Asian Journal of Chemistry Vol. 21, No. 2 (2009), 1069-1080

Kinetic and Mechanism Investigation of the Reactions of Triphenylphosphine, Dialkyl Acetylenedicarboxylates and NH-Acids by Ultra Violet

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The work undertaken to carry out kinetic studies of the reactions between triphenylphosphine, dialkyl acetylenedicarboxylates in the presence of NH-acid, such as 2-acetylpyrrole or 2-pyrrolecarbaldehyde. To determine the kinetic parameters of the reactions, 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 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 NH-acids) 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[1-6]. 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[7-19]. A facile synthesis of the reaction between triphenylphosphine (**1**), dialkyl acetylendicarboxylates (**2**) and 2-acetylpyrrole (**3a**) or 2-pyrrolecarbaldehyde (**3b**) (as NH-acids) have been earlier reported[20] 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 the reactions was undertaken by the UV spectrophotometer technique. Numerous kinetic investigations over a large area of different reactions have been previously reported using the UV instrument[21-27]. On the basis of the well established chemistry of trivalent phosphorus nucleophiles[1], it is reasonable to assume that phosphorus ylide **4** results from the initial addition of triphenylphosphine to the acetylenic ester **2** (**2c**, **2d** or **2e**) (rate constant k_2) and subsequent protonation of the 1:1 adduct by the NH-acids **3** (**3a** or **3b**)(rate constant k_3) to form phosphoranes **4** (**4ac**, **4ad**, **4ae**, **4bc**, **4bd** or **4be**) (rate constant k_4) (Figs. 1 and 2).

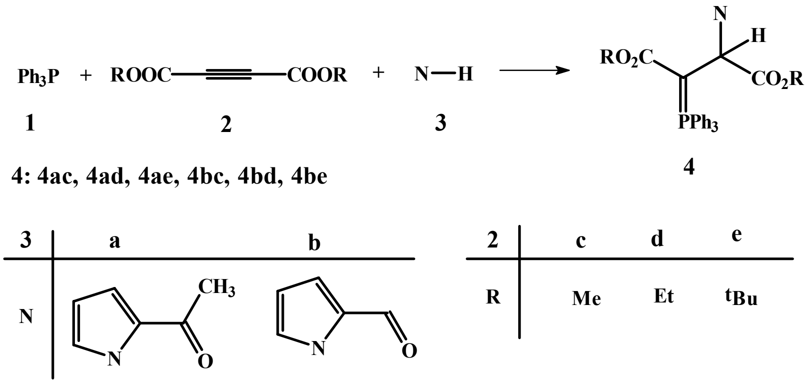

Fig. 1. Reaction between triphenylphosphine **1**, dialkyl acetylenedicarboxylate **2** (**2c**, **2d** or **2e**) and NH-acids **3** (**3a** or **3b**) for generation of stable phosphorus ylides **4** (**4ac**, **4ad**, **4ae**, **4bc**, **4bd** or **4be**)

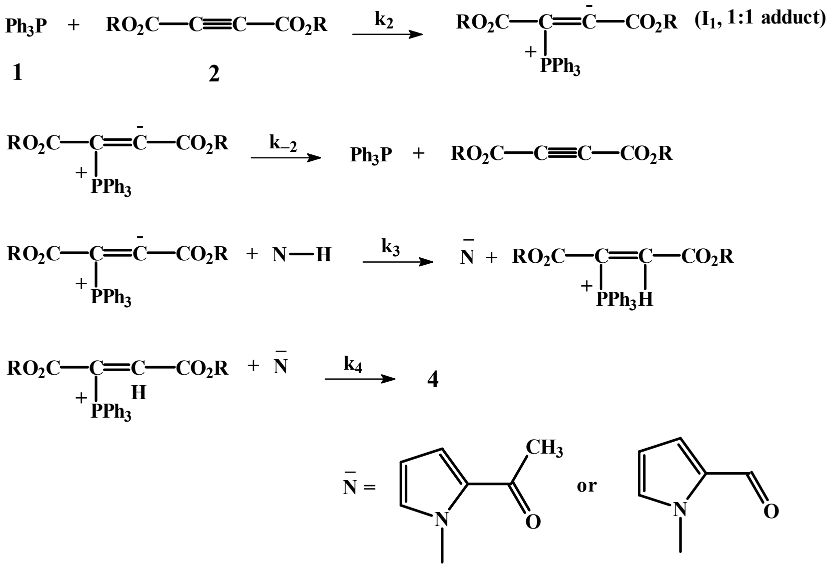

Fig. 2. Proposed mechanism for the reaction between **1**, **2** (**2c**, **2d** or **2e**) and (**3a** or **3b**) on the basis of literatures[7-19] for generation of phosohorus ylides **4** (**4ac**, **4ad**, **4ae**, **4bc**, **4bd** or **4be**)

EXPERIMENTAL

Dialkyl acetylenedicarboxylates, triphenyl-phosphine, 2-acetylpyrrole or 2-pyrrolecarbaldehyde were purchased from Fulka (Buchs, Switzerland) and used without further purifications. All extra pure solvents including the *n*-hexane 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.

Method: 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**, **2e** and **3a** have been prepared in *n*-hexane 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. Figs. 3-5 show the ultraviolet spectra of compounds **1**, **2e** and **3a**, respectively. In the second experiment, first 1 mL aliquot from the 3×10^{-3} M solutions of compounds **1** and **3a** 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 **2e** was added to the mixture and the reaction monitored by recording scans of the entire spectra every 12 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 340 nm (corresponding mainly to the compound **4ae** (product) as shown in Fig. 6). At this wavelength, compounds **1**, **2e** and **3a** 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 **2e** and 2-acetylpyrrole **3a** at 340 nm in the presence of *n*-hexane as solvent. Since the spectrophotometer cell of the UV equipment had a 10 mm light-path cuvette, the UV/Vis spectra of compound 4ae was measured over the concentrations range (2×10^{-4} M $\leq M_{\mathbf{4ae}} \leq 10^{-3}$M) to check a linear relationship between absorbance values and concentrations.

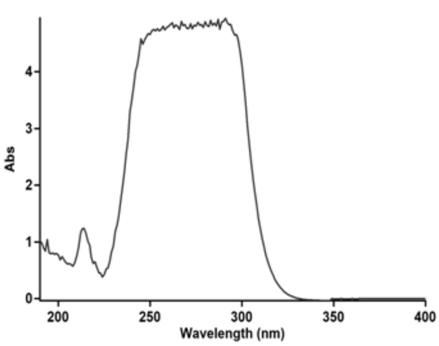

Fig. 3. UV spectrum of 10^{-3} M triphenylphosphine **1** in *n*-hexane

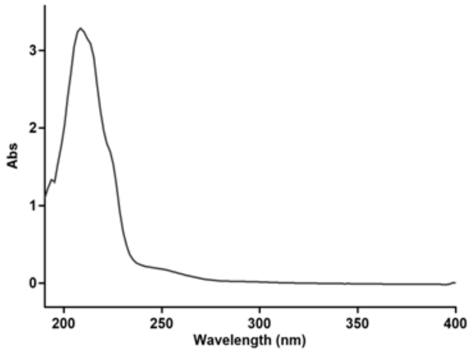

Fig. 4. UV spectrum of 10^{-3} M di-*tert*-butyl acetylenedicarboxylate **2e** in *n*-hexane

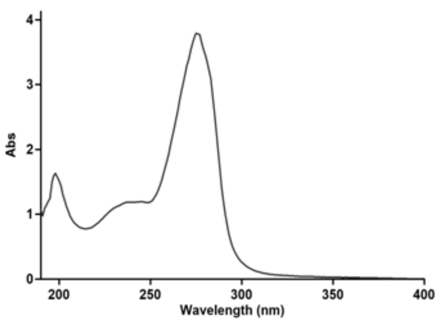

Fig. 5. UV spectrum of 10^{-3} M 2-acetyl-pyrrole **3a** in *n*-hexane

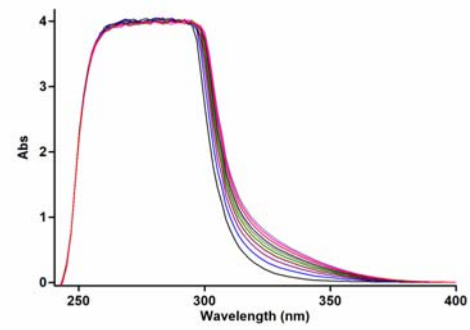

Fig. 6. UV spectra of the reaction between **1**, **2e** and **3a** with 10^{-3} M concentration of each compound as reaction proceeds in *n*-hexane

Thus, 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 kinetic of reaction between compounds **1**, **2e** and **3a** by the UV/Vis spectrophotometry technique. This will be discussed according to the following procedure (Fig. 2).

For each kinetic experiment, first 1 mL aliquot from each freshly made solution of 3×10^{-3} M compounds **1** and **3a** in *n*-hexane were pipetted into a quartz cell and then 1 mL aliquot of 3×10^{-3} M solution of reactant **2e** was added to the mixture, keeping the temperature at 5 ºC 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**, **2e** and **3a**. The infinity absorbance (A_∞) that is the absorbance at reaction completion, can be obtained from Fig. 7 at t =156 min. With respect to this value, zero and first or second curve fitting could be automatically drawn for the reaction by the software[27] 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 340 nm which exactly fits the experimental curve (dotted line) as shown in Fig. 8.

Thus the reaction between compounds **1**, **2e** and **3a** follows second-order kinetic. The second-order rate constant ($k_2 = 88.4$ mol^{-1} K^{-1}) is then automatically calculated using standard equation[27] within the program at 5 ºC. It was necessary to remember that another kinetic studies under same concentration of each reactant were also carried out in a series of separate experiment 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 previous experiment. In addition, the overall order of reaction was also 2.

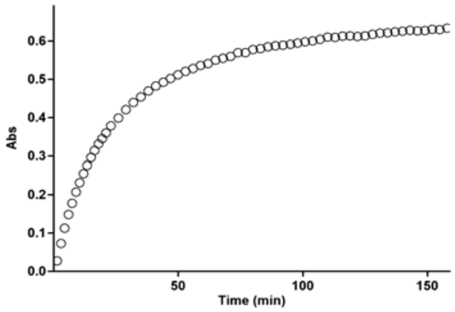

Fig. 7. Experimental absorbance change (dotted line) against time for the reaction between compounds **1**, **2e** and **3a** at 340 nm and 5 ºC in *n*-hexane

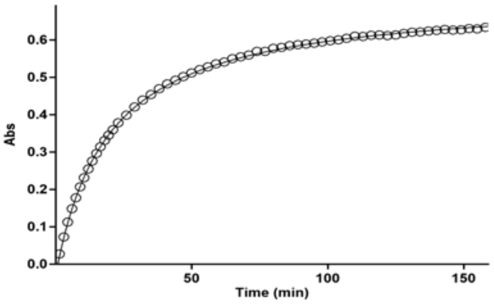

Fig. 8. Second order fit curve (solid line) accompanied by the original experimental curve (dotted line) for the reaction between **1**, **2e** and **3a** at 340 nm and 5 ºC in *n*-hexane

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 arrange various experiments with different temperature and solvent polarity under same condition with previous experiment. For this purpose, ethyl acetate with 6 dielectric constant was chosen as suitable solvents which not only could be dissolved all compounds but also does not react with them. The effects of solvent 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 was increased at higher temperature. In addition, the rate of reactions between (**1**, **2e** and **3a**) and (**1**, **2e** and **3b**) were accelerated in a high dielectric constant environment (ethyl acetate) in comparison with a low dielectric constant environment (*n*-hexane) 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 behaviour is shown in Fig. 9. The activation energy of reactions between (**1**, **2e** and **3a**) and (**1**, **2e** and **3b**) were obtained 33.2 and 32.1 kJ/mol respectively from the slop of Figure.

TABLE-1
VALUES OF OVERALL SECOND ORDER RATE CONSTANT FOR TWO REACTIONS (**1**, **2e** AND **3a**) AND (**1**, **2e** AND **3b**) IN THE PRESENCE OF DIFFERENT SOLVENTS AT DIFFERENT TEMPERATURES

	Solvent	ε	K_2 M^{-1} min^{-1}			
			5 ºC	10 ºC	15 ºC	20 ºC
3a	*n*-Hexane	2	20.8	26.3	33.5	43.6
	Ethyl acetate	6	38.8	50.7	63.8	78.5
3b	*n*-Hexane	2	25.6	33.4	42.1	52.3
	Ethyl acetate	6	44.2	54.5	68.2	83.2

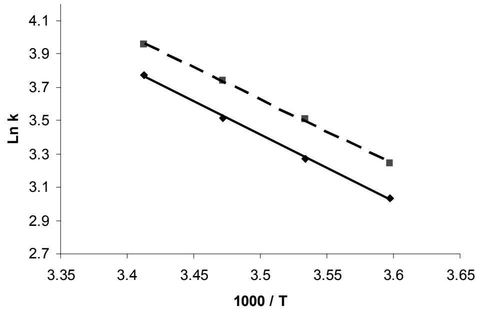

Fig. 9. Dependence of second order rate constant (Ln k) on reciprocal temperature for the two reactions between compounds (**1**, **2e** and **3a**) (—) and (**1**, **2e** and **3b**) (----) measured at wavelength 340 nm in *n*-hexane in accordance with Arrhenius equation

Effect of concentration: To determine reaction order with respect to triphenylphosphine **1** and dialkyl acetylenedicarboxylate **2** (**2e**), in a series of another separate experiments, all kinetic studies were carried out in the presence of excess **3** (**3a**). Under this condition the rate equation may therefore be expressed as:

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

in this case (3×10^{-2} M of **3a** instead of 3×10^{-3} M) using the original experimental absorbance *versus* time data (Fig. 10) provides a second order fit curve (full line) against time at 340 nm which exactly fits the experimental curve (Fig. 11). 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 **3a** was separately led to same fit curve and rate constant. In fact the experimental data were 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 (I). It is therefore appeared that the reaction is zero and second order with respect to **3a** (NH-acid) and sum of **1** and **2** ($\alpha + \beta = 2$), respectively. To determine reaction order with respect to dialkyl acetylenedicarboxylate **2** (**2e**) separate experiment was performed in the presence of excess of **1** (rate = $k'_{obs}\,[3]^{\gamma}\,[2]^{\beta}$, $k'_{obs} = k_2\,[1]^{\alpha}$ (2)). The original experimental absorbance *versus* time data has been shown in Fig. 12. This provides a pseudo first order fit curve (full line) at 340 nm which exactly fits the experimental curve (dotted line) as shown in Fig. 13. 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** (**2e**) ($\beta = 1$). Due to 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 five reactions (**1**, **2c** and **3a**), (**1**, **2d** and **3a**), (**1**, **2c** and **3b**), (**1**, **2d** and **3b**), (**1**, **2e** and **3b**). Based on the above results the simplified scheme of the proposed reaction (Fig. 2) as a possible explanation is shown in **Scheme-I**. 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 rate of law can be expressed as follows:

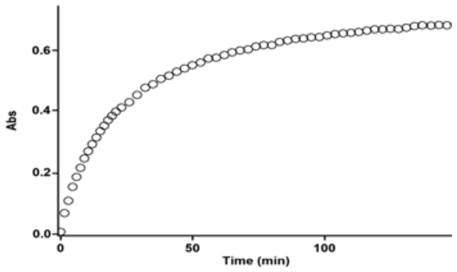

Fig. 10. Experimental absorbance change *vs.* time for the reaction between **1** and **2e** in the presence of excess **3a** (10^{-2} M) at 340 nm and 5 ºC in *n*-hexane

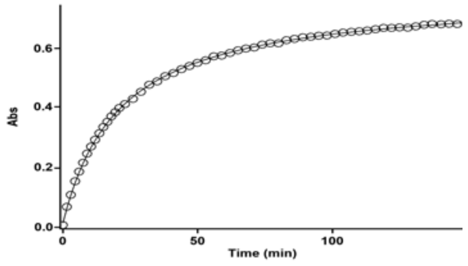

Fig. 11. Pseudo second order fit curve (solid line) for the reaction between **1** and **2e** in the presence of excess **3a** (10^{-2} M) at 340 nm and 5 ºC in *n*-hexane

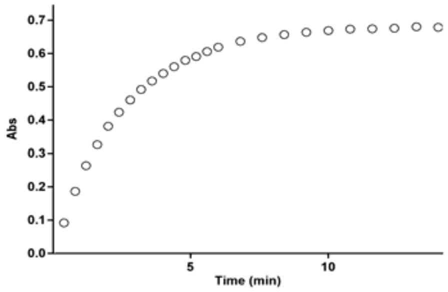

Fig. 12. Experimental absorbance change *vs.* time for the reaction between **2e** and **3a** in the presence of excess **1** (10^{-2} M) at 340 nm and 5 ºC in *n*-hexane

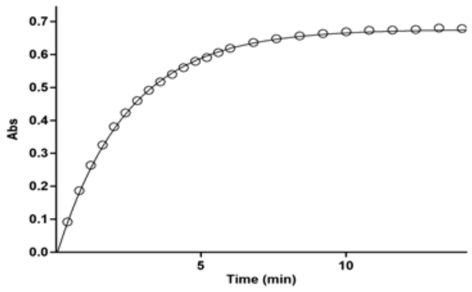

Fig. 13. Pseudo first order fit curve (solid line) for the reaction between **2e** and **3a** in the presence of excess **1** (10^{-2} M) at 340 nm and 5 ºC in *n*-hexane

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

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

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

$$I_2 + N^- \xrightarrow{k_2} 4\ (\text{product, ylide})$$

Scheme-I: Simplified scheme for the proposed reaction mechanism

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

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:

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

because it was assumed that k_3 is relevant to the rate determining step, it is reasonable to make the following assumption:

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

so the rate of law becomes:

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

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 order of reaction with respect to 2-acetylpyrrole **3a** is one whereas it was practically obtained equal to zero. For this reason, it therefore appeared 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 powerful ion dipole bonds to the ethyl acetate as solvent (high dielectric constant) in the reaction medium. But formation of transition state of reaction between two ions carries a dispersed charge which is divided between the attacking 2-acetylpyrrole 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 practically up the reaction. 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:

$$\text{rate} = k_4 [I_2][N^-]$$

by application of steady state for $[I^-]$ and $[N^-]$, replace their values in above equation, this equation is obtained:

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

this equation is independent of rate constant of fourth step (k_4) and is confirmed that why the fourth step would not be effected upon a change in the solvent medium. Addition to these, it was earlier suggested that kinetic studies of phenomena of ionic species are so fast[29]. 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**, **2d** or **2e**)), as we see (Fig. 2), have no charge and could not form powerful ion-dipole bonds to the ethyl acetate as a solvent (high dielectric constant) in the reaction medium. But the transition state carries a dispersed charge which is 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 reactans and therefore E_a is reduced which speed up the reaction. From the experimental result, it is found that solvent with high dielectric constant exert a power full 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 (*n*-hexane). 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** (**2c**, **2d** or **2e**) and **3** (**3a** or **3b**). Two steps involving **3** and **4** are not determining step according to the discussed effects, although these effects altogether 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** from the reaction mechanism (Fig. 14) is given by:

$$\frac{d[4]}{dt} = \frac{d[\text{ylide}]}{dt} = \text{rate} = k_4[I_2][N^-] \tag{5}$$

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

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

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

to obtain a suitable expression for $[I_2]$ to put into eqn. 5, it is 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 $\frac{d[I_1]}{dt}$ and $\frac{d[I_2]}{dt}$ are zero and obtained expressions for $[I_2]$ and $[I_1]$ as follows:

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

$$\frac{d[I_1]}{dt} = 0 \qquad [I_1] = \frac{k_2[1][2]}{k_{-2} + k_3[3]} \tag{7}$$

We can now replace $[I_1]$ in the eqn. 6 to obtain this equation:

$$[I_2] = \frac{k_2 k_3[1][2][3]}{k_4[N^-]\left[k_{-2} + k_3[3]\right]}$$

the value of $[I_2]$ can be put into eqn. 5 to obtain the rate eqn. 8 for proposed mechanism:

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

experimental data were 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:

$$\text{rate} = k_2\,[1][2] \tag{9}$$

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

Further kinetic investigations

Effect of structure of NH-acids: Reproducible experiments were investigated under the same conditions with previous experiment in the presence of other NH-acids such as 2-pyrrolecarbaldehyde **3b** instead of **3a**. Practically, experimental data were indicate that change within the structure of NH-acid has no effect on the priority of the rate determining step of the reaction and step 1 (rate constant k_2) is still the rate determining step in the presence of new NH-acid **3b** and order of reaction with respect to it is still zero. Because of the chemical activity of NH-acid is dependent on its structure, this provide opportunity in order to change the rate constant k_3 (NH-acid participate in this step) and also subsequent alteration of overall rate constant of reaction (eqn. 8). The overall rate constant of reactions have been shown in Table-1.

Effect of structure of dialkyl acetylenedicarboxylates: To confirm the above observations, further experiments were performed with diethyl acetylenedicarboxylate **2d** and dimethyl acetylenedicarboxylate **2c**, respectively. The values of the second-order rate constant (k_2) for the reactions between (**1**, **2c** and **3a**), (**1**, **2d** and **3a**), (**1**, **2c** and **3b**) and (**1**, **2d** and **3b**) 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 340 nm for only two reactions (**1**, **2d** and **3a**) and (**1**, **2c** and **3a**) are shown in Figs. 14 and 15, respectively.

TABLE-2
VALUE OF OVERALL SECOND ORDER RATE CONSTANTS FOR TWO REACTIONS (**1**, **2d** and **3a**) AND (**1**, **2d** and **3b**) IN THE PRESENCE OF ALL SOLVENTS AT DIFFERENT TEMPERATURES

	Solvent	ε	K_2 M^{-1} min^{-1}			
			5 ºC	10 ºC	15 ºC	20 ºC
3a	*n*-Hexane	2	125.3	140.6	160.1	185.1
	Ethyl acetate	6	239.1	265.1	294.6	329.9
3b	*n*-Hexane	2	152.3	169.8	189.5	212.6
	Ethyl acetate	6	288.9	315.3	345.8	381.9

TABLE-3
VALUE OF OVERALL SECOND ORDER RATE CONSTANTS FOR TWO REACTIONS (**1**, **2c** AND **3a**) AND (**1**, **2c** AND **3b**) IN THE PRESENCE OF *n*-HEXANE AND ETHYL ACETATE AT DIFFERENT TEMPERATURES

	Solvent	ε	K_2 M^{-1} min^{-1}			
			5 °C	10 °C	15 °C	20 °C
3a	*n*-Hexane	2	181.4	200.7	223.5	252.1
	Ethyl acetate	6	346.6	373.7	404.8	441.0
3b	*n*-Hexane	2	226.2	247.3	270.8	297.9
	Ethyl acetate	6	417.9	448.2	480.6	516.5

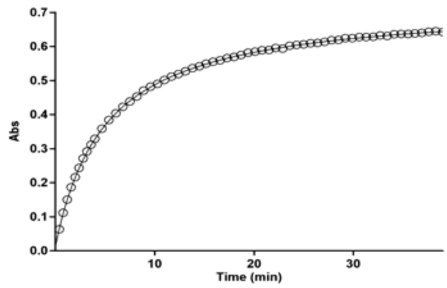

Fig. 14. Second order fit curve (solid line) accompanied by the original exp-erimental curve (dotted line) for the reaction between compounds **1**, **2d** and **3a** at 340 nm in *n*-hexane

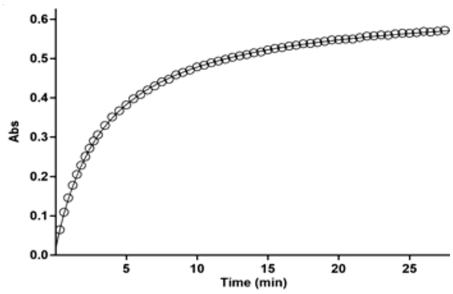

Fig. 15. Second order fit curve (solid accompanied by the original experimental curve (dotted line) for the reaction between compounds **1**, **2c** and **3a** at 340 nm in *n*-hexane

Conclusion

The kinetic investigation of the reactions between triphenylphosphine **1**, dialkyl acetylenedicaroxylates **2** (**2c**, **2d** or **2e**), with 2-acetylpyrrole **3a** or 2-pyrrole-carbaldehyde **3b** were undertaken by the UV spectrophotometery. The results can be summarized as follow: (**1**) The appropriate wavelengths and concentrations were successfully determined to follow kinetic investigations. (**2**) The overall order of all the 6 reactions followed second-order kinetic and order of reaction with respect to triphenylphosphine, dialkyl acetylenedicarboxylate and 2-acetylpyrrole or 2-pyrrole-carbaldehyde were obtained 1, 1 and 0, respectively. (**3**) The values of second-order rate constant of all the reactions were automatically calculated with respect to the standard equation within 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 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. (**6**) 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. (**7**) Reproductive experiments with different structure of NH-acids (**3a** and **3b**) were indicated that they participate in the fast step of reactions.

ACKNOWLEDGEMENT

The authors sincerely thank the University of Systan and Baluchestan for providing financial support of this work.

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(*Received*: 22 December 2007; *Accepted*: 19 September 2008) AJC-6876