Theoretical, kinetics and mechanism investigation of the reaction between triphenylphosphine, di-tert-butyl acetylenedicarboxilate and OH-acid

S. M. Habibi Khorassani,[a]* A. Ebrahimi,[a] M. T. Maghsoodlou,[a] M. Moradian,[b] M. A. Kazemian[a] and P. Karimi[a]

[a]*Department of Chemistry, The University of Sistan and Balouchestan, P. O. Box 98135-674, Zahedan, Iran*
[b]*Department of Chemistry, Islamic Azad University of Ghaemshahr, Ghaemshahr, Iran*

Abstract: Kinetic studies were made of the reaction between triphenylphosphine, di-tert-butyl acetylenedicarboxylate in the presence of OH-acid, such as 2-hydroxy-4-methoxybenzaldehyde. To determine the kinetic parameters of the reaction, it was monitored by UV spectrophotometery. The second order fits were automatically drawn by the software associated with a Cary UV spectrophotometer model Bio-300 at appropriate wavelength. The values of the second order rate constant (k_2) were calculated using standard equations within the program. At the temperature range studied the dependence of the second order rate constant (Ln k_2) on reciprocal temperature was in a good agreement with Arrhenius equation. This provided the relevant plots to calculate the activation energy of the reaction. Furthermore useful information were obtained from studies of the effect of solvent and concentration of reactants on the rate of reaction. Proposed mechanism was confirmed according to the obtained results and steady state approximation and first step (k_2) of reaction was recognized as a rate determining step on the basis of experimental data. In addition, assignment of more stable isomers (*Z* or *E*) were investigated using the theoretical study.

Keywords: Phosphorus ylide; OH-acid; UV spectrophotometry; Kinetic parameters; Triphenylphosphine, *Z*- and *E*- isomer, Theoretical calculations

Introduction

Phosphorous ylides are reactive systems, which have a role in many valuable reactions of organic synthesis [1-12]. These are most often obtained in excellent yields from the 1:1:1 addition reaction between triphenylphosphine, dialkyl acetylendicarboxylates, in the presence of CH, SH or OH-acid [13-19]. A facile synthesis of the reaction between triphenylphosphine **1**, dialkyl acetylenedicarboxilate **2** and 2-hydroxy-4-methoxybenzaldehyde **3** (as a OH-acid) has been earlier reported [20] but the kinetic studies of this reaction has not yet been investigated.

In order to gain further insight into the reaction mechanism, a kinetic study of the reaction between triphenylphosphine **1**, di-tert-butyl acetylenedicarboxylate **2c** and 2-hydroxy-4-methoxybenzaldehyde **3** as an OH-acid was undertaken by the UV spectrophotometer technique. Numerous kinetic investigations over a large area of different NH-acids or SH-acid have previously been reported using

the UV technique [21-27]. Herein we wish to describe a kinetic investigation of the ylide reaction in the presence of OH-acid. In addition, an "atoms in molecules" (AIM) analysis at the HF/6-31G level of theory has been performed in order to gain a better understanding of the most geometrical parameters of both the *Z*-**4(a, c)** and the *E*-**4(a, c)** phosphorus ylides.

Results and Discussion

On the basis of the well established chemistry of trivalent phosphorus nucleophiles [1-6], it is reasonable to assume that phosphorus ylide **4** (Figure 1) results from the initial addition of triphenylphosphine to di-*tert*-butylacetylenedicarboxylate **2c** (rate constant k_2) and subsequent protonation of the 1:1 adduct by the OH-acid **3** (rate constant k_3) to form phosphoranes **4** (rate constant k_4) (see Figure 2).

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*Corresponding author. Fax: +(98) 5412446565; E-mail: *smhabibius@yahoo.com*

Figure 1 (i) Reaction between triphenylphosphine **1**, di-*tert*-butylacetylenedicarboxilate **2** and **3** for generation of stable phosphorus ylids **4** in accord with previous work reported in literature [20]. **(j)** *Z* and *E* isomers (major and minor) of stable phosphorus ylides **4a-b** are shown for 2-hydroxy-4-methoxybenzaldehyde. **(k)** Only one isomer (major) of stable phosphorus ylide **4c** (*Z*-**4c**).
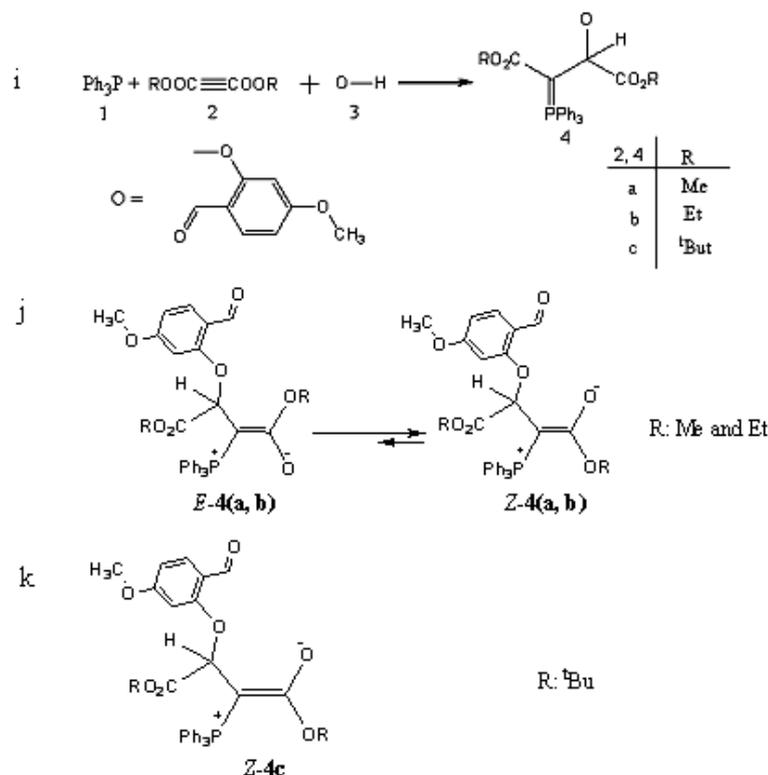
Figure 2 Mechanism proposed for the reaction between **1**, **2c** and **3** on the basis of literature [13-20] for generation of phosphorus ylides **4c**.
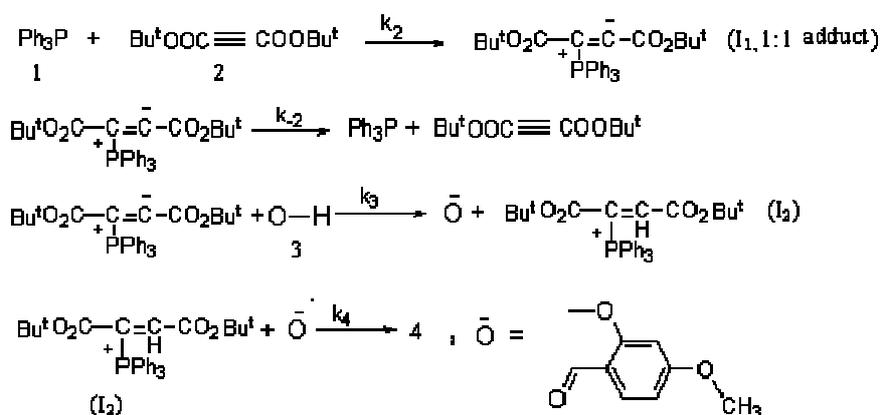
Experimental procedures

Chemicals and apparatus
Di-*tert*-butylacetylenedicarboxylate, triphenylphosphine and 2-hydroxy-4-methoxybenzaldehyde were purchased from Fulka (Buchs, Switzerland) and used without further purification. All extra pure solvents including 1,2-dichloroethane and THF also obtained from Merk (Darmstadt, Germany). A Cary UV/Vis spectrophotometer model Bio-300 with a 10 mm light-path black quartz spectrophotometer cell was employed throughout the current work.

Methods
First it was necessary to find the appropriate wavelength in order to follow the kinetic study of the reaction. For this purpose, in the first experiment, 3×10^{-3}M solution of compounds **1, 2c** and **3** have been prepared in 1,2-dichloroethane solvent. Approximately 3 mL aliquot from each reactant was pipetted into a 10 mm light path quartz spectrophotometer cell and the relevant spectra were recorded over the wavelength range 190-400 nm. The ultraviolet spectra of compounds **1, 2c** and **3** were recorded respectively. In the second experiment, 1mL aliquot from the 3×10^{-3}M solutions of compounds **1** and **3** were first pipetted into a quartz spectrophotometer cell (as there is no reaction between them), later 1mL aliquot of 3×10^{-3}M solution of reactant **2c** was added to the mixture and the reaction monitored by recording scans of the entire spectra every 4 min over the whole reaction time at the ambient temperature. The ultra-violet spectra shown in Figure **3** are typical. From this, the appropriate wavelength was found to be 360 nm (corresponding mainly to the compound **4c** (product) as shown in Figure **3**). At this wavelength, compounds **1, 2c** and **3** have relatively no absorbance value. This provided a good opportunity in order to fully investigate the kinetic of the reaction between triphenylphosphine **1**, di-*tert*-butyl acetylenedicarboxylate **2c** and 2-hydroxy-4-methoxybenzaldehyde **3** at 360 nm in the presence of 1,2-dichloroethane solvent.

Figure 3 The UV spectra of the reaction between 10^{-3} M of each compounds **1, 2c** and **3** as reaction proceeds in 1,2-dichloroethane.
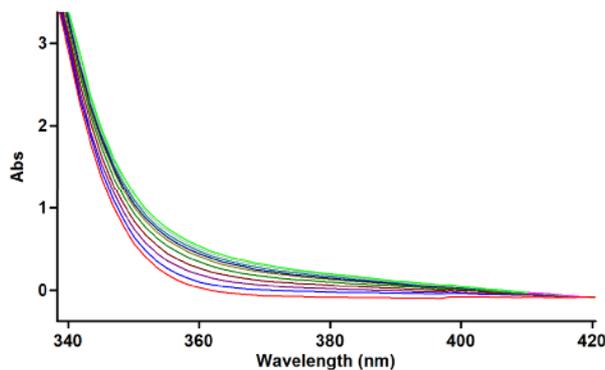
Since the spectrophotometer cell of the UV equipment had a 10 mm light-path cuvette, the UV/Vis spectra of compound **4c** was measured over the concentrations range (2×10^{-4}M $\leq$ M$_{4c}$ $\leq$ 10^{-3}M) to check a linear relationship between absorbance values and concentrations. Therefore, the UV/Vis experiments may be carried out over this concentrations range. With respect to this concentrations range and identification of suitable wavelength in preliminary investigations, it seems that practical conditions have been found that allow an investigation of kinetics of reaction between compounds **1, 2c** and **3** by the UV/Vis spectrophotometry technique. The following procedure was employed. For each kinetic experiment, first 1mL aliquot from each freshly made solution of 3×10^{-3}M compounds **1** and **3** in 1,2-dichloroethane were pipetted into a quartz cell, then 1mL aliquot of 3×10^{-3}M solution of reactant **2c** was added to the mixture, keeping the temperature at 10.0ºC, and the reaction kinetics was followed plotting UV absorbance against time measurement. Figure **4** shows the absorbance change *versus* time for the 1:1:1 addition reaction between compounds **1, 2c** and **3**. The infinity absorbance (A$_\infty$) that is the absorbance at reaction completion, can be obtained from Figure **4** at higher than t =80 min. With respect to this value, zero, first or second curve fitting could be automatically drawn for the reaction by the software [28] associated with the UV instrument. Using the original experimental absorbance *versus* time data provided a second order fit curve (solid line) at 360 nm that exactly fits the experimental curve (dotted line) as shown in Figure **5**.

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Figure 4 Experimental absorbance change (dotted line) against time at 360 nm for the reaction between compounds **1, 2c** and **3** at 10.0 ºC in 1,2-dichloroethane.
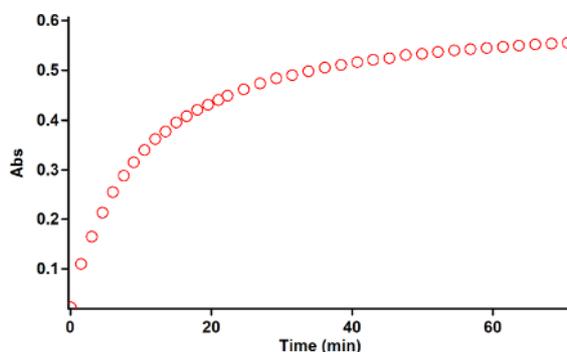
Figure 5 Second order fit curve (solid line) accompanied by the original experimental curve (dotted line) for the reaction between **1, 2c** and **3** at 360 nm and 10.0 ºC in 1,2-dichloroethane.
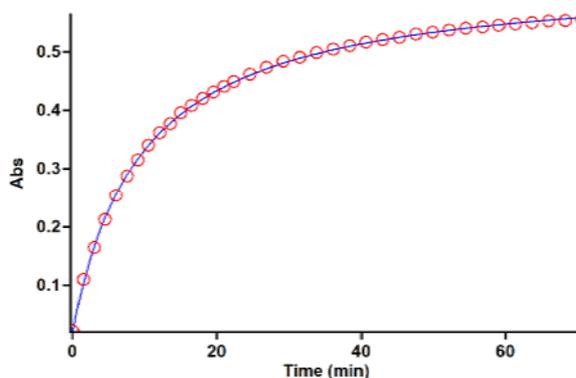
Thus the reaction between compounds **1**, **2c** and **3** follows second-order kinetic. The second order rate constant (k_2) is then automatically calculated using standard equation [28] within the program at 10.0ºC. Note that all kinetic studies under same concentration of each reactant as mentioned previously were also carried out in a series of separate experiment with 5×10^{-3} M and 7×10^{-3} M respectively. As expected the second order rate constant was independent of concentrations and its value was same as previous experiment. In addition, the overall order of reaction was also 2.

Effect of solvents and temperature
To determine the effect of change in temperature and solvent environment on the rate of reaction, it was necessary to carry out various experiments using different temperature and solvent polarity but otherwise under same condition as the previous experiment. Tetrahydrofuran (THF) with 7.4 dielectric constant was

chosen as a suitable solvent as it not only could be dissolved all compounds but also did not react with them. The effects of solvents and temperature on the rate constant are given in Table **1**. This shows that the rate of reaction in each solvent was increased at higher temperature. In addition, the rate of reaction between **1**, **2c** and **3** were decreased in a low dielectric constant environment (THF) in comparison with a hight dielectric constant environment (1,2-dichloroethane) at all temperature investigated. In the temperature range studied, the dependence of the second-order rate constant (Ln k_2) of the reaction on reciprocal temperature are consistent with the Arrhenius equation. This behavior is shown in Figure 6, gives the activation energies for reaction between **1**, **2c** and **3** as (30.14 kJ/mol), (34.54 kJ/mol) and (38.74 kJ/mol) in 1,2-dichloroethane, mixture of 1,2-dichloroethane and THF (50/50%) and THF, respectively.

Table 1 The values of second order rate constant for the reaction between compounds **1, 2c** and **3** in the presence of different solvents at all temperatures investigated.

solvent	ε	k_2/M. S			
		5.0ºC	**10.0ºC**	**15.0ºC**	**20.0ºC**
1,2-dichloroethane Mix[a]	10.03	55.1	66.5	83.6	107.3
(50/50%)	(7.4< ε <10.03) 7.4	44.2	57.4	75.7	94.3
THF		32.4	41.3	55.3	76.4

[a]Mixture of 1, 2-dichloroethane and THF

Figure 6: Dependence of second order rate constant (Ln k_2) on reciprocal temperature for the reaction between compounds **1, 2c** and **3** in 1,2-dichloroethane (solid line), mix (50/50%) (dotted line) and THF (dash line) measured at wavelength 360 nm in accordance with Arrhenius equation
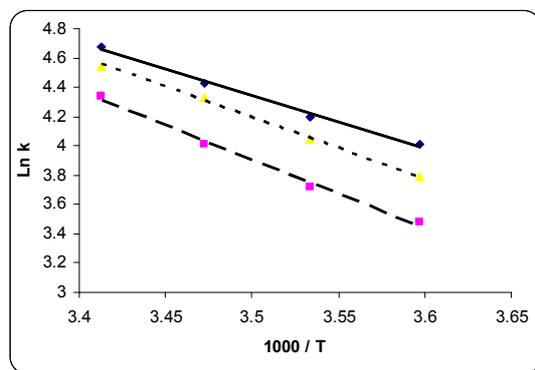
Effect of concentration

To determine reaction order with respect to triphenylphosphine **1** and di-*tert*-butyl-acetylenedicarboxilate **2c**, in a series of other separate experiments, all kinetic studies were carried out in the presence of excess **3**. Under this condition the rate equation may therefore be expressed as:

$$rate = k_{obs} [1]^\alpha [2c]^\beta, \quad k_{obs} = k_2 [3]^\gamma \quad \text{or} \quad Ln\, k_{obs} = Ln\, k_2 + \gamma\, Ln[3] \tag{I}$$

in this case (3×10^{-2} M of **3** instead of 3×10^{-3} M) using the original experimental absorbance *versus* time data provided a second order fit curve (solid line) again time at 360 nm which exactly fits the experimental curve (Figure **7**). The value of rate constant was same with that of the previous experiment (3×10^{-3} M). Repeating the experiments with 5×10^{-2}M and 7×10^{-2}M of **3** gave separately the same fit curve and rate constant. In fact the experimental data were indicated that the reaction is zero and second order with respect to **3** (OH-acid) and sum of **1** and **2c** (α + β = 2) respectively.

Figure 7 Pseudo second order fit curve (solid line) for the reaction between **1** and **2c** in the presence of exess **3** (10^{-2} M) at 360 nm and 10.0 ˚C in 1,2-dichloroethane.
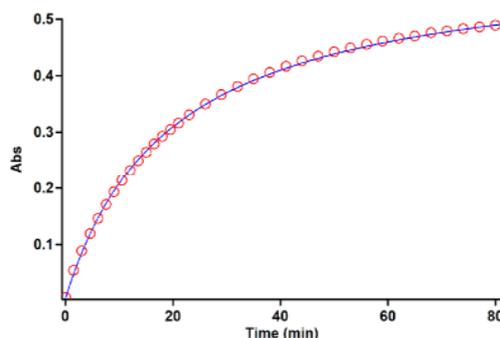
To determine reaction order with respect to di-*tert*-butyl acetylenedicarboxylate **2c** separate experiment was performed in the presence of excess of **1** with these rate of law equations:

$$rate = k'_{obs}[3]^{\gamma}[2]^{\beta}, \quad k'_{obs} = k_2[1]^{\alpha} \qquad (II)$$

Using the original experimental absorbance *versus* time data provides a pseudo first order fit curve at 360 nm which exactly fits the experimental curve (dotted line) as shown in Figure **8**.

Figure 8: Pseudo first order fit curve (solid line) for the reaction between **2c** and **3** in the presence of excess **1** (10^{-2} M) at 360 nm and 10.0 ˚C in 1,2-dichloroethane.
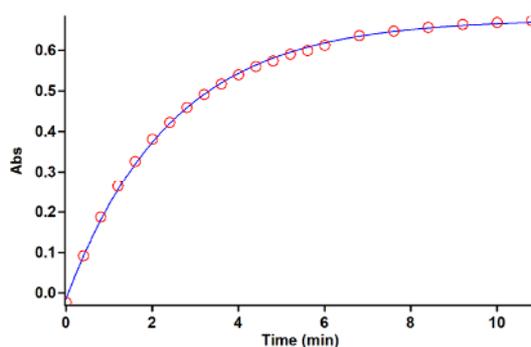
As a result, since $\gamma = 0$ (as determined in previous experiment), it is reasonable to accept that the reaction is first order with respect to compound **2c** ($\beta = 1$). Because the overall order of reaction is 2 ($\alpha + \beta + \gamma = 2$) it is obvious that $\alpha = 1$ and order of triphenylphosphine **1** must be equal to 1. Based on the above results the simplified scheme for the proposed reaction mechanism [13-20] as a possible explanation is shown in Figure **9.**

Figure 9 The simplified scheme for the proposed reaction mechanism.
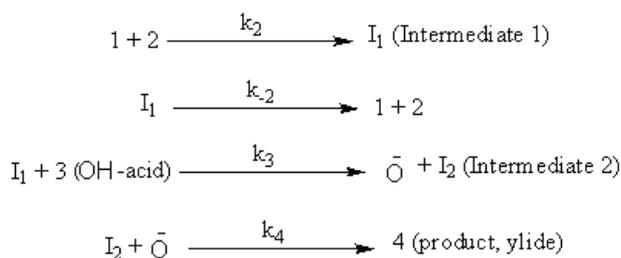
The experimental results indicate that the third step (rate constant k_3) is possibly fast. In contrast, it may be assumed that the third step is the rate determining step for the proposed mechanism. In this case rate of law can be expressed as follows:

$$rate = k_3[I_1][3] \qquad (III)$$

the steady state assumption can be employed for $[I_1]$ which is generated following equation:

$$[I_1] = \frac{k_2[1][2]}{k_{-2} + k_3[3]}$$

The value of $[I_1]$ can be replaced in equation (III) to obtain this equation:

$$rate = \frac{k_2 k_3[1][2][3]}{k_{-2} + k_3[3]}$$

Because it was assumed that k_3 is relevant to the rate determining step, it is reasonable to make the following assumption: $k_{-2} \gg k_3[3]$

So the rate of low becomes: $rate = \dfrac{k_2 k_3[1][2][3]}{k_{-2}}$

Final equation is indicated that overall order of reaction is 3 which is not compatible with experimental overall order of reaction (=2). In addition, according to this equation, the order of reaction with respect to 2-hydroxy-4-methoxybenzaldehyde **3** is 1 whereas it was actually equal to zero. For this reason, it therefore appeared that third step is fast. If we assume that fourth step (rate constant k_4) is the rate determining step for the proposed medium. In this case, there are two species ions to consider in the rate determining step namely phosphonium ion (I_2) and 2-hydroxy-4-methoxybenzaldehyde ion (O^-). The phosphonium and 2-hydroxy-4-methoxybenzaldehyde iones, as we see in Figure **2**, have full positive and negative charges and form very powerful ion dipole bonds to the 1,2-dichloroethane as the solvent (with a high dielectric

constant) in the reaction medium. But formation of transition state of the reaction between two ions carries a dispersed charge which here is divided between the attacking 2-hydroxy-4-methoxybenzaldehyde and the phosphonium ions. Bonding of solvent (1,2-dichloroethane) to this dispersed charge is much weaker than to the concentrated charge of 2-hydroxy-4-methoxybenzaldehyde and phosphonium ions. The solvent thus stabilize the species ions more than it does in the transition state, and therefore E_a is higher which slow down the reaction. But, conversely, 1,2-dichloroethane actually speeds up the reaction. For this reason, the fourth step which is independent of a change in the solvent medium could not be presented as the rate determining step. Furthermore the rate law of formation of the product (fourth step) for a proposed reaction mechanism with application of steady state assumption can be expressed by:

$$rate = \frac{k_2 k_3 [1][2][3]}{k_{-2} + k_3 [3]} \qquad (IV)$$

This equation is independent of rate constant of fourth step (k_4) and is confirms why the fourth step would not be effected by a change in the solvent medium. In addition, it has been suggested that kinetic studies of phenomena of ionic species are very fast [29,30]. If the first step (rate constant k_2) was the rate determining step, in this case, two reactants (triphenylphosphine **1** and di-*tert*-butyl acetylenedicarboxilate **2c**), as we see in Figure **2**, have no charge and could not form powerful ion-dipole bonds to the 1,2-dichloroethane as the solvent (with a high dielectric constant) in the reaction medium. But the transition state carries a dispersed charge which here is divided between the attacking **1** and **2c**. Bonding of solvent to this dispersed charge is much stronger than to the reactants with lack charge. The solvent thus stabilizes the transition state more than it does the reactans, and therefore E_a is reduced which speed up the reaction. Our experimental result, shows that solvent with high dielectric constant exert a power full effect on the rate of reaction (in fact, the first step has rate constant k_2 of proposed mechanism) but the opposite occurs with the solvent of low dielectric constant (THF, see table 1). The result of the current work (effect of solvent and concentration of compounds, in particular, the concentration of OH-acid) provided a useful evidence for steps 1 (k_2), 3 (k_3) and 4 (k_4) of the reaction between triphenylphosphine **1**, dialkyl acetylenedicarboxylate **2c** and 2-hydroxy-4-methoxybenzaldehyde **3**. Two steps involving 3 and 4 are not rate determining step although discussed effects taken altogether are compatible with the first step (k_2) of

the proposed mechanism and would allow this to be the rate determining step. However a good kinetic description of the experimental result using a mechanistic scheme based upon the steady state approximation is frequently taken as evidence of its validity. By application of this, the rate formation of product **4c** from the reaction mechanism in Figure **9**, a simplified version of Figure **2**, is given by:

$$\frac{d[4]}{dt} = \frac{d[ylide]}{dt} = rate = k_4 [I_2][O^-] \qquad (V)$$

We can apply the steady-state approximation to $[I_1]$ and $[I_2]$:

$$\frac{d[I_1]}{dt} = k_2 [1][2] - k_{-2} [I_1] - k_3 [I_1][3] \qquad ,$$

$$\frac{d[I_2]}{dt} = k_3 [I_1][3] - k_4 [I_2][O^-]$$

to obtain a suitable expression for $[I_2]$ to put into equation (V) we can assume that, after an initial brief period, the concentration of $[I_1]$ and $[I_2]$ achieve a steady state with their rates of formation and rates of disappearance just balanced. Therefore $\dfrac{d[I_1]}{dt}$ and $\dfrac{d[I_2]}{dt}$ are zero and we can obtain expressions for $[I_2]$ and $[I_1]$ as follows:

$$\frac{d[I_2]}{dt} = 0 \quad , \qquad [I_2] = \frac{k_3 [I_1][3]}{k_4 [O^-]} \qquad (VI)$$

$$\frac{d[I_1]}{dt} = 0 \quad , \qquad [I_1] = \frac{k_2 [1][2]}{k_{-2} + k_3 [3]} \qquad (VII)$$

We can now replace $[I_1]$ in the equation (VI) to obtain this equation:

$$[I_2] = \frac{k_2 k_3 [1][2][3]}{k_4 [O^-] \big[k_{-2} + k_3 [3] \big]}$$

The value of $[I_2]$ can be put into equation (V) to obtain the rate equation (VIII) for proposed mechanism:

$$rate = \frac{k_2 k_3 k_4 [1][2][3][O^-]}{k_4 [O^-] \big[k_{-2} + k_3 [3] \big]} \quad or$$

$$rate = \frac{k_2 k_3 [1][2][3]}{\big[k_{-2} + k_3 [3] \big]} \qquad (VIII)$$

Table 2: The relative energy (kcal/mol) for both the Z and the *E* isomers of ylides **4a** and **4c** calculated at the HF/6-31G and B3LYP/6-311++G(d,p) levels**.**

Isomer	HF	B3LYP
Z-**4a**	0.00	0.00
E-**4a**	3.52	2.31
Z-**4c**	0.00	0.00
E-**4c**	5.29	4.83

Experimental data have indicated that steps 3 (k_3) and 4 (k_4) are fast but in contrast step 1 (k_2) is slow, it is therefore reasonable to make the following assumption:

$$k_3\ [3] \gg k_{-2}$$

So the rate equation becomes:

$$rate = k_2\ [1][2]$$

This equation which was deduced from the mechanistic scheme (shown in Figure **9**), by applying the steady-state approximation, is compatible with the results obtained by the UV spectrophotometery.

Theoretical studies
Recently, different reports have been published on the synthesis of stable phosphorus ylides from the reaction between triphenylphosphine and reactive acetylenic esters in the presence of N-H, C-H or O-H heterocyclic compounds. The ylides **4a-b** (Figure 1) usually exist in solution as a mixture of two isomers, while ylide like compound **4c** exhibit one isomer. Determination of the more stable isomer is impossible by the ^{31}P, ^{13}C and ^{1}H NMR techniques. For this reason quantum mechanical calculations have been performed in order to gain a better understanding of the most important geometrical parameters and also relative energies of both isomers.

Calculations

Structure and Stabilities
In order to determine which is the more stable form of both the *Z*-**4(a, c)** and the *E*-**4(a, c)** isomers of ylides, their structures were first optimized at HF/6-31G level of theory [31] by using the Gaussian 98 program package [32]. Also, the relative energies of the two isomers have been calculated at the HF/6-31G and B3LYP/6-311++G (d,p) levels (See Figures **10** and **11**). The relative stabilization energies for both the *Z*-**4(a, c)** and the *E*-**4(a, c)** isomers are reported in Table **2**. As can be seen, *Z*-**4c** and *Z*-**4a** isomers are more stable forms in both HF and B3LYP levels.
Further investigation was undertaken in order to determine more effective factors on the stability of both

isomers, on the basis of AIM calculations[33] at the HF/6-31G level of theory by the AIM2000 program package.[34] As noted in the literature[35], the ranges of $\rho(r)$ and $\nabla^2\rho(r)$ are 0.002-0.035e/a_0^3 and 0.024-0.139 e/a_0^5, respectively, if H-bonds exist. The number of hydrogen bonds in both categories (*Z*-**4a** and *E*-**4a**) and (*Z*-**4c** and *E*-**4c**) are (8 and 6) and also (14 and 11), respectively. In addition, the ranges of their electron densities are in (0.0026 - 0.0140 and 0.0028 - 0.0183 au) and also (0.0015 - 0.0124 and 0.0032 -0.0167 au), respectively. With respect to the large number of hydrogen bonds in both *Z* and *E* isomers it is difficult to make a precise decision for determination of more stable isomer (see Tables 3 and 4).

Figure 10: Intramolecular hydrogen bonds (dotted lines) in the *Z*-**4a** and the *E*-**4a** isomers of stable ylide **4a**.
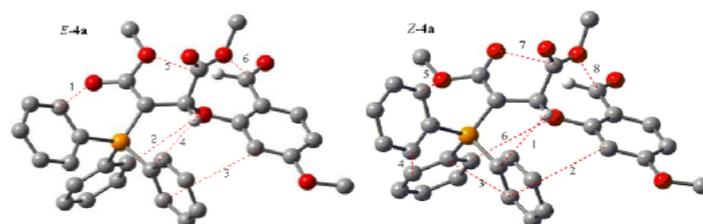
Figure 11: Intramolecular hydrogen bonds (dotted lines) in the *Z*-**4c** and the *E*-**4c** isomers of stable ylide **4c**.
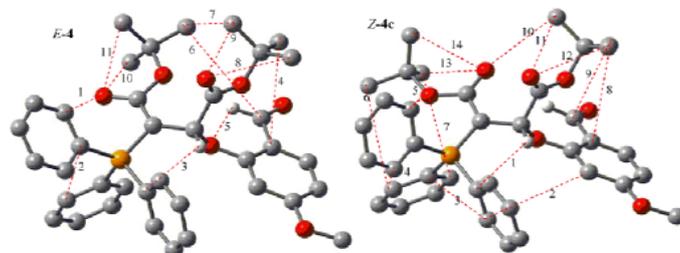
On the basis of theoretical calculations (Table **2**), the difference between relative stability of the *E*-**4a** and the *Z*-**4a** isomers (2.31kcal/mol) in the gas phase is small, while it is considerably greater in the *E*-**4c** and the *Z*-**4c** (4.83kcal/mol). Perhaps this noticeable difference is taken more in solution media for **4c,** and for this reason it is possible to observe only one isomer of **4c** (*Z* or *E*). Nevertheless, the result of our calculations is different for the ylides **4a** or **4b** (observed as the two isomers), which may be attributed to the negligible difference in relative stability of *Z*-**4a** and *E*-**4a** isomers. Perhaps this negligible difference is not taken more considerably for**4a** or **4b** in solution media, and for this reason it is possible to see the two isomers of **4a** or **4b** (both *Z* and

E isomers). In recent case [20] (synthesis of ylides **4a** and **4b**), the ^{1}H, ^{13}C and ^{31}P NMR experimental data showed the two isomers for ylide **4a** and **4b** which were consistent with the obtained result from the theoretical investigations.

Table 3: The values of $\rho \times 10^{-3}$ and $\nabla^2\rho \times 1C^3$ for both the *Z*-**4a** and the *E*-**4a** isomers of ylide **4a** calculated at the hydrogen bond critical points. All quantities are in atomic units.

E-**4a**	ρ	$\nabla^2\rho$	Z-**4a**	ρ	$\nabla^2\rho$
1	8.85	-9.14	1	6.83	-7.40
2	8.34	-7.67	2	8.67	-8.43
3	2.15	-1.73	3	2.05	-1.67
4	21.07	-23.06	4	21.45	-23.41
5	14.23	-15.38	5	46.36	-41.18
6	9.91	-10.40	6	15.21	-18.39
7	14.70	-18.01			
8	3.95	-4.75			
9	42.65	-40.31			

Table 4: The values of $\rho \times 10^{-3}$ and $\nabla^2\rho \times 1C^3$ for both the *Z*-**4c** and the *E*-**4c** isomers of ylide **4c** calculated at the hydrogen bond critical points. All quantities are in atomic units

E-**4c**	ρ	$\nabla^2\rho$	Z-**4c**	ρ	$\nabla^2\rho$
1	8.54	-8.02	1	8.82	-8.77
2	8.35	-8.72	2	6.75	-7.30
3	2.18	-1.75	3	2.10	-1.70
4	21.58	-23.43	4	2.50	-2.13
5	14.87	-18.16	5	1.98	-1.66
6	47.11	-44.27	6	4.60	-5.35
7	10.62	-10.34	7	21.51	-23.49
8	10.99	-10.75	8	15.21	-18.37
9	2.62	-3.04	9	48.43	-42.90
10	11.95	-11.48	10	10.63	-10.37
11	13.44	-12.91	11	11.08	-10.86
			12	3.76	-4.23
			13	12.23	-11.81
			14	12.68	-12.21

Conclusions

Kinetic investigation of the reaction between triphenylphosphine and di-*tert*-butyl acetylenedicarboxilate in the presence of 2-hydroxy-4-methoxybenzaldehyde was undertaken by the UV spectrophotometery. The results can be summarized as follow:
1. The appropriate wavelength and concentrations were successfully determined in order to follow kinetic investigations.

2. The overall order of reaction followed second-order kinetic and order of reaction with respect to triphenylphosphine, di-*tert*-butyl acetylenedicarboxylate and 2-hydroxy-4-methoxybenzaldehyde (OH-acid) were obtained 1, 1 and zero respectively.

3. The values of second-order rate constant of the reaction were automatically calculated with respect to the standard equation using the software associated with Cary-300 UV equipment. This provided the relevant plots to calculate the activation energy of the reaction.

4. The rate of reaction was increased in media of higher dielectric constant solvent; this can be related to differences in stabilization of the reactants and the activated complex in transition state by solvent.

5. With respect to the experimental data, the first step of proposed mechanism was recognized as a rate determining step (k_2) and this was confirmed based upon the steady state approximation. **6.** The assignments of the Z and E isomer as the major or minor forms in both ylides **4a** and **4c** were undertaken by AIM method. Quantum mechanical calculation was clarified how ylide **4a** or **4b** exist in solution as a mixture of two isomers. These results have also provided useful evidence for the ylide **4c**. Noticeable differences between the most important geometrical parameters (for instance, relative energy) provide a suitable chance for **4c** which appear as a single isomer *Z*-**4c** in solution.

Acknowledgments

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