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# Direct esterification of *p*-nitrobenzoic acid with *n*-butanol using diethyl chlorophosphate in pyridine: A DFT study

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# ABSTRACT

Direct esterification reaction mechanism of the *p*-nitrobenzoic acid with *n*-butanol have been studied using density functional theory (DFT) by B3LYP and M06 with a 6-311++G(d,p) basis set, with the polarized continuum model (PCM) to simulate the solvent effects of pyridine. This project sheds light on the detailed processes of the title reaction proceeding along two channels: with the diethyl chlorophosphate (**DECP**) absence (channel a) and presence (channel b). The calculated results have demonstrated that channel b smoothes the reaction by reducing the energy barrier, which is in good agreement with the experimental observations. Especially, in channel b, for yield of the important intermediate of carboxylate-phosphate anhydride (**CPA**), two possible mechanisms have been proposed: channel b1 suggests the carboxylic acid **R1** reacts with **DECP** via a four-membered ring transition state, while channel b Snotiate to its relative carboxylate radical anion **R1**′ before reacting with **DECP** by the S<sub>N</sub>2 mechanism. The calculated results indicated that channel b2 shows the more energy-favorable mechanism. The natural bond orbital (NBO) charge analysis has been implemented to gain more information about the electronic properties and to prove the feasibility of each reaction step. Moreover, the reasons for how and why the introduction of **DECP** could make the reaction easier to occur have also been clarified.

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# 1. Introduction

The esterification reaction of carboxylic acid with alcohol is one of the most important and commonly employed reactions in organic synthesis [1]. Since the first reported by Fischer [2], a great number of useful esterification methods have been developed, including the non-catalyzed ways by using specific dehydrating reagents [3] and the catalyzed ways promoted by Lewis acids [4], solid acids [5–7], metal compounds (the metal triflates [8–13] or the metal halides [14-16]) and so on. The mixed anhydride method is also one of the well known ways for carboxylic group activation, representatively involving activation with a reactive acid chloride such as the Yamaguchi reagent [17]. The use of mixed carboxylate-phosphate anhydride in the presence of base [18] has been reported mainly in the synthesis of macrocyclic lactones, by employing the less reactive, more selective monochloro-disubstituted phosphates to activate the corresponding seco-acid derivatives. However, this method has attracted little attention [18a] despite the availability of the required reagents and the selective mixed anhydride formation in the presence of free hydroxyl groups. In particular, the reactive reagent phenyl dichlorophosphate has been exploited in both ester [19] and thioester [20] bond forming processes.

Recently, Won and co-workers [21] found that the (6-oxo-6Hpyridazin-1-yl) phosphoric acid diethyl esters were efficient and selective coupling agents for equimolar esterification of carboxylic acids and alcohols, which appears reminiscent of some of the lactonization difficulties encountered with the use of the Yamaguchi macrolactonization method. In problematic cases, Yonemitsu and co-workers [22] reported that the use of excess DMAP and mild heating, so as not to promote symmetrical carboxylic anhydride formation, was highly effective in promoting the mixed-anhydride pathway. Inspired by the study of Yonemitsu group on mixedanhydride, McNulty and co-workers [23] hypothesized that the disubstituted pyridazine compound was not to be required, and the pyridine base allowed formation of the mixed anhydride CPA directly from DECP (Scheme 3) and the carboxylic acid. Particularly, they successfully activated this pathway of using only pyridine to allow for a simple and a direct synthesis of a range of esters and amides. All the side products appearing in this method are water soluble and therefore allow for the straightforward isolation of high purity products.

Even though some valuable experimental results have demonstrated the esterification reactions in different promoting ways, theoretical investigations on the reaction mechanism, especially

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about the details at the molecular level under solvent constrained conditions, are quite limited until now. Then why the esterification of the carboxylic acid with the alcohol cannot be arisen directly under a mild condition? How and why the introduction of **DECP** could make the reaction easier to occur? How about the form (Neutral or Anionic) of the reactant when it is involved in the reaction? All these questions motivate the present work.

In this project, a theoretical study on the detailed mechanism of the esterification has been carried out. Based on the experimental results [23], the *p*-nitrobenzoic acid (denotes as **R1**, Scheme 1) and the *n*-butanol (denotes as **R2**, Scheme 1) have been chosen as the objects of investigation. All calculations were carried out by using density functional theory (DFT), which has been widely used in the study of mechanism [24].

### 2. Computational details

All theoretical calculations were performed using the Gaussian 03 [25] program. All structures of each reactant, product, transition state, and intermediate were optimized by B3LYP/6-311++G(d,p) [26–28], using polarized continuum model (PCM) [29–33] to simulate the solvent effects of pyridine (chosen from the available experiment [23]). Compared with other levels of theory, the B3LYP method has been recognized to be sufficiently accurate for predicting reliable geometries and vibrational frequencies of the stationary points [34–36]. But in recent studies by Truhlar et al., the M06 functional were found to perform as well for energies, geometries and vibrational frequencies [37–40]. In order to verify a suitable DFT method for our studied system, the M06 method has also been employed to optimize all the involved stationary





Scheme 2. Proposed mechanism for channel a.

points with the 6-311++G(d,p) basis set considering the solvent effects with PCM. The corresponding vibrational frequency calculations were then performed respectively at the same level with geometric optimations including the solvent effects simulated by PCM, in order to confirm that all the reactants, intermediates and products have no imaginary frequencies, and each transition state has one, and only one imaginary frequency. All energies reported in this paper include the zero-point vibrational energy (ZPVE) correction. To corroborate which are the correspondent minima linked by the considered transition state, normal coordinate analysis are performed on these transition state structures by intrinsic reaction coordinate (IRC) routes [41] in both reactant and product directions. The electronic properties of the complexes were discussed using the natural bond orbital (NBO) analysis at the same level by the NBO 3.1 program [42].

## 3. Results and discussion

We begin by first investigating the mechanism for the title reaction proceeding with **DECP** absence (channel a, Scheme 2). Second, the mechanism for the title reaction proceeding with **DECP** presence (channel b, Scheme 3) is investigated, which have been proposed to occur through two possible mechanisms (channel b1 and channel b2, Scheme 3).

# 3.1. Channel a: reaction with DECP absence

When **DECP** is absent, there is only one step for the esterification of **R1** with **R2** via the transition state **TS1** to yield the ester product **P**. The optimized structures and geometrical parameters for R1, R2, TS1, P and H<sub>2</sub>O are presented in Fig. 1, and the NBO charges distributed on the C1, O2 atoms of **R1** and O4, H5 atoms of **R2** are shown in Table 1. The opposite charges distributed on the C1 atom (0.800 e) of **R1** and O4 atom (-0.771 e) of **R2** suggest the electrostatic attraction between C1 and O4. Similarly, the opposite charges on the H5 atom (0.472 e) of R2 and O2 (-0.680 e) atom of **R1** indicate the mutual attraction between H5 and O2. As a result, one four-membered ring (C1O2H5O4) configuration presented in TS1, in which the distances of C1...O4 and O2···H5 reach to 1.756 Å and 1.189 Å, respectively. At the same time, the bond lengths of C1-O2 and O4-H5 are elongated from 1.345 Å in **R1** and 0.963 Å in **R2** to 1.784 Å and 1.225 Å in **TS1**, respectively. After that, the four-membered ring configuration disappears with the departure of one molecule of water  $H_2O$ . The bonds of C1-O4 in P and O2-H5 in H<sub>2</sub>O are fully formed (1.338 Å and 0.964 Å, respectively), indicating generation of the carboxylic ester product.

The energy barrier for channel a is 48.20 kcal/mol, which is too high to be crossed for the esterification reaction under the available experimental conditions [23]. The energy of **P** plus  $H_2O$  is



Scheme 3. Proposed mechanisms for channel b (channel b1 and channel b2).



**Fig. 1.** Optimized geometries of the **R1**, **R2**, **TS1**, **P**, **H**<sub>2</sub>**O** and the potential energy profile of channel a calculated by B3LYP along with energies in parentheses calculated by M06 (hydrogen atoms not involved in reaction sites are omitted; distance in Å, energy in kcal/mol).

 Table 1

 NBO charges (unit: e) distributed on C1, O2, H3, O4 and H5 of R1 and R2.

	C1	02	H3	04	H5
R1	0.800	-0.680	0.505	_	_
R2	—	-	—	_0.771	0.472

4.86 kcal/mol lower than that of the reactants, indicating that the esterification reaction is exothermic.

# 3.2. Channel b: reaction with **DECP** presence

As shown in Scheme 3, there are two steps involved in channel b: (i) generation of the mixed anhydride **CPA** by reaction of **R1** with **DECP**, (ii) the **CPA** reacts with **R2** to yield the ester product **P**.

## 3.2.1. Generation of CPA

Two possible mechanisms have been proposed for this step (Scheme 3). First, **R1** reacts with **DECP** directly by the four-membered ring mechanism via the transition state **TS21** (channel b1). Second, as the base conditions are available, it is reasonable to hypothesize **R1** is dissociated to its relative carboxylate radical anion **R1**', before it reacts with **DECP** to yield **CPA** by the S<sub>N</sub>2 mechanism (channel b2).

In channel b1, the mechanism is very similar with that of channel a. The different properties of NBO charges distributed on the O2 atom (-0.680 e) of **R1** (Table 1) and P6 atom (2.275 e) of **DECP** (Table 2) suggest the electrostatic attraction between O2 and P6, while the opposite charges on the H3 atom (0.505 e) of **R1** (Table 1) and Cl7 atom (-0.314 e) of **DECP** (Table 2) indicate the mutual attraction between H3 and Cl7. Homoplastically, the transition state **TS21** with one four-membered ring (O2P6Cl7H3) configuration presents. The distances of O2…P6 and H3…Cl7 reach to 2.820 Å and 1.963 Å in **TS21**, respectively. At the same time, the

Table 2

NBO charges (unit: e) distributed on C1, O2, P6 and Cl7 of R1', DECP and CPA.

	C1	02	P6	Cl7
R1′ DECP CPA	  0.819	-0.797 - -0.815	 2.275 _	_ _0.314 _

bond lengths of O2–H3 and P6–Cl7 are elongated from 0.970 Å in **R1** and 2.077 Å in **DECP** to 1.009 Å and 3.606 Å in **TS21**, respectively. The departure of one molecule of chlorine hydride **HCl** leads to breaking of the four-membered ring configuration. With the bond of P6–O2 being fully formed (1.666 Å), the **CPA** is generated. The energy barrier of channel b1 is 41.99 kcal/mol, which is also too high to be crossed under the available experimental conditions [23].

In channel b2 (Fig. 2), **R1**' reacts with **DECP** by the  $S_N 2$  mechanism via the transition state **TS22**. That is, the nucleophilic attack of **R1**' to **DECP** and the departure of the chloride anion (**CA**) go through a synchronous mechanism. The positive charge on the P6 atom (2.275 e, Table 2) and the negative one on the O2 atom (-0.797 e, Table 2) have demonstrated the reaction of **R1**' with **DECP**. The distance of P6...O2 is shortened to 1.849 Å in **TS22**, and the bond length of P6–Cl7 is elongated from 2.077 Å in **DECP** to 2.353 Å in **TS22**. Finally, the mixed anhydride **CPA** is generated. The energy barrier of channel b2 is 19.49 kcal/mol (Fig. 2), which is very easy to be crossed under the experimental conditions [23].

Obviously, the energy barrier of this step of channel b2 (19.49 kcal/mol) is 22.50 kcal/mol lower than that of channel b1 (41.99 kcal/mol). Therefore, the anhydride intermediate **CPA** should be generated by the  $S_N 2$  mechanism.

# 3.2.2. Yield of **P**

Since the mixed carboxylate-phosphate anhydride **CPA** has been prepared, the following discussion would be focused on the yield of the ester product **P** by reaction of **CPA** with **R2**. The calculated results demonstrate that this process proceeds through the four-membered ring mechanism, because the alcohol hydrogen H5 of **R2** is not easy to be dissociated under the available experimental conditions [23].

Analogously with channel a, the NBO charges distributed on the C1 atom (0.819 e), O2 atom (-0.815 e) of **CPA** and on the H5 atom (0.472 e), O4 atom (-0.771 e) of **R2** (Table 1) suggest the electrostatic attractions between C1, O4 and H5, O2, respectively. In consequence, one four-membered ring (C1O2H5O4) configuration is constructed in **TS3** as well as in **TS1**. The four-membered ring configuration disappears with the departure of one molecular of **DEHP**. The bonds of C1–O4 in **P** and O2–H5 in **DEHP** are fully formed (1.338 Å and 0.966 Å, respectively), indicating yield of the carboxylic ester product **P**. The energy barrier of this step is 28.93 kcal/mol (Fig. 2).

As mentioned above, the rate-limiting step for channel b1 occurs in the first step (generation of **CPA**) and the energy barrier is 41.99 kcal/mol (Fig. 2), while for channel b2, the rate-limiting step occurs in the second step (yield of **P**) and the energy barrier is 28.93 kcal/mol (Fig. 2). Obviously, channel b2 shows the more energy-favorable mechanism.

Taken channel a and channel b into account, the energy barrier of the rate-limiting step for channel b (28.93 kcal/mol, channel b2), is 19.27 kcal/mol lower than that for channel a (48.20 kcal/mol). That is, the way proceeding with **DECP** presence is much more energy favorable.

In addition, the M06 functional was also used to recalculate all the reactants, product, transition states and intermediates. The corresponding geometric parameters have been shown in Support-



Fig. 2. Optimized geometries of the R1, R1', DECP, TS21, TS22, CPA, TS3, DEHP and the potential energy profile of channel b1 (black), channel b2 (blue) calculated by B3LYP along with energies in parentheses calculated by M06 (hydrogen atoms not involved in reaction sites are omitted; the 4-nitrobenzene group is omitted as the purple asterisk in TS21, TS22, CPA, and TS3; distance in Å, energy in kcal/mol) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

ing Information. The results demonstrate that the obtained geometries of the stationary points by M06 are very similar with those obtained by B3LYP, except for **TS22**, an anion transition state. As representations, some key bond lengths of **CPA**, **TS22** and **TS3** are listed in Table 3. In **CPA**, the two listed bond lengths are less than 1% shorter than those calculated by B3LYP. While in **TS3**, the average change value of the four listed bond lengths is 3.6%. However, in **TS22**, the length of P6–Cl7 is 20.9% longer than the B3LYP result, a very notable change. Furthermore, the calculated results have indicated that the energy barriers (Figs. 1 and 2, numbers in magenta with brackets) of every step in the present system calculated by M06 are all lower than those by B3LYP. Remarkably, in the step via **TS22**, the energy barrier is 5.78 kcal/mol lower than the B3LYP result, which is consistent with the notable structural change.

# 3.3. How DECP effects?

Based on the results and discussions mentioned above, the title reaction proceeding with **DECP** presence is thought to be much more energy favorable than that of with its absence. Then, how does **DECP** effect? Why its introduction could smooth the reaction greatly?

Comparing channel a with channel b, we can discover that due to the introduction of **DECP**, the carboxylic acid **R1** is converted to the mixed anhydride **CPA** in fact before it reacts with the alcohol **R2**. The H3 atom is substituted by the phosphate group, which makes the bond of C1–O2 looser (as the bond length is elongated from 1.345 Å to 1.370 Å, Table 4) and therefore breaking of the

Table 4 Bond lengths (unit: Å) of C1–O2 and O4–H5 in R1, R2, DECP, TS1 and TS3.

-	1.370	1.794	2.012
	_ 0.963	- 1.370 0.963 -	- 1.370 1.794 0.963 - 1.221

bond becomes easier. Consequently, when go through the transition state **TS3** in channel b, the bond of C1–O2 is broken with great priority than O4–H5. That is, the two bonds are broken almost in the step-by-step way. However, when go through **TS1** in channel a, the two bonds are broken almost synchronously. Table 4 gives the specific data to prove it. For channel a via **TS1**, the bond length of C1–O2 is elongated by 33.4% (from **R1** to **TS1**), and that of O4– H5 is elongated by 26.8% (from **R2** to **TS1**). While for channel b via **TS3**, the bond length of C1–O2 is elongated by 46.9% (from **CPA** to **TS3**), but that of O4–H5 is elongated by only 2.4% (from **R2** to **TS3**). Obviously, the process going in the step-by-step way is much easier to be achieved. Therefore, introduction of **DECP** has activated the carboxylic acid, loosen the bond of C1–O2, and changed the transition state that the reaction goes though, so reducing of the energy barrier will become necessity.

## 4. Conclusions

In this paper, the esterification reaction of carboxylic acid **R1** with alcohol **R2** proceeding in two channels has been studied using density functional theory. The optimized geometries and the po-

Table 3

Some key bond lengths (unit:	A) of CPA, TS22 and TS3	calculated by B3LYP and M06.
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	СРА	СРА		TS22		TS3		
	C1-02	O2-P6	O2-P6	P6-C17	C1-02	02-H5	04-H5	C1-04
B3LYP M06	1.370 1.359	1.666 1.651	1.849 1.819	2.353 2.845	2.012 1.930	1.743 1.820	0.986 0.983	1.794 1.690

tential energy surface information have been obtained by the B3LYP and M06 functionals with a 6-311++G(d,p) basis set, using PCM to simulate the solvent effects of pyridine. The calculated results indicate that: (i) the reaction proceeding with **DECP** presence smoothes the esterification because the energy barrier is greatly reduced by 19.27 kcal/mol, (ii) there is only one step in channel a via a four-membered ring mechanism, while channel b consists of two steps: generation of **CPA** and yield of **P**, (iii) in channel b, the agent **CPA** is generated by the S<sub>N</sub>2 mechanism rather than the four-membered ring ones, because the energy barrier of the latter is too high to be crossed, (iv) in the present system, the geometric parameters calculated by M06 and B3LYP are very similar except for **TS22**. The energy barriers are all lower than those by B3LYP, and the notable change in energy barrier via **TS22** might be due to the remarkable change in its structure.

Moreover, it is demonstrated that with the introduction of **DECP**, the way of bonds (C1–O2 and O4–H5) breaking via the transition state has been changed, from almost synchronous one (**TS1**) to the almost step-by-step one (**TS3**), resulting in the esterification reaction being able to proceed along a more energy favorable channel (channel b). All computational results are in good agreement with the experimental results.

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# Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.comptc.2010.09.003.

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