# Kinetic study and mechanism investigation of the reactions between triphenylphosphine, dialkyl acetylene dicarboxylates and NH-acid such as Harman

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## ABSTRACT

The Kinetic studies were made of the reactions between triphenylphosphine, dialkyl acetylenedicarboxylates in the presence of NH-acid, such as harman. To determine the kinetic parameters of the reactions, they were monitored by UV spectrophotometery. The second order fits were automatically drawn and 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 all reactions. Furthermore, useful information were obtained from studies of the effect of solvent, structure of reactants (different alkyl groups within the dialkyl acetylenedicarboxylates) and also concentration of reactants on the rate of reactions. 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.

**Key words**: Phosphorus ylide; NH-acid; UV spectrophotometry;
Kinetic parameters; Rate constant.

## 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 strong CH, SH or NH-acids.[13-25] A facile synthesis of the reaction between triphenylphosphine 1, dialkyl acetylendicarboxylates 2 (2a, 2b or 2c) and harman 3 (as NH-acid) have been earlier reported[26] but the kinetic studies of these reactions have not yet been investigated . In order to gain further insight into the reaction mechanism, a kinetic study of these reactions was undertaken by the UV spectrophotometery technique. Numerous kinetic investigations over a large area of different reactions have previously been reported using the UV instrument.[27-34] On the basis of the well established chemistry of trivalent phosphorus nucleophiles,[1-6] it is reasonable to assume that phosphorus ylide 4 (4a, 4b or 4c) results from the initial addition of triphenylphosphine to the acetylenic ester 2 (2a, 2b  or 2c ) (rate constant $k_2$) and subsequent protonation of the 1:1 adduct by the NH-acid 3 (rate constant $k_3$) to form phosphoranes 4 (rate constant $k_4$) (Fig. 1 and 2).

## EXPERIMENTAL

*Chemicals and apparatus used*: dialkyl acetylenedicarboxylates, triphenylphosphine, harman were purchased from Fulka (Buchs, Switzerland) and used without further purifications. All extra pure solvents including the 1,4-dioxan and ethyl acetate also obtained from Merk (Darmstadt, Germany). A Cary UV/Vis spectrophotometer model Bio-300 with a 10 mm light-path 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, $3 \times 10^{-3}$M solution of compounds **1, 2c** and **3** have been prepared in 1,4-dioxan as 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. Figures **3, 4** and **5** show the ultraviolet spectra of compounds **1, 2c** and **3** respectively. In the second experiment, first 1mL aliquot from the $3 \times 10^{-3}$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 $3 \times 10^{-3}$M solution of reactant **2c** was added to the mixture and the reaction monitored by recording scans of the entire spectra every 6 min over the whole reaction time at the ambient temperature. The ultra-violet spectra shown in Figure **6** are typical. From this, the appropriate wavelength was found to be 365 nm (corresponding mainly to the compound **4c** (product) as shown in Figure **6**). At this wavelength, compounds **1, 2c** and **3** have relatively no absorbance value. This provided good opportunity in order to fully investigate the kinetic of the reaction between triphenylphosphine **1**, di-*tert*-butyl acetylenedicarboxylate **2c** and harman **3** at 365 nm
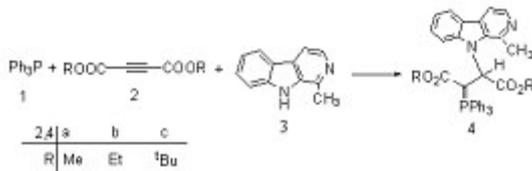


**Fig. 1: The reaction between triphenylphosphine 1, dialkyl acetylenedicarboxylate 2 (2a, 2b or 2c) and NH-acid 3 for generation of stable phosphorus ylides 4 (4a, 4b or 4c).**
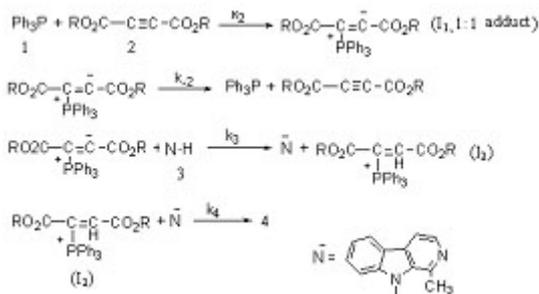


**Fig. 2: Proposed mechanism for the reaction between 1, 2 (2a, 2b or 2c) and 3 on the basis of literatures[13-26] for generation of phosohorus ylides 4 (4a, 4b or 4c)**
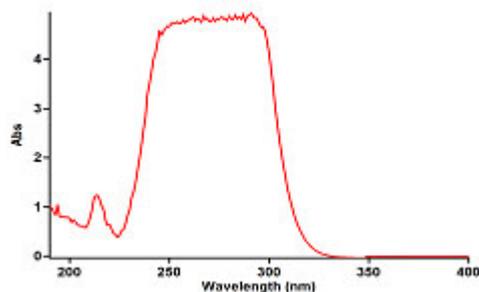


**Fig. 3: The UV spectrum of $10^{-3}$M triphenyl- phosphine 1 in 1,4-dioxan.**
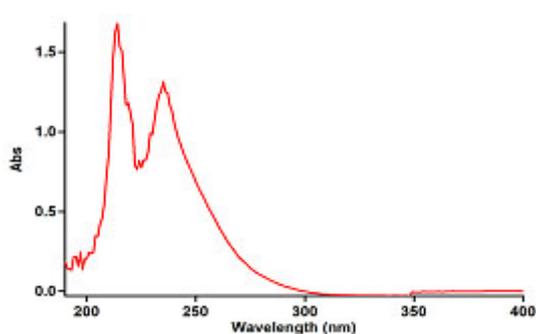


**Fig. 4: The UV spectrum of $10^{-3}$M di-*tert*-butyl acetylenedicarboxylate 2c in 1,4-dioxan.**
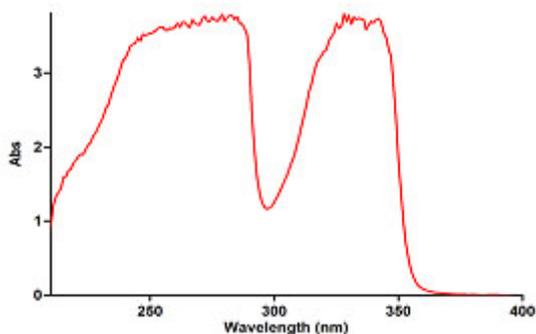
**Fig. 5: The UV spectrum of $10^{-3}$M harman 3 in 1, 4-dioxan.**
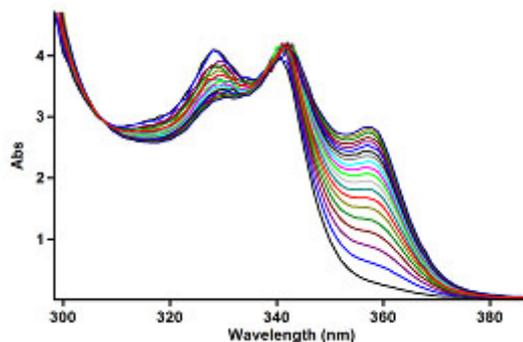


**Fig. 6: The UV spectra of the reaction between 1, 2c and 3 with $10^{-3}$M concentration of each compound as reaction proceeds in 1, 4-dioxan.**

in the presence of 1,4-dioxan as solvent. 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 ($2 \times 10^{-4}$M $\geq$ M$_{4c}$ $\geq 10^{-3}$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 kinetic 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 $3 \times 10^{-3}$M compounds 1 and 3 in 1,4-dioxan were pipetted into a quartz cell, then 1mL aliquot of $3 \times 10^{-3}$M solution of reactant 2c was added to the mixture, keeping the temperature at 12.0°C and the reaction kinetics were followed plotting UV absorbance against time measurement. Fig. 7 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

Fig. 7 at t =181 min. With respect to this value, zero and first or second curve fitting could
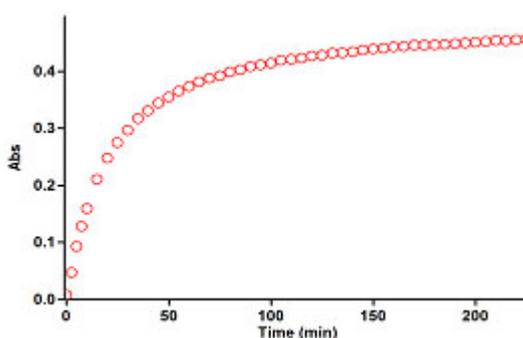


**Fig. 7: The experimental absorbance change (dotted line) against time for the reaction between compounds 1, 2c and 3 at 365 nm and 12.0°C in 1,4-dioxan.**
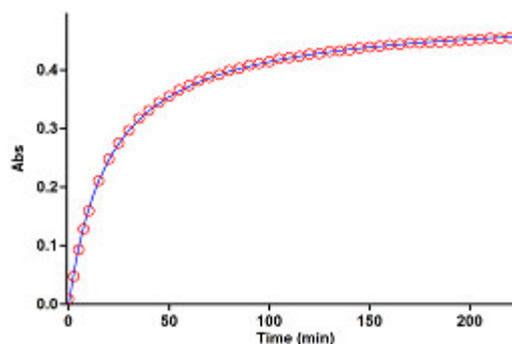


**Fig. 8: Second order fit curve (solid line) accompanied by the original experimental curve (dotted line) for the reaction between 1, 2c and 3 at 365 nm and 12.0°C in 1,4-dioxan.**

be automatically drawn for the reaction by the software[35] associated with the UV instrument. In this case using the original experimental absorbance versus time data provided a second order fit curve (solid line) at 365 nm that exactly fits the experimental curve (dotted line) as shown in Fig. 8.

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 equetion[35] within the program at 12.0°C. Not that all kinetic studies under same concentration of each reactant were also carried out in a series of separate experiment with concentration of $5 \times 10^{-3}$ M and $7 \times 10^{-3}$ 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.

### RESULT AND DISCUSSION

#### 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. For this purpose, ethyl acetate with 6 dielectric constant was chosen as suitable solvent as it not only dissolved all the compounds but also does not react with them. The effects of solvent 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 was accelerated in a high dielectric constant environment (ethyl acetate) in comparison with a low dielectric constant environment (1,4-dioxan) at all temperature investigated. In the temperature range studied, the dependence of the second-order rate constant (Ln $k_2$) of the reactions on reciprocal temperature are consistent with the Arrhenius equation. This behavior is shown in Figure 9, gives the activation energy of reaction between 1, 2c and 3 was obtained (28.3 kJ/mol) from the slop of Figure.

#### Effect of concentration

To determine reaction order with respect to triphenylphosphine 1 and dialkyl acetylenedicarboxylate 2 (2c), in a series of other separate experiments, all kinetic studies were
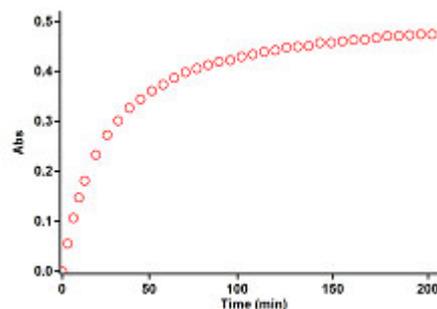
**Fig. 10: The experimental absorbance change versus time for the reaction between 1 and 2c in the presence of excess 3 ($10^{-2}$M) at 365 nm and 12.0°C in 1,4-dioxan.**

**Fig. 9: Dependence of second order rate constant (Ln k) on reciprocal temperature for the reaction between compounds 1, 2c and 3 measured at wave length 365 nm in 1,4-dioxan in accordance with Arrhenius equation.**
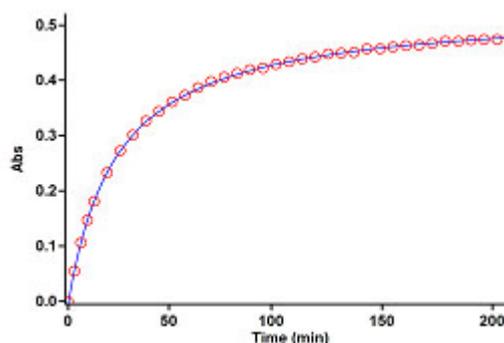
**Fig. 11: Pseudo second order fit curve (solid line) for the reaction between 1 and 2c in the presence of excess 3 ($10^{-2}$ M) at 365 nm and 12.0°C in 1,4-dioxan.**

carried out in the presence of excess **3**. Under this condition the rate equation may therefore be expressed as: rate = $k_{obs}$ $[1]^{\alpha}$ $[2]^{\beta}$, $k_{obs}$ = $k_2$ $[3]^{\gamma}$ or $Lnk_{obs}$ $Lnk_2$ + $\gamma Ln[3]$

in this case ($3 \times 10^{-2}$ M of **3** instead of $3 \times 10^{-3}$ M) using the original experimental absorbance versus time data (Figure **10**) provides a second order fit curve (solid line) against time at 365 nm that exactly fits the experimental curve (Figure **11**). The value of rate constant was same with that of the previous experiment ($3 \times 10^{-3}$ M). Repeating the experiments with $5 \times 10^{-2}$ M and $7 \times 10^{-2}$M of **3** was separately led to same fit curve and rate constant. In fact, the experimental data indicated that observed pseudo second order rate constant ($k_{obs}$) is equal to the second order rate constant ($k_2$), this is possible when $\gamma$ is zero in equation (I). It is therefore appeared that the reaction is zero and second order with respect to **3** (NH-acid) and sum of **1** and **2** (**2c**) ($\alpha + \beta = 2$) respectively.

To determine reaction order with respect to dialkyl acetylenedicarboxylate **2** (**2c**) separate experiment was performed in the presence of excess of **1** (rate $_=$ $k'_{obs}$ $[3]^{\gamma}$ $[2]^{\beta}$, $k'_{obs}$ $_=$ $k_2$ $[1]^{\alpha}$ (II)). The original experimental absorbance versus time data has been shown in Figure **12** and provide a pseudo first order fit curve (solid line) at 365 nm that exactly fits the experimental curve (dotted line) as shown in Figure **13**. 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 **2** (**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. This observation was also obtained for other two reactions (**1**, **2b** and **3**) and (**1**, **2a** and **3**). Based on the above results the simplified scheme of the proposed reaction mechanism (Figure **2**) as a possible explanation is shown in Figure **14**. The experimental results indicate that the third step (rate constant $k_3$) is possibly fast. In contrast, it may

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

| Solvent | ε | $K_2.M^{-1}.min^{-1}$ | | | | |
|---|---|---|---|---|---|---|
| | | 12.0°C | 17.0°C | 22.0°C | 27.0°C | |
| 1,4-dioxanethyl acetate | 2 | | 40.5 | 50.4 | 60.3 | 74.1 |
| | 6 | 81.3 | 94.7 | 116.2 | 138.0 | |
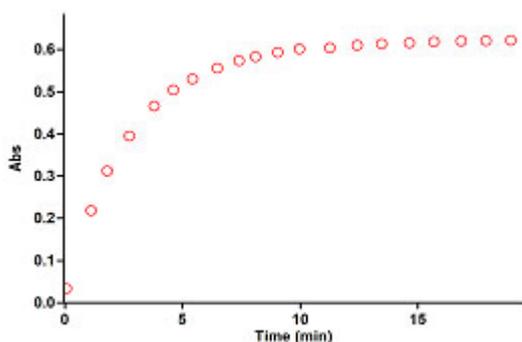


**Fig. 12: The experimental absorbance change versus time for the reaction between 2c and 3 in the presence of excess 1 ($10^{-2}$M) at 365 nm and 12.0°C in 1,4-dioxan.**
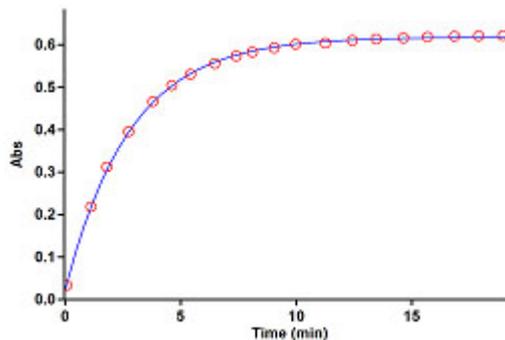


**Fig. 13: Pseudo first order fit curve (solid line) for the reaction between 2c and 3 in the presence of excess 1 ($10^{-2}$ M) at 365 nm and 12.0°C in 1,4-dioxan.**

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:

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

The final equation is indicated that overall

**Table 2: The value of overall second order rate constants for the reaction between 1, 2b and 3 in the presence of all solvents and temperatures investigated**

| Solvent | ε | $K_2.M^{-1}.min^{-1}$ | | | |
|---|---|---|---|---|---|
| | | 12.0°C | 17.0°C | 22.0°C | 27.0°C |
| 1,4-dioxanethyl acetate | 2 | 236.4 | 264.1 | 307.0 | 357.5 |
| | 6 | 349.6 | 396.5 | 440.3 | 499.8 |

**Table 3: The value of overall second order rate constants for the reaction between 1, 2a and 3 in the presence of all solvents and temperatures investigated**

| Solvent | ε | $K_2.M^{-1}.min^{-1}$ | | | |
|---|---|---|---|---|---|
| | | 12.0°C | 17.0°C | 22.0°C | 27.0°C |
| 1,4-dioxanethyl acetate | 2 | 482.1 | 526.4 | 591.8 | 663.7 |
| | 6 | 511.2 | 563.1 | 628.4 | 711.3 |

$$1 + 2 \xrightarrow{\ k_2\ } I_1 \text{ (Intermediate 1)}$$

$$I_1 \xrightarrow{\ k_{-2}\ } 1 + 2$$

$$I_1 + 3 \text{ (NH-acid)} \xrightarrow{\ k_3\ } N^- + I_2 \text{ (Intermediate 2)}$$

$$I_2 + N^- \xrightarrow{\ k_4\ } 4 \text{ (product, ylide)}$$
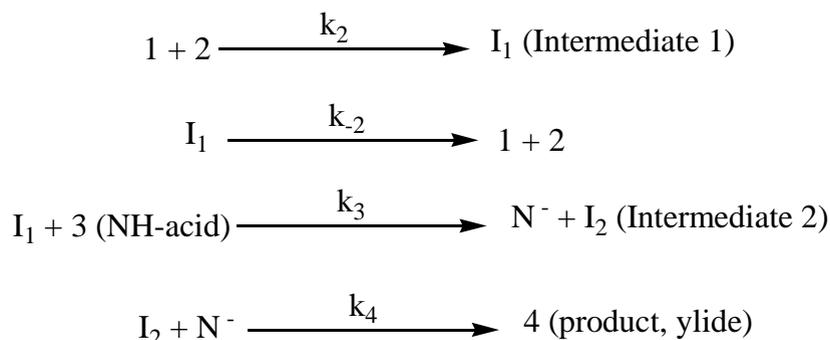
**Fig. 14: The simplified Scheme for the proposed reaction mechanism.**

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 harman **3** is one 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 mechanism, in this case, there are two species ions to consider in the rate determining step namely phosphonium ion ($I_2$) and $N^-$. The phosphonium and $N^-$ ions, as we see in Figure **2**, have full positive and negative charges and form very powerful ion dipole bonds to the ethyl acetate as the solvent (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 $N^-$ and the phosphonium ions. Bonding of solvent (ethyl acetate) to this dispersed charge is much weaker than to the concentrated charge of $N^-$ 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, ethyl acetate speeds actually up the reaction. For this reason, the fourth step that 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 = $k_4$ [$I_2$][$N^-$] by

application of steady state for [$I^-$] and [$N^-$], replace their values in above equation, the following

equation is obtained: $rate = \dfrac{k_2 k_3 [1][2][3]}{k_{-2} + k_3[3]}$

this equation is independent of rate constant of fourth step ($k_4$) and confirms why the fourth step would not be affected by a change in the solvent medium. In addition, it has been suggested that kinetic studies of phenomena of ionic species are very fast.[36-37] If the first step (rate constant $k_2$) were the rate determining step. In this case, two reactants (triphenylphosphine **1** and dialkyl acetylenedicarboxylate **2** (**2c**)), as we see (Figure 2), have no charge and could not form powerful ion-dipole bonds to the ethyl acetate 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 **2**. Bonding of solvent to this dispersed charge is much stronger than to the reactants which lack charge. The solvent thus stabilizes the transition state more than it does the reactants, and therefore $E_a$ is reduced which speed up the reaction. Our experimental result, shows that the solvent

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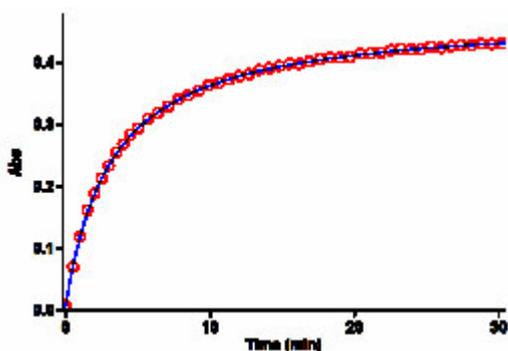


**Fig. 15: Second order fit curve (solid line) accompanied by the original experimental curve (dotted line) for the reaction between 1, 2b and 3 at 365 nm and 12.0°C in 1,4-dioxan**
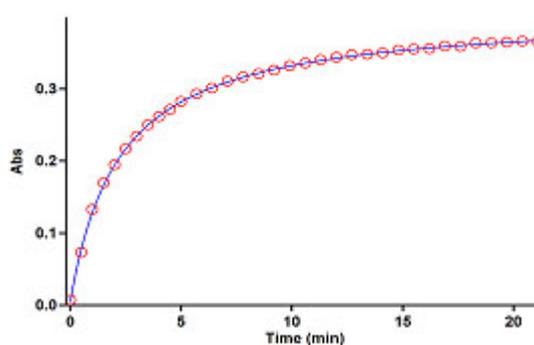


**Fig. 16: Second order fit curve (solid line) accompanied by the original experimental curve (dotted line) for the reaction between 1, 2a and 3 at 365 nm and 12.0°C in 1,4-dioxan.**

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 solvent of low dielectric constant (1,4-dioxan). The result of the current work (effect of solvent and concentration of compounds, in particular, the concentration of NH-acid) provided useful evidence for steps 1 ($k_2$), 3 ($k_3$) and 4 ($k_4$) of all reactions between triphenylphosphine **1**, **2** (**2a**, **2b** or **2c**) and **3**. Two steps involving 3 and 4 are not rate determining step, although the discussed effects taken together are compatible with the first step ($k_2$) of proposed mechanism and would allow this to be the rate determining step. However, a good kinetic description of the experimental result using 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 **4** (**4a**, **4b** or **4c**) from the reaction mechanism (Figure **14**) is given by:

$$\frac{d[4]}{dt} = \frac{d[ylide]}{dt} = rate = k_4[I_2][N^-] \quad ...(5)$$

we can apply the steady-state approximation to $[I_1]$ and $[I_2]$;

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

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

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 $\frac{d[I_1]}{dt}$ and $\frac{d[I_2]}{dt}$ are zero and we can obtain expressions for $[I_2]$ and $[I_1]$ as follows:

$$\frac{d[I_2]}{dt} = 0 \qquad [I_2] = \frac{k_3[I_1][3]}{k_4[N^-]} \quad ...(6)$$

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

...(7)

We can now replace $[I_1]$ in the equation (VI) which is generate following equation:

$$[I_1] = \frac{k_2 k_3[1][2][3]}{k_4[N^-][k_{-2} + k_3[3]]}$$

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

$$rate = \frac{k_2 k_3 k_4[1][2][3][N^-]}{k_4[N^-][k_{-2} + k_3[3]]} \quad or \quad rate = \frac{k_2 k_3[1][2][3]}{[k_{-2} + k_3[3]]} \quad ...(8)$$

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: $k_3[3] >> k_{-2}$

so the rate equation becomes:

$$rate = k_2[1][2] \qquad (IX)$$

This equation which was obtained from a mechanistic scheme (shown in Figure **14**) by applying the steady-state approximation is compatible with the results obtained by the UV spectrophotometery.

**Further kinetic investigations**
**Effect of structure of dialkyl acetylenedi carboxylates**

To confirm the above observations, further experiments were performed with diethyl acetylenedicarboxylate **2b** and dimethyl acetylenedicarboxylate **2a** respectively. The values of the second-order rate constant ($k_2$) for the reactions between (**1**, **2b** and **3**) and (**1**, **2a** and **3**) are reported in Tables **2** and **3** respectively for all solvents and temperature investigated. The original experimental absorbance curves (dotted line) accompanied by the second order fit curves (solid line) at 365 nm for both reactions are shown in Figures **15** and **16**.

As can be seen from the Tables **2** and **3** the behavior of diethyl acetylenedicarboxylate **2b** and dimethyl acetylenedicarboxylate **2a** are as same as the di-*tert*-butyl acetylenedicarboxylate **2c** with respect to the reaction with **1** and **3**. The rate of both recent reactions were also accelerated in high dielectric constant environment and high temperature, nevertheless the rate of them under the same conditions are approximately 4 to 6 time greater than the reaction with di-*tert*-butyl

acetylenedicarboxylate **2c** (see Tables **1, 2** and **3**). It seems that both inductive and steric factors of bulky alkyl groups within the structure of dialkyl acetylenedicarboxylate would tend to reduce the rate of overall reactions (see equation IX). As a result of this, it appears that the dialkyl acetylenedicarboxylates participate in the rate determining step of reaction (rate constant k$_2$) and in addition on concentrations, structures of them (strict and inductive factors) affects the rate of this step. In the case of dimetyl acetylenedicarboxylate **2a**, less steric and also less inductive effects of dimethyl groups both together exert a powerful effect on the rate of reaction.

## Conclusions

Kinetic investigation of the reactions between triphenylphosphin **1**, dialkyl acetylenedicaroxylates **2** (**2a, 2b** or **2c**) with harman **3** was undertaken using UV spectrophotometery. The results can be summarized as follow; **1**. The appropriate wavelengths and concentrations were successfully determined in order to follow kinetic investigations. **2**. The overall order of all three reactions followed second-order kinetic and order of reaction with respect to triphenylphosphine, dialkyl acetylenedicarboxylate and harman were obtained 1, 1 and zero respectively. **3**. The values of second-order rate constant of all reactions were automatically calculated with respect to the standard equation using the software associated with Cary-300 UV equipment. **4**. The rate of all reactions were 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**. The rate of all reactions were accelerated at high temperature and the activation energy of the reaction with di-*tert*-butylacetylenedicarboxylate **2c** (28.3 kJ/mol) was higher than the two reactions which were followed by the diethyl acetylenedicarboxylate **2b** (19.7 kJ/mol) and dimethyl acetylenedicarboxylate **2a** (16.2 kJ/mol) in 1,4-dioxan. **6**. The more steric factor in bulky alkyl groups accompanied by its more inductive effect within the structure of dialkyl acetylenedicarboxylate would tend to reduce the overall reaction rates. **7**. 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.

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