodynamically favoured. In addition, we have noticed that the values of the free enthalpy variation of reaction $\Delta G_r$ which corresponds to the reaction of formation the product $P_{Cl}$ is higher in absolute value than the value of the free enthalpy variation of reaction corresponds to the reaction of formation of the product $P_C$. This indicates that the attack on the chlorine atom is more favoured.

We found that the values of $\Delta H_r$ for the formation reactions of the compounds $P_C$ and $P_{Cl}$ are negative. Therefore, they are exothermic.

We also noted that the value of $\Delta E_r$ for the $P_{Cl}$ compound formation reaction is larger in absolute value than the value for the $P_C$ compound formation reaction. This again confirms that the most favourable site of attack is the chlorine atom.

**4.2. KINETIC STUDY**

**4.2.1. Energy study of transition states**

In order to demonstrate the type of nucleophilic attack of the phosphorus atom of $P(OEt)_3$ on $CCl_4$ most favourable kinetically, determined the energies of the transition states ($TS_{Cl}$ and $TS_C$) of the reaction of $CCl_4$ with $P(OEt)_3$.

The surface of the potential energy (SEP) corresponding to the two modes of attack shows that: the energy of the transition state corresponding to the attack on the chlorine atom $TS_{Cl}$ is 15,687 Kcal/mol below the energy of the transition state corresponding to the attack on carbon $TS_C$ (Figure 2). The activation energies corresponding to the two modes of attack: 53.965 Kcal/mol for $A_C$ and 38.278 Kcal/mol for $TS_{Cl}$. Therefore, the attack on the chlorine atom is kinetically more favoured than the attack on the carbon atom.

**Figure 2.** Energy profile in (a.u.) for the reaction between $CCl_4$ and $P(OEt)_3$
The structure of the transition state associated with the reaction path \((A_C)\) is more stable than that associated with the reaction path \((A_{Cl})\). Two transition state structures optimized by DFT/B3LYP/6-311G(d,p) are shown in Figure 3.

Triethylphosphite \((P(OEt)_3)\) tends to react more with chlorine than with carbon because of the difference in length between the \(P - CCl_3\) and \(P - Cl\) bonds at the transition state \(d(P - Cl) < d(P - CCl_3)\) (Figure 3).

\[\text{Figure 3. Bond lengths for the transition states of the reaction of } P(OEt)\text{ with CCl}_4.\]

4.2.2. Determination of the reaction path (IRC)

To ensure that the transition states are correct, we studied the evolution of the molecular system along the reaction path between \(\text{CCl}_4\) and \(P(OEt)_3\). When performing the IRC (Intrinsic Reaction Coordinate) calculation, one must ensure that the transition state is related to the minima (reagents and products) Figure 4.

\[\text{Figure 4: The IRC of the reaction between CCl}_4\text{ and } P(OEt)_3 \text{ calculated by DFT/B3LYP/6-311G(d,p).}\]
5. CONCLUSION

In this work, we have demonstrated by the method DFT/B3LYP/6-311G(d,p), by determining the variation of free enthalpies $\Delta Gr$, whatever the mode of attack of phosphorus on $\text{CCl}_4$, the corresponding variations of free enthalpies $\Delta Gr$ are negative. This shows that these nucleophilic attacks are thermodynamically possible.

The calculation of the global indices and the gap énergétique $\text{HOMO/LUMO}$ shows that the reagent $\text{P(OEt)}_3$ plays the role of nucleophile and the tétrachlorométhane $\text{CCl}_4$ plays the role of electrophile. The difference in electrophilicity $\Delta \omega > 1$, we are talking about a polar process.

The variation of enthalpy of reaction $\Delta H_r$ is very exothermic for the reaction of formation of the product $\text{PCl}_3$. Therefore this reaction is more favoured because the products formed are stable and their formation releases energy.

The thermodynamic and kinetic study, show that the stable products of the reaction of tétrachlorométhane $\text{CCl}_4$ with triéthylphosphite $\text{P(OEt)}_3$ are the products coming from the attack on the halogen Cl.

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COMPETING INTEREST STATEMENT

The authors declare that there is no conflict of interests regarding the publication of this paper. Also, they declare that this paper or part of it has not been published elsewhere.

ADDITIONAL INFORMATION

No additional information is available for this paper.

REFERENCES