

Turkish Comp Theo Chem (TC&TC)

Volume(Issue): 10(1) – Year: 2026 – Pages: 44-55

e-ISSN: 2602-3237

https://doi.org/10.33435/tcandtc.1580012



Received: 11.11.2024 Accepted: 06.02.2025 Research Article Mechanistic investigation of the reaction between triphenylphosphine with Dimethylacetylenedicarboxylate in the presence of 2-indolinone as NH-acid

Mohammad Zakarianezhad^{a, 1},Batoul Makiabadi^b, Majid Moradian^c, Sahar Darvisholadi^a

^aDepartment of Chemistry, Payame Noor University, Tehran, Iran ^bDepartment of Chemical Engineering, Sirjan University of Technology, Sirjan, Iran ^cDepartment of Chemistry, Qaemshahr Branch, Islamic Azad University, Qaemshahr, Iran

Abstract: Stable phosphorus ylids are usually synthesized as a mixture of two E- and Z- isomeric forms with different percentages. Experimental methods and techniques cannot find a reason for the presence of these products in different proportions. Therefore, in this project, we are trying to find evidence for the preference of one of the E- and Z-structural isomers. For this purpose, the mechanism of the reaction between triphenylphosphine R1 and dimethyl acetylenedicarboxylate R2 was investigated in the presence of 2-indolinone as NH-acid, based on quantum mechanical calculations. Theoretical studies were performed to evaluate the energy levels of all structures participating in the mechanism. All structures optimized at the B3LYP/6-311++g(d,p) levels. Two kinetic pathways I and II are predicted for the reaction. Based on the results, pathway I has a kinetic preference over pathway II. The first step of the reaction was recognized as a rate-determining step in the reaction mechanism. The results of the calculations well proven the preference of geometrical isomer P-E over P-Z, and the Z/E ratio was seen to be kinetically controlled. To investigate the solvent effect on the energy level of structures, condensed phase calculations in dichloromethane were carried out with the polarizable continuum model (PCM). The natural bond orbital (NBO) method is applied for a better understanding of molecular interaction.

Keywords: Triphenylphosphine; dimethyl acetylene dicarboxylate; 2-indolinone; Z- and E-rotamers, density functional theory

1. Introduction

Multicomponent reactions have attracted much attention due to their molecular diversity and ability to construct complex chemical and biological compounds in single operations [1-3]. These reactions have found increasing application in synthetic organic chemistry [4-6]. The surprising chemistry that results from the addition of nucleophiles to activated acetylene compounds has attracted considerable interest. Typically, addition of nucleophiles devoid of an acidic hydrogen atom results in a 1:1 zwitterionic intermediate that can undergo further transformations to produce a stable product [7]. Organophosphorus chemistry is an essential field of organic chemistry, which was used to develop new methods in organic synthesis and to to their well-recognized chemical and biological properties [8]. Groups such as triphenylphosphine, pyridine, amines, and isocyanides can form zwitterions well [9-11]. MCRs are important systems in organic chemistry due to their application in the synthesis of organic products, such as phosphorus ylides and natural products with biological and pharmaceutical properties [12-18]. The reaction of electron-deficient acetylene esters with triphenylphosphine (TPP) in organic compounds containing acidic hydrogen produces phosphorus ylides [19,20]. Some phosphorus ylides exist as a mixture of two Z- and E-rotational isomers, and show a dynamic ¹H NMR effect that is kinetically important [21-24]. Determining the product structure and the percentage of each

¹ Corresponding Authors

e-mail: m.zakarianejad@yahoo.com & mzakarianejad@pnu.ac.ir

rotamer and also measurement of the conversion energy of rotamers are useful pieces of information that come from ¹H, ¹³C and, ³¹P NMR spectroscopy. Despite the valuable information obtained from spectroscopic techniques in experimental studies, investigating the reasons for the quantitative majority of either *E*- or *Z*-rotamer over each other requires further theoretical study. After conducting numerous studies on the kinetics and mechanism of various reactions [25-38], a theoretical studies on the reaction between triphenylphosphine **R1**, dimethyl acetylene dicarboxylate **R2** and 2indolinone **R3** (as a NH-acid) for generation of phosphorus ylides **P** will be conducted. (Figure 1) [39]. In this project, possible kinetic pathways for the reaction will be predicted. All structures along the reaction pathway, including reactants, intermediates, transition states, and products, will be optimized. Then, the competitive pathways are investigated kinetically and thermodynamically, and the preferred kinetic pathway will be identified. The reason for the preference of one of the E- or Z-rotamer will be determined. Finally, the rate-determining step will be identified and the overall reaction rate equation will be obtained.



Figure 1. The reaction between triphenylphosphine R1, dimethyl acetylendicarboxylates R2 and 2-indolinone R3 for generation of stable phosphorus ylides P(P-E or P-Z)

2. Computational Method

All Geometrical structures were optimized at B3LYP/6-311++G(d,p) level of theory using Gaussian 09 [40]. The corresponding frequencies of the structures were estimated at the same level of theory to check the stationary points without imaginary frequencies and, the transition states with only one imaginary frequency. Also, the intrinsic reaction coordinate (IRC) approach [41,42] is performed to ensure that the given transition state connects with the corresponding reactants and products. Calculations have been carried out in the gas phase and consider solvent effects (dichloromethane) with the polarizable continuum model (PCM) [43-47]. Natural bond orbital (NBO) analysis was carried out at B3LYP/6-311++G(d,p) level of theory using version 3.1 of the NBO package [48-50].

3. Results and discussion

3.1. Investigation of the mechanism and potential energy levels of the reactions in the gas phase

According to the investigations, the reaction was initiated by the nucleophilic proximity of the P17 atom of the triphenylphosphine (R1) to the C9 atom of the dimethyl acetylenedicarboxylate (R2). The proximity of the nucleophile P17 was studied in four different directions, and accordingly two different pathways I and II are predicted for the reaction. The pathway in which the triphenylphosphine $(\mathbf{R1})$ is oriented in the opposite direction to the COMe group of dimethyl acetylenedicarboxylate (R2) and produces the Eisomer is called I and the pathway in which the two groups are oriented in the same direction and produces the Z-isomer is called II. Optimized structures of all reaction components (including reactants, transition states, intermediates, and products) for pathways I and II in the presence of 2-indolinone (R3) are shown in Figure 2. Also, relative zero point correction energy (ΔE_0), relative enthalpy (Δ H), relative entropy (Δ S), and relative Gibbs free energy (ΔG) in the gas phase are reported in Table 1. The reaction proceeds by passing through the TS1-I and TS1-II transition states and creating I1-I and I1-II intermediates. At this step of the reaction, the P17-C9 bond formed. Structures I1-I and I1-II were converted to I1'-I and **I1'-II** to reduce the steric effect. This configuration change, by passing **TS2-I** and **TS2-II** transition states, leads to a decrease in the potential energy level of **I1'** relative to that of **I1**. After the reaction, NH-acid approaches the C8 atom in the **I1'** structure through the H51 atom. The transfer of H51 from the NH-acid to the C8 atom in the **I1'-II** and **I1'-II** intermediates, leading to the formation of **I2-I** and **I2-II** intermediates. Finally, by passing through the transition states **TS3-I** and **TS3-II**, it lead to the formation of products **P-E** and **P-Z**. The C8-H51 and N52-C8 bonds formed during this three-step reaction.

Table. 1 Relative zero point correction energy
(ΔE_0) , relative enthalpy (ΔH), Relative entropy
(ΔS) , and relative Gibbs free energy (ΔG) in the
gas phase at standard temperature.

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Structure	Δ E 0 (kJ/mol)	Δ H (kJ/mol)	ΔG (kJ/mol)
Ts1-I	51.84	111.70	51.55
I1-I	48.60	112.11	48.37
I1'-I	40.25	100.21	40.11
I2-I	9.39	117.23	11.70
Ts3-I	44.60	157.66	45.26
P- <i>E</i>	-82.28	40.52	-84.06
Ts1-II	67.74	127.90	67.35
I1-II	63.55	125.98	63.57
I1'-II	50.88	109.69	51.13
I2-II	17.01	125.79	19.22
Ts3-II	48.17	161.00	48.91
P-Z	-85.73	37.46	-87.63

The relative enthalpy and relative Gibbs free energy of the overall reaction in pathways **I** and **II** in the presence of 2-indolinone (**R3**) with values of - 84.06(40.52) kJ/mol and -87.63(37.46) kJ/mol indicate exothermicity and spontaneity of the reaction. The values reported in parentheses belong to the results obtained in dichloromethane solvent. The potential energy diagrams for two paths **I** and **II** are shown in Figure **3**.

As mentioned, the overall reaction in each kinetic pathway consists of three steps. The first and second steps of the reaction mechanism (including all structures and all energy levels) are the same in the presence of reactant R3.

Figure 2. Optimized geometry of all structures in the presence of 2-indolinone R3 at B3LYP/6-311++g(d,p) level of theory.

Figure **3**. The potential energy profile of the reaction in two paths I and II in the presence of 2-indolinone R3, both in the gas phase and in dichloromethane solvent (The values reported in parentheses belong to the results obtained in the presence of dichloromethane)

With the presence of reactant R3 in the third step of the reaction, the energy levels of this step will change relative to each other. Comparison of the potential energy levels in Figure 3 shows that except for the product, all structures, including intermediates and transition states in pathway I are more stable than pathway II. The energy barrier of the first step in both paths of I and II is 51.84 (52.14) and 67.74 (59.86) kJ/mol, respectively. The energy barrier in the second step in both paths of I and II is 5.93 (3.93) and 7.95 (9.94) kJ/mol. The energy barriers of the third step are 35.21 (31.45) and 31.16 (30.07) kJ/mol in pathways I and II, respectively. Comparison of energy barriers in all kinetic pathways shows that the first step of the reaction is known as the rate-determining step of the reaction, with a significant difference in energy barrier compared to other steps. Comparison of the results in paths I and II shows that path I is more kinetically preferable than path II with a lower energy barrier of 15.9 (7.72) kJ/mol. However, theoretical results show that the P-E resulting from the preferred kinetic path I is slightly more unstable than P-Z, as much as 3.45 (2.45) kJ/mol. In experimental research, the synthesis of stable

phosphorus ylide in the presence of 2-indolinone (R3) also shows the majority of the product with an E-structural isomer (70%) [44]. To find out the reason for preference of P-E, it is necessary to investigate the reaction mechanism in details.

The changes in energy levels of structures in two different kinetic pathways I and II are shown in Figure 3. Each of these two kinetic pathways results in a product with a different structural isomer. As can be seen from this figure, the first step of the mechanism has the highest energy barrier in both paths. The barrier height of the first step of pathway I is lower than pathway II, with a value of 15.90 (7.72) kJ/mol. Due to the kinetic preference of path I, it is evident that the reaction often proceeds from path I to produce the product P-E. Furthermore, it is logical that all intermediates in the kinetic path II can move to kinetic path I. It is desirable that I1-II turns into I1-I or I1'-II turns into I1'-I as more stable structures, and this task is accomplished by passing through Ts4 and Ts5 structures with the potential energy barriers of 14.31 (11.19) and 15.81 (19.84) kJ/mol, respectively (Figure 4). Also, I2-II is converted to the more stable intermediate I12-I

by crossing Ts6 with the barrier height of 20.57 (23.16) kJ/mol.

Therefore, the reaction precedes through pathway I to produce P-E as the main product. Although the energy diagram reported in Figure 3 clearly shows the reason for the preference of product P-E over P-Z, there is still an issue. The issue is that the product P-Z is more stable than the P-E, and the unstable product P-E will likely change to the stable product P-Z by rotating around the O-C-C-P dihedral angle. The scanning results in Figure 4 show that

transforming P-E to P-Z requires an energy barrier of 70.00(77.13) kJ/mol in passing from Ts7, which is relatively high. Thus, this configuration change is not desirable. Crossing a high energy barrier to achieve a low stability of 3.46 (2.45) kJ/mol does not appear to be favorable both kinetically and thermodynamically. Therefore, the thermodynamic instability of P-E compared to P-Z cannot affect the majority of the product P-E.

Figure 4. Potential energy diagram (kJ/mol) for conversion of $(\mathbf{P} - \mathbf{E} \rightarrow \mathbf{P} - \mathbf{Z}, \mathbf{I1} - \mathbf{II} \rightarrow \mathbf{I1} - \mathbf{I}, \mathbf{I1}' - \mathbf{II} \rightarrow \mathbf{I1}' - \mathbf{I}$ and $\mathbf{I2} - \mathbf{II} \rightarrow \mathbf{I2} - \mathbf{I}$) at the B3LYP/6-311++G(d,p) level of theory.

		1			
structure	gas	dichloromethane	structure	gas	dichloromethane
R 1	1.39	1.88	P- <i>E</i>	4.58	8.10
R2	2.72	3.19	TS1-II	11.63	5.13
R3	6.38	8.19	I1-II	8.78	8.20
Ts1-I	3.36	5.13	Ts2-II	8.48	12.05
I1-I	5.68	8.20	I1'-II	9.83	8.33
Ts2-I	5.61	8.16	I2-II	10.95	10.82
I1'-I	6.10	8.33	TS3-II	11.63	12.08
I2-I	5.79	10.30	P-Z	7.89	10.15
TS3-I	7.58	12.05			

Table 2. Dipole moment values (μ) related to the structures participating in the reaction mechanism in the gas phase and in the presence of dichloromethane in the presence of 2-indolinone

3.2 Investigation of potential energy levels in the solvent phase

In order to investigate the effect of solvent on potential energy levels, comprehensive phase calculations were performed for dichloromethane solvent with dielectric constant of 9/00 using polarizable continuum model (PCM). The values reported in parentheses in Figures 3 and 4 are related to the calculations in the solution phase. The dipole moment (μ) of a molecule indicates its

polarity and distribution of charges. The dipole moment values (μ) of the structures involved in the reaction mechanism in the gas phase and in the presence of the dichloromethane solvent are reported in Table 2. Results show that all structures in the gas phase have significant dipole moment and in all structures, dipole moment value increased in the presence of dichloromethane compared to the gas phase. These structures can have favorable interactions with polar solvent molecules and align

and stabilize the dipole moment of the molecule, thus increasing the dipole moment of the structures. The results also show that the dipole moment of all structures (intermediates, transition states and product) in kinetic path **II** has a higher value than kinetic path **I** in both gas and solution phases. Key factors that influence bipolar moments include: bond polarity, bond length, molecular geometry, molecular symmetry, and molecular size. Almost all of these parameters change with the configuration of the molecule. Therefore, it can be expected that the dipole moments of the structures in the two kinetic pathways 1 and 2 will be different from each other. The calculations in the solution phase show that in the presence of 2-indolinone **R3**, the energy level of all structures in kinetic pathways **I** and **II**, except **Ts1-I** and **I2-I**, are decreased compared to the gas phase. Studies conducted in the gas and solution phases show that the energy barrier of the first reaction step in pathways I and II is higher in both the gas phase and the solvent phase than in the second and third steps.

3.3 Calculation of the reaction rate constant

According to the results, the first step of the reaction was identified as the rate-determining step, thus, the mechanism of the reaction can be proposed in Figure **5** according to kinetic evidence.

Figure 5. The reaction mechanism between triphenylphosphine **R1** and dimethyl acetylenedicarboxylate **R2** in the presence of 2-Indolinone **R3**.

Using the approximation of the rate-determining step we will have:

$$rate = \frac{d[P]}{dt}$$

$$= k_3[N^-][12]$$
(1)

$$\frac{d[11]}{dt} = k_1[R1][R2]$$
(2)
= $-k_2[11][R3]$

$$\frac{d[N^{-}]}{dt} = k_2[R3][I1]$$
(3)
= $-k_3[N^{-}][I2]$

$$[N^{-}][I2] = \frac{k_2[R3][I1]}{-k_3} \tag{4}$$

$$rate = k_1[R1][R2] \tag{5}$$

This rate equation well displays that the overall reaction rate constant is independent of the concentration of reactant **R3** and depends only on the concentration of reactants **R1** and **R2**. According to the conventional transition state theory (CTST), the values of the rate constant k(T)

for elementary bimolecular reactions in the gas phase are expressed by;

$$k = \kappa \sigma \frac{k_{BT}}{h} \frac{Q_{TS}}{Q_R} exp \left[\frac{-(E_{TS} - E_R)}{RT} \right]$$
(6)

 Q_{TS} and Q_R are the partition functions of the transition states and the reactants, $k_{\rm B}$ is the Boltzmann constant, κ is the transmission coefficient. The E_{TS} and E_R are energies of the transition state and the reactants with zero-point energy correction involved. The tunneling corrections were expressed as the ratio of the quantum mechanical to classical barrier crossing rate, assuming an unsymmetrical, one-dimensional Eckart function barrier [51]. The overall reaction rate constant was calculated using equation (5). The rate constant of the first step of the reaction as the overall rate constant of the reaction at 298.15 K for the pathways I and II is 6.79×10^{-27} and, 9.86×10^{-30} cm³.molecule⁻¹.s⁻¹, respectively. The results show that the energy required for the reaction (the sum of the energies of the first, second and third phase steps) in the presence of indoline-2-one in the gas phase and in the solution in paths I and II is 92.98(87.52) kJ/mol and 106.85(99.87) kJ/mol, respectively (the values in parentheses are related

to calculations in solvent phase). These results indicate that the reaction in the presence of indoline-2-one is more energy-efficient in path **I**, both in the gas phase and in solution.

3.4 NBO analysis

The electronic charge analysis of the atoms involved in the gas phase reaction was performed by NBO software at B3LYP/6-311++G(d,p) theoretical level and the results are reported in Table 3. The results show that the P17, C18, C29 and C40 atoms have electronic charge of 0.847, -0.329, -0.329 and -0.329 e, respectively. This result indicates that the P-C bonds are polarized in this reactant. In the TS1-I, the electronic charge of P17 decreased to 1.057 e, indicating a charge transfer from P17 atom to the C9 atom. Although the electronic charge of atoms C18, C29 and, C40 in TS1-I increases slightly (-0.377, -0.367, -0.361), it does not appear to cause the electronic charge reduction of the P17 atom. The decrease in the electronic charge of the P17 atom is due to its transfer to the C9 atom due to the formation of a stronger C9-P17 bond. By forming the P17-C9 bond in I1-I, the electronic charge of the P17 is further reduced to 1.493 e.

Table 3. NBO data calculated at B3LYP/6-311 ++ G (d, p) level of theory

R	1	R	2	R3'		I1-I	
atom	charge	atom	charge	atom	charge	atom	charge
qP(17)	0.847	qO(5)	-0.527	qH(51)	0.409	qP(17)	1.493
qC(18)	-0.329	qC(6)	0.731	qN(52)	-0.623	qO(5)	-0.571
qC(29)	-0.329	qO(7)	-0.549	qC(53)	0.613	qC(6)	0.664
qC(40)	-0.329	qC(8)	-0.008	qO(54)	-0.531	qO(7)	-0.665
		qC(9)	-0.036	qC(55)	0.479	qC(8)	-0.084
				qO(56)	-0.480	qC(9)	-0.512
TS	1-I	I1-	II	TSI	l-II	P	-E
qP(17)	1.057	qP(17)	1.500	qP(17)	1.271	qH(51)	0.262
qC(1)	-0.204	qO(5)	-0.571	qC(1)	-0.204	qN(52)	-0.551
qO(5)	-0.556	qC(6)	0.662	qO(5)	-0.554	qC(53)	0.616
qC(6)	-0.680	qO(7)	-0.667	qC(6)	-0.688	qO(54)	-0.564
qO(7)	-0.629	qC(8)	-0.077	qO(7)	-0.634	qC(55)	0.336
qC(8)	-0.344	qC(9)	-0.535	qC(8)	-0.074	qO(56)	-0.516
qC(9)	0.524			qC(9)	-0.307		

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$\alpha C(10)$	0 477	aC(10)	0.764
qC(10)	0.477		0.704
qO(11)	-0.632	qO(11)	-0.568
qO(12)	-0.532	qO(12)	-0.563
qC(13)	-0.205	qC(13)	-0.201
СТ	-0.316	СТ	-0.549

Investigation of the electronic charge of the C9 in the TS1-I shows that the charge of this atom not only did not increase compared to the dimethyl acetyl dicarboxylate (R2) (-0.036 e) but also decreased to 0.524 e. In contrast, the electronic charge of C8 increases from -0.008 a.u. in dimethyl acetylene dicarboxylate ($\mathbf{R2}$) to -0.344 e in the TS1-I structure. This result shows that the electronic charge of the P17 atom was transferred to the C8 atom. It is expected that the electronic charge of the C8 will also be increased by further reducing the electronic charge of P17 due to the forming a P-C bond in the I1-I structure. However, the results show that the electronic charge of this atom not only does not increase but also decreases substantially (-0.084). Due to that, the electronic charge of the C8 atom substantially increased to -0.512 e. This result is replicated in TS1-II and I1-II structures and thus indicates that the C9-P17 bond in structures I1-II and I1-I is also highly polarized. The overall result is that the reduction of the electronic charge of the P17 in the TS1-I and TS1-II structures is due to its transfer to the C8 atom, but in the I1-I and I1-II structures, it is due to its transfer to the C9 atom. The charge transfer values in TS1-I and TS1-II structures are -0.316 e and -0.549 e, respectively, indicating an increase in the amount of charge transfer in TS1-II compared to that in TS1-I. This increase in charge transfer with the decrease in charge of the P17 atom in the TS1-II structure and the decrease in the C9-P17 bond length in the **TS1-II** structure (2.202 Å) compared to that of the TS1-I structure (2.237 Å), confirms this claim. The results show that the charge amount of N52 in the structure of 2indolinone (R3) is -0.623 e, which decreases to -0.551 e in the **P-E** and -0.498 e in the **P-Z**. Meanwhile, the N52 charge in **R3** is -0.616 e, which decreases to -0.528 e in **P-E** and -0.486 e in **P-Z**. The results indicate the electron-withdrawing nature of the C=O group in the 2-indolinone (R3) structure.

4. Conclusions

A mechanistic investigation of the reaction between triphenylphosphine **1** and dimethyl acetylenedicarboxylate **2** in the presence of a 2indolinone as NH-acid **3** was investigated theoretically, with the results summarized as follows:

- 1. Theoretical studies showed that the reaction proceeded via three steps. The first step of the proposed mechanism (k1) was recognized as the rate-determining step.
- The lower barrier height in the ratedetermining step, as well as the higher kinetic stability of path I compared to path II, well justified and established the preference for P-*E*.
- Quantum calculations have shown well that due to the high energy barrier of converting P-*E* to P-Z, thermodynamic stability is not the reason for preference of P-*E* over P-Z. However, the Z/*E* ratio was seen to be kinetically controlled.

Acknowledgment

The author sincerely thanks the Payame Noor University and The Sirjan University of Technology for providing financial support for this work.

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