KINETIC STUDY AND MECHANISM: AN INVESTIGATION OF THE REACTIONS BETWEEN TRIPHENYLPHOSPHINE, DIALKYL ACETYLENEDICARBOXYLATES AND NH-ACID SUCH AS 2-AMINOBENZIMIDAZOLE BY UV

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ABSTRACT

The works undertaken were to carry out kinetic studies of the reactions between triphenylphosphine, dialkyl acetylenedicarboxylates in the presence of NH-acid, such as 2-aminobenximidazole. To determine the kinetic parameters of the reactions, they were monitored by UV spectrophotometry. 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 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 take part 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

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triphenylphosphine **1**, dialkyl acetylendicarboxylates **2** (**2a, 2b** or **2c**) and 2-aminobenzimidazole **3** (as NH-acid) have been earlier reported[26] but the kinetic studies of these reactions have not been investigated yet. In order to gain further insight into the reaction mechanism, a kinetic study of these reactions was undertaken by the UV spectrophotometry technique. Numerous kinetic investigations over a large area of different reactions have been previously 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 and 2-aminobenzimidazole were purchased from Fulka (Buchs, Switzerland) and used without further purifications. All extra pure solvents including the 1,4-dioxan and ethyl acetate were 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, 3×10^{-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 wavelengths range 190-400 nm. Fig. **3, 4** and **5** show the ultraviolet spectra of compounds **1, 2c** and **3,** respectively. In the second experiment, first 1 mL aliquot from the 3×10^{-3}M solutions of compounds **1** and **3** were pipetted into a quartz spectrophotometer cell (because there is no reaction between them), later 1 mL aliquot of 3×10^{-3}M solution of reactant **2c** was added to the mixture and the reaction was monitored by recording scans of the entire spectra every 15 min over the whole reaction time at the ambient temperature. The ultra-violet spectra shown in Fig. 6 are typical. As can be seen from this figure, the appropriate wavelength can be chosen 330 nm (corresponding mainly to the compound **4c** (product) as shown in Fig. 6). At this wavelength, compounds **1, 2c** and **3** have relatively no absorbance value. This provided good opportunity in order to fully investigate the kinetics of the

reaction between triphenylphosphine **1**, di-*tert*-butyl acetylenedicarboxylate **2c** and 2-aminobenzimidazole **3** at 330 nm 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 (2×10^{-4} M $\leq$ M$_{4c}$ $\leq$ 10^{-3} M) to check a linear relationship between absorbance values and concentrations.

2,4	a	b	c
R	Me	Et	^tBu
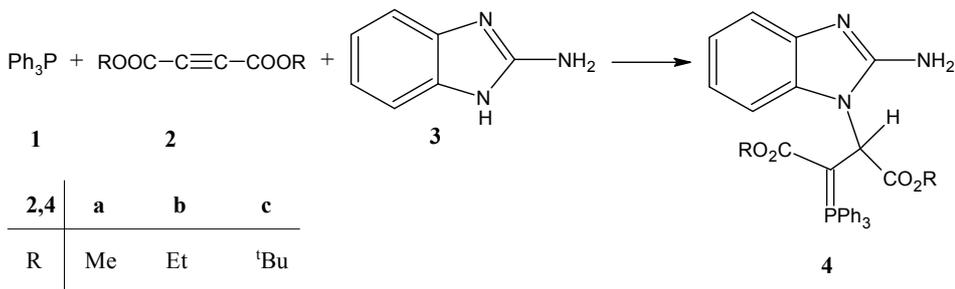
Fig. 1: The reaction between triphenylphosphine 1, dialkyl acetylenedicarboxylate 2 (2a, 2b or 2c) and NH-acid 3 for generation of stable phosphorus ylides 4 (4a, 4b or 4c)
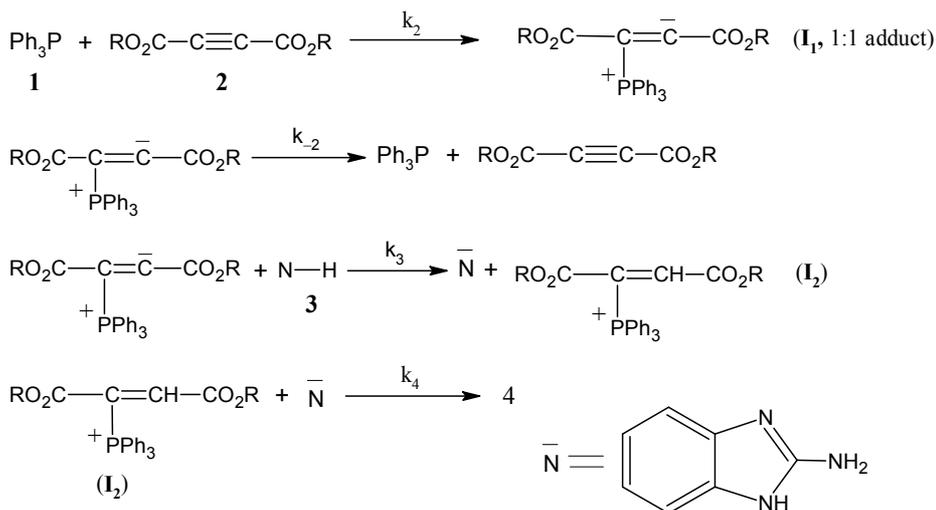
Fig. 2: Proposed mechanism for the reaction between 1, 2 (2a, 2b or 2c) and 3 on the basis of literatures[13–26] for generation of phosohorus ylides 4 (4a, 4b or 4c)

Therefore, the UV/Vis experiments may be carried out over this concentrations range. With respect to the obtained concentrations range and identification of suitable wavelength in preliminary investigations, it seems that practical conditions have been

found to allow an investigation of kinetics of reaction between compounds **1**, **2c** and **3** by the UV/Vis spectrophotometry technique. This will be discussed according to the following procedure-
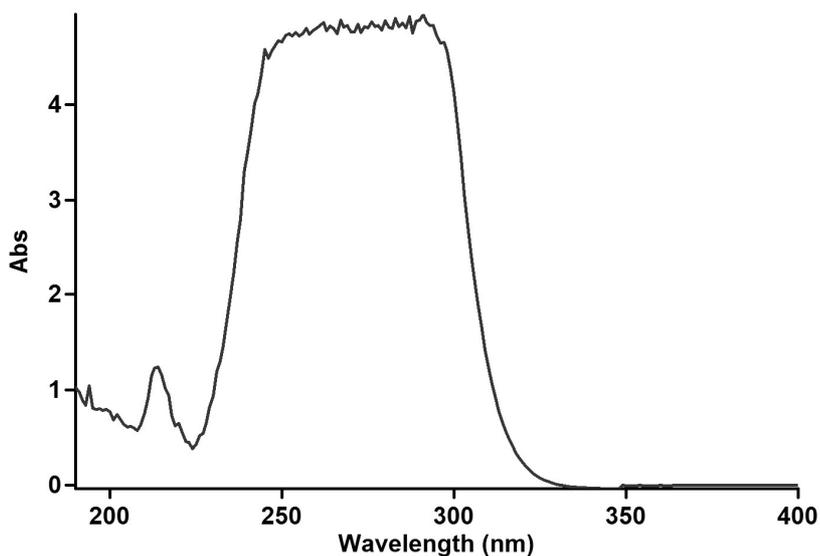

**Fig. 3: The UV spectrum of 10^{-3} M triphenylphosphine 1 in 1,4-dioxan**
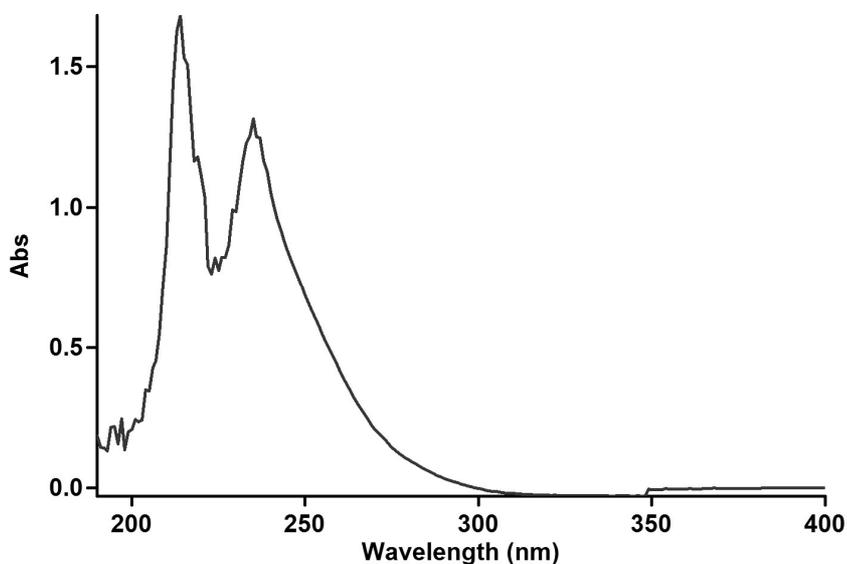
Fig. 4: The UV spectrum of 10^{-3}M di-*tert*-butyl acetylenedicarboxylate 2c in 1, 4-dioxan
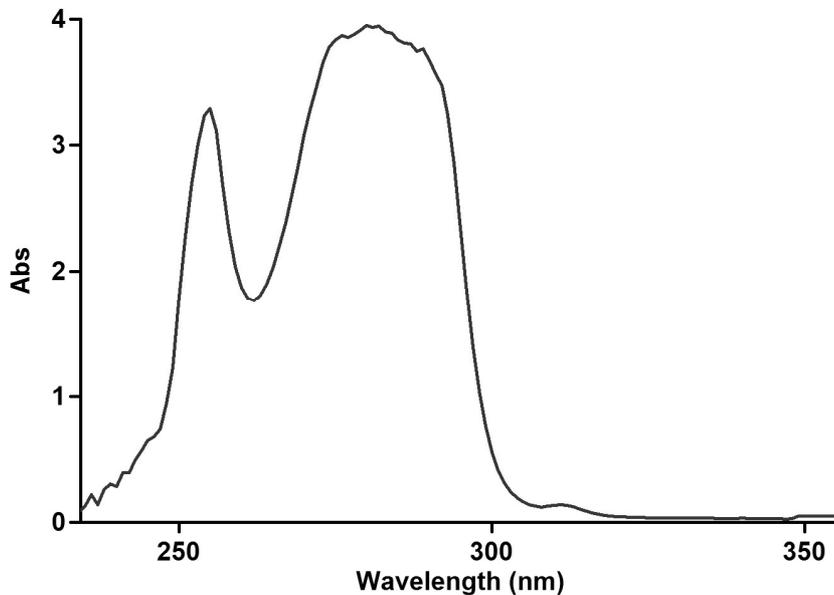
**Fig. 5 The UV spectrum of 10^{-3} M 2-aminobenzimidazole 3 in 1, 4-dioxan**
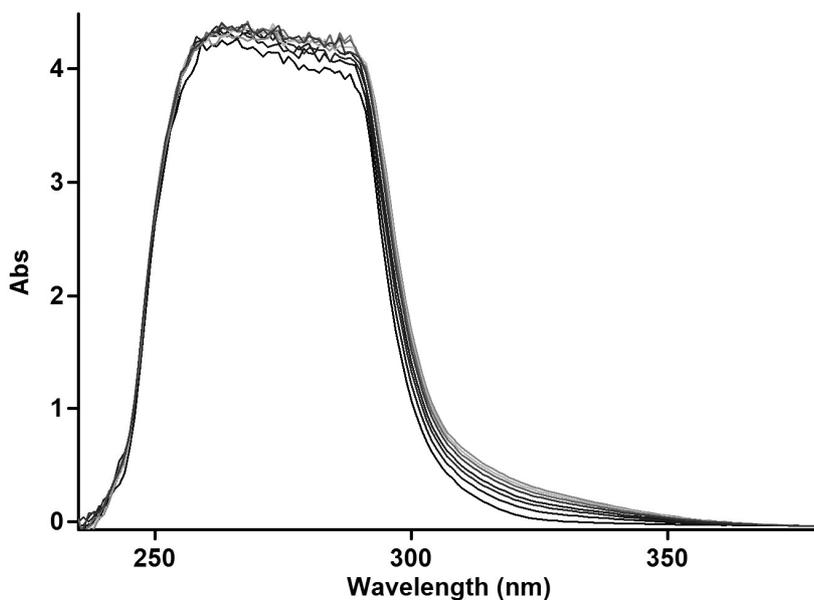
Fig. 6: The UV spectra of the reaction between 1, 2c and 3 with 10^{-3} M concentration of each compound as reaction proceeds in 1, 4-dioxan

For each kinetic experiment, first 1 mL aliquot from each freshly made solution of 3×10^{-3} M compounds **1** and **3** in 1,4-dioxan were pipetted into a quartz cell, then 1 mL aliquot of 3×10^{-3} M solution of reactant **2c** was added to the mixture, keeping the temperature at 12.0 °C and the reaction kinetics were followed via 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_∞), that is the absorbance at reaction completion, can be obtained from Fig. **7** at t =222 min. With respect to this value, zero and first or second curve fitting could 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 (full line) at 330 nm, which exactly fits the experimental curve (dotted line) as shown in Fig. **8**.
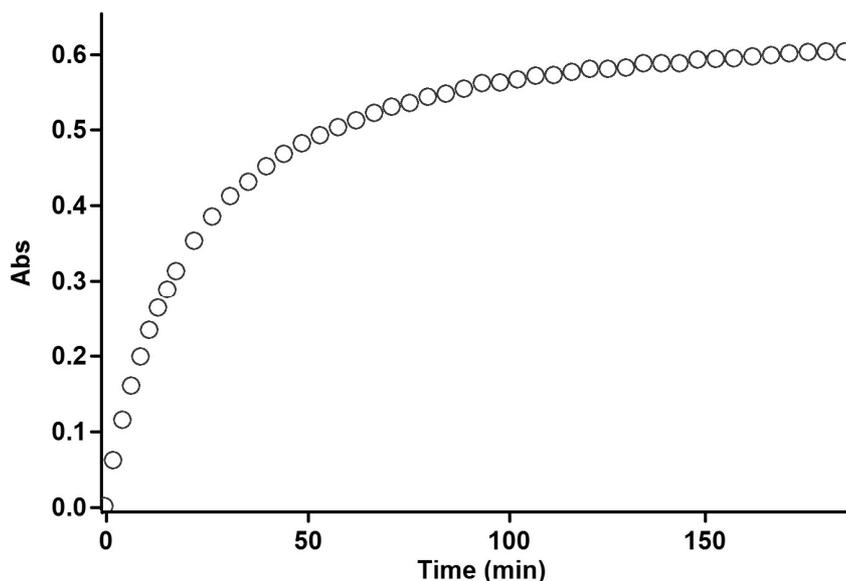

Fig. 7: The experimental absorbance change (dotted line) against time for the reaction between compounds 1, 2c and 3 at 330 nm and 12.0ºC in 1,4-dioxan.

Thus the reaction between compounds **1**, **2c** and **3** follows second-order kinetics. The second-order rate constant (k_2) is then automatically calculated using standard equetion[35] within the program at 12.0ºC. It was necessary to remember that another kinetic studies under same concentration of each reactant were also carried out in a series of separate experiments with concentration of 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 in previous experiment. In addition, the overall order of reaction was also 2.
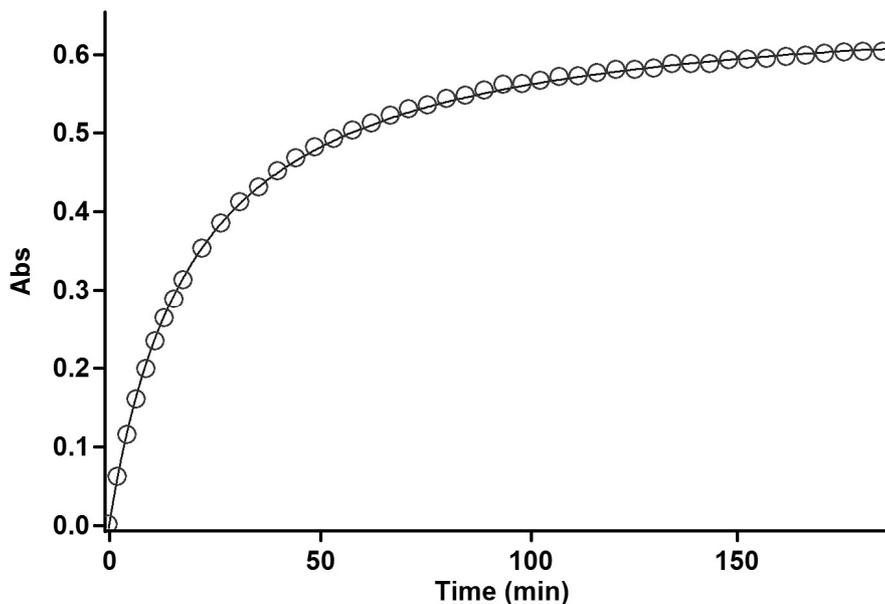
Fig. 8: Second order fit curve (full line) accompanied by the original experimental curve (dotted line) for the reaction between 1, 2c and 3 at 330 nm and 12.0ºC in 1, 4-dioxan

RESULTS 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 with different temperature and solvent polarities under same conditions with previous experiment. For this purpose, ethyl acetate with 6 dielectric constant was chosen as suitable solvent, which not only could dissolve all compounds but also does not react with them. The effects of solvents and temperature on the rate constant are given in Table **1**. As can be seen from this table, the rate of reaction in each solvent 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 temperatures 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 Fig. **9**. The activation energy of reaction between **1**, **2c** and **3** was obtained (26.1 kJ/mol) from the slope of straight line**.**

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}			
1,4-Dioxan	2	55.4	67.0	79.3	96.7
Ethyl acetate	6	64.6	77.5	91.0	108.7
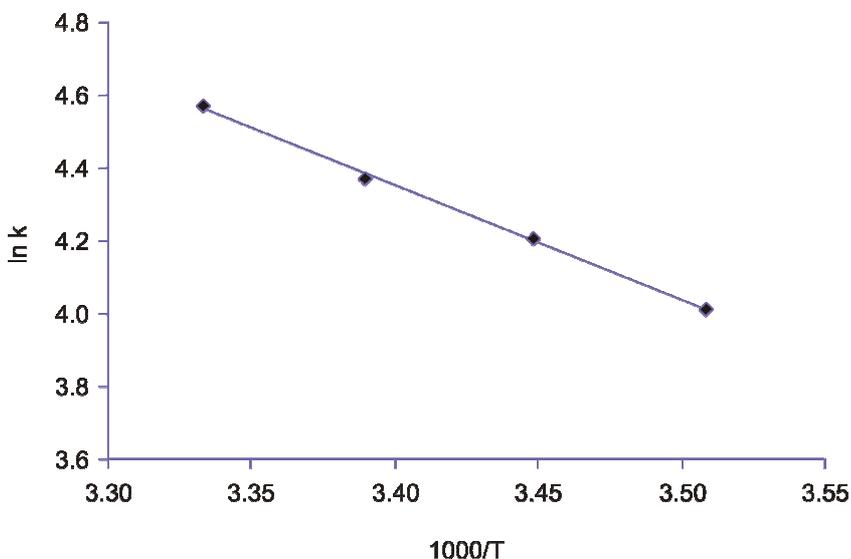
Fig. 9: Dependence of second order rate constant (ln k) on reciprocal temperature for the reaction between compounds 1, 2c and 3 measured at wavelength 330 nm in 1,4-dioxan in accordance with Arrhenius equation.

Effect of concentration

To determine reaction order with respect to triphenylphosphine **1** and dialkyl acetylenedicarboxylate **2 (2c)**, in a series of another 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:

$$\text{rate} = k_{obs} \; [\mathbf{1}]^{\alpha} \; [\mathbf{2}]^{\beta} \; , \; k_{obs} = k_2 \; [\mathbf{3}]^{\gamma} \; \text{or ln } k_{obs} = \ln k_2 + \gamma \ln[\mathbf{3}] \quad …(1)$$

In this case (3×10^{-2} M of **3** instead of 3×10^{-3} M) using the original experimental absorbance versus time data provides a second order fit curve (full line) against time at 330 nm, which exactly fits the experimental curve. The value of rate constant was same to that

of the previous experiment (3×10^{-3} M). Repeat experiments with 5×10^{-2} M and 7×10^{-2} M of **3** 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 γ is zero in equation (1). 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.

$$\text{rate} = k'_{obs} [\mathbf{3}]^{\gamma} [\mathbf{2}]^{\beta}, \; k'_{obs} = k_2 [\mathbf{2}]^{\alpha}, \qquad \qquad \ldots(2)$$

The original experimental absorbance versus time data has been shown in Fig. **10**. This provides a pseudo first order fit curve (full line) at 330 nm which exactly fits the experimental curve (dotted line) as shown in Fig. 11. As a result of this, since $\gamma = 0$ (was determined in previous experiment), it is reasonable to accept that the reaction is first order with respect to compound **2** (**2c**) ($\beta = 1$). Due to the overall order of reaction is 2 ($\alpha + \beta + \gamma = 2$), it is obvious that $\alpha = 1$ and the 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 (Fig. 2) as a possible explanation is shown in Fig. 12.
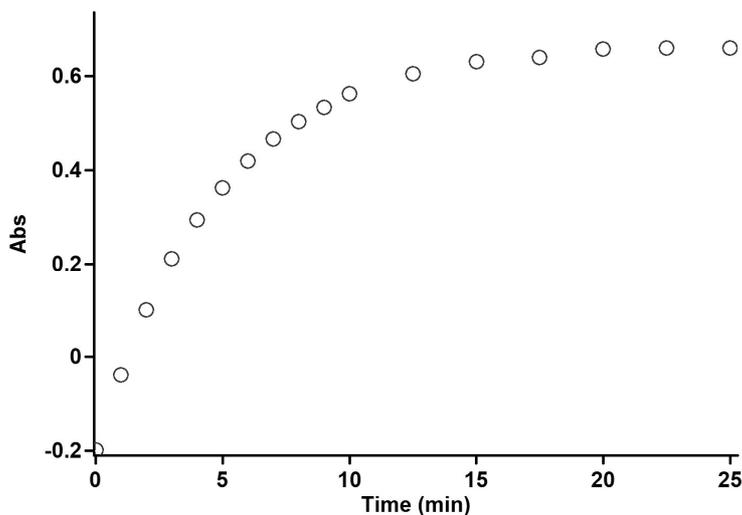

Fig. 10: The experimental absorbance change versus time for the reaction between 2c and 3 in the presence of excess of 1 (10^{-2} M) at 330 nm and 12.0°C in 1, 4-dioxan
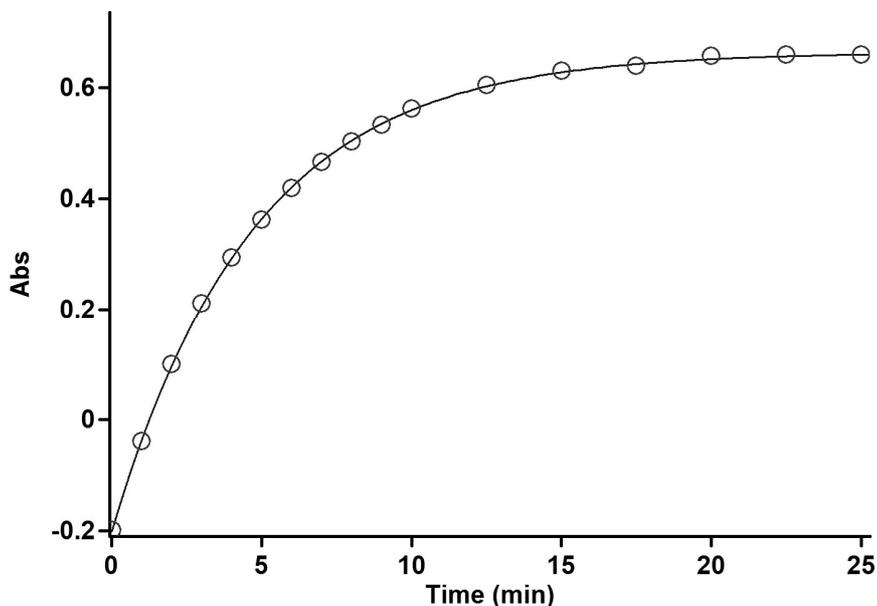
Fig. 11: Pseudo first order fit curve (full line) for the reaction between 2c and 3 in the presence of excess 1 (10^{-2} M) at 330 nm and 12.0ºC in 1, 4-dioxan.

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

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

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

$$I_2 + N^- \xrightarrow{\ k_4\ } 4 \text{ (Product, ylide)}$$
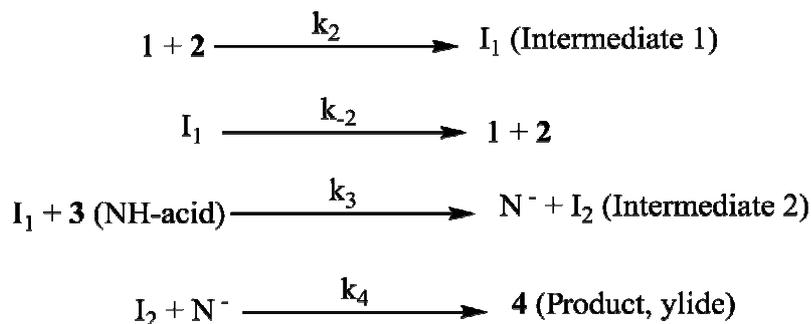
Fig. 12 The simplified scheme for the proposed reaction mechanism.

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 slow and it could be the rate determining step for the proposed mechanism. In this case, the rate law can be expressed as follows:

$$\text{rate} = k_3 [I_1][3] \qquad \qquad …(3)$$

The steady state assumption can be employed for $[I_1]$ which generates the

following equation-

$$[I_1] \ = \ \frac{k_2[\mathbf{1}][\mathbf{2}]}{k_{-2} + k_3[\mathbf{3}]} \qquad \qquad \dots(4)$$

The value of $[I_1]$ can be replaced in equation (3) to obtain this equation:

$$rate \ = \ \frac{k_2 k_3[\mathbf{1}][\mathbf{2}][\mathbf{3}]}{k_{-2} + k_3[\mathbf{3}]} \qquad \qquad \dots(5)$$

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

$$rate \ = \ \frac{k_2 k_3[\mathbf{1}][\mathbf{2}][\mathbf{3}]}{k_{-2}} \qquad \qquad \dots(6)$$

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-aminobenzimidazole **3** is one whereas it was practically obtained equal to zero. For this reason, it therefore, appears that third step is presumably fast step. 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 (Fig. 2), have full positive and negative charges and form very powerful ion dipole bonds to the ethyl acetate as solvent (high dielectric constant) in the reaction mechanism. But formation of transition state of reaction between two ions carries a dispersed charge which is here 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 the transition state, and therefore, E_a is raised which slow down the reaction. Conversely, ethyl acetate speeds up the reaction practically. For this reason, the fourth step could not be presented as the rate determining step. Furthermore, the rate law of formation of product (fourth step) for proposed reaction mechanism can be expressed:

$$rate \ = \ k_4 [I_2][N^-] \qquad \qquad \dots(7)$$

By application of steady state for $[I^-]$ and $[N^-]$, replacing their values in above equation, the equation (8) is obtained

$$rate = \frac{k_2 k_3 [\mathbf{1}][\mathbf{2}][\mathbf{3}]}{k_{-2} + k_3 [\mathbf{3}]} \qquad \ldots(8)$$

This equation is independent of rate constant of fourth step (k_4) and it is confirmed that why the fourth step would not be effected upon a change in the solvent medium. In addition to these, it was earlier suggested that kinetic studies of phenomena of ionic species are so fast.[36, 37] If the first step (rate constant k_2) to be rate determining step. In this case, two reactants (triphenylphosphine **1** and dialkyl acetylenedicarboxylate **2** (**2c**)), as we see (Fig. 2), have no charge and could not form powerful ion-dipole bonds to the ethyl acetate as solvent (high dielectric constant) in the reaction medium. But the transition state carries a dispersed charge which is here divided between the attacking **1** and **2**. Bonding of solvent to this dispersed charge is much stronger than to the reactants with lack of 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. From the experimental results, it is found that solvent with high dielectric constant exert a powerful effect on the rate of reaction (in fact, first step with rate constant k_2 of proposed mechanism) but in the opposite to the solvent with low dielectric constant (1,4-dioxan). The result of the current work (effect of solvent and concentration of compounds) provided a 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 steps according to the discussed effects, although these effects are compatible with first step (k_2) of proposed mechanism and would allow to be the rate determining step. However, a good kinetic description of experimental result by 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 **4** (**4a, 4b** or **4c**) from the reaction mechanism (Fig. 12) is given by:

$$\frac{d[\mathbf{4}]}{dt} = \frac{d[ylide]}{dt} = rate = k_4 [I_2][N^-] \qquad \ldots(9)$$

the steady-state approximation can be applied to $[I_1]$ and $[I_2]$;

$$\frac{d[I_1]}{dt} = k_2 [\mathbf{1}][\mathbf{2}] - k_{-2}[I_1] - k_3 [I_1][\mathbf{3}] \qquad \ldots(10)$$

$$\frac{d[I_2]}{dt} = k_3 [I_1][\mathbf{3}] - k_4 [I_2][N^-] \qquad \ldots(11)$$

To obtain a suitable expression for $[I_2]$ to put into equation (9), it can be assumed 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 it can be obtained expressions for $[I_2]$ and $[I_1]$ as follows:

$$\dfrac{d[I_2]}{dt} = 0 \qquad\qquad [I_2] = \dfrac{k_3[I_1][\mathbf{3}]}{k_4[N^-]} \qquad\qquad \text{...(12)}$$

$$\dfrac{d[I_1]}{dt} = 0 \qquad\qquad [I_1] = \dfrac{k_2[\mathbf{1}][\mathbf{2}]}{k_{-2}+k_3[\mathbf{3}]} \qquad\qquad \text{...(13)}$$

Now replace $[I_1]$ in the equation (12) which generates following equation:

$$[I_2] = \dfrac{k_2\,k_3[\mathbf{1}][\mathbf{2}][\mathbf{3}]}{k_4[N^-]\big[k_{-2}+k_3[\mathbf{3}]\big]} \qquad\qquad \text{...(14)}$$

The value of $[I_2]$ can be put into equation (9) to obtain the rate equation (15) for proposed mechanism:

$$rate = \dfrac{k_2\,k_3\,k_4[\mathbf{1}][\mathbf{2}][\mathbf{3}][N^-]}{k_4[N^-]\big[k_{-2}+k_3[\mathbf{3}]\big]} \quad \text{or} \quad rate = \dfrac{k_2\,k_3[\mathbf{1}][\mathbf{2}][\mathbf{3}]}{\big[k_{-2}+k_3[\mathbf{3}]\big]} \qquad \text{...(15)}$$

Experimental data were indicated that steps 3 (k_3) and 4 (k_4) are fast but in contrast, the step 1 (k_2) is slow. It is, therefore, reasonable to make the following assumption: $k_3[\mathbf{3}] \gg k_{-2,}$ so the rate equation becomes:

$$rate = k_2[\mathbf{1}][\mathbf{2}] \qquad\qquad \text{...(16)}$$

This equation, which was obtained from a mechanistic scheme (shown in Fig. **12**) by applying the steady-state approximation, is compatible with the results obtained by the UV spectrophotometery.

Further kinetic investigations

Effect of structure of dialkyl acetylenedicarboxylates

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 temperatures investigated. The original experimental absorbance curves (dotted line) accompanied by the second order fit curves (full line) at 330 nm for both reactions are shown in Fig. 13 and 14.

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}			
1,4-Dioxan	2	311.9	345.1	387.0	447.5
Ethyl acetate	6	345.8	380.9	425.7	487.0

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}			
1,4-Dioxan	2	452.1	486.4	551.7	623.7
Ethyl acetate	6	491.2	540.1	605.4	676.3
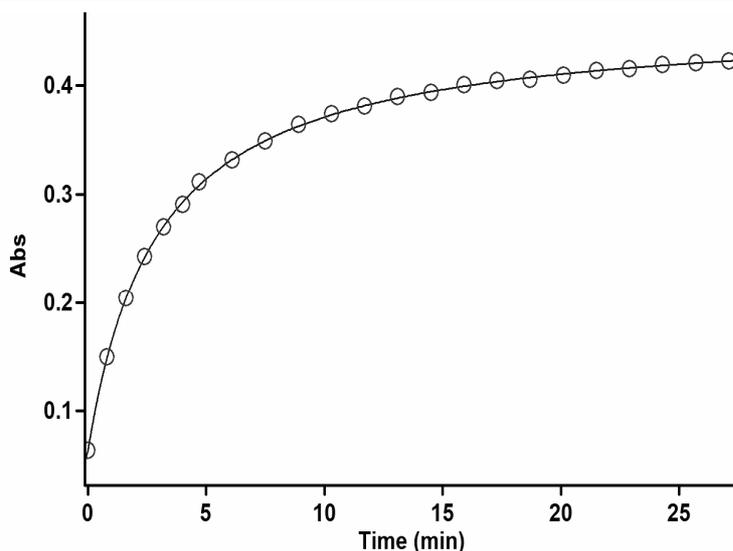
Fig. 13: Second order fit curve (full line) accompanied by the original experimental curve (dotted line) for the reaction between 1, 2b and 3 at 330 nm and 12.0ºC in 1, 4-dioxan
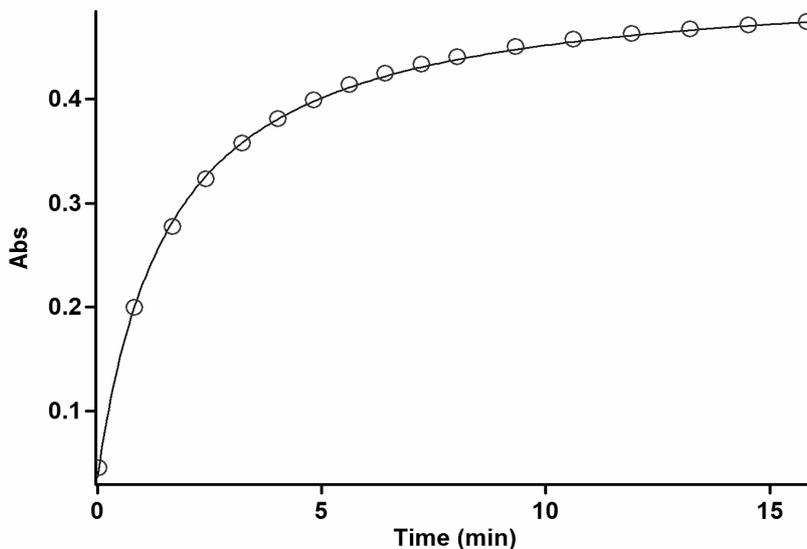
Fig. 14: Second order fit curve (full line) accompanied by the original experimental curve (dotted line) for the reaction between 1, 2a and 3 at 330 nm and 12.0ºC in 1,4 dioxan

As can be seen from the Tables **2** and **3,** the behavior of diethyl acetylenedicarboxylate **2b** and dimethyl acetylenedicarboxylate **2a** are 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 these under the same conditions are approximately 6 to 8 times greater than the reaction with di-*tert*-butyl acetylenedicarboxylate **2c** (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 (equation 16). 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 triphenylphosphine **1**, dialkyl acetylenedicaroxylates **2** (**2a, 2b** or **2c**) with 2-aminobenzimidazole **3** were undertaken by the UV spectrophotometery. The results can be summarized as follow; (**i**). The appropriate wavelengths and concentrations were successfully determined to follow kinetic investigations, (**ii**). The overall order of all three reactions followed second-order kinetics

and order of reaction with respect to triphenylphosphine, dialkyl acetylenedicarboxylate and 2-aminobenzimidazole were obtained 1, 1 and zero, respectively, **(iii)**. The values of second-order rate constant of all reactions were automatically calculated with respect to the standard equation within the software associated with Cary-300 UV equipment, **(iv)**. 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, **(v)**. The rate of all reactions were accelerated at high temperature, and the activation energy of the reaction with di-*tert*-butylacetylenedicarboxylate **2c** (26.1 kJ/mol) was higher than the two reactions which were followed by the diethyl acetylenedicarboxylate **2b** (16.9 kJ/mol) and dimethyl acetylenedicarboxylate **2a** (15.5 kJ/mol) in 1,4-dioxan, **(vi)**. 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 rate of overall reactions and **(vii).** With respect to the experimental data first step of proposed mechanism was recognized as a rate determining step (k_2) and reaction mechanism was confirmed based upon the obtained experimental results and also steady state approximation.

ACKNOWLEDGMENTS

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