Journal of the Iranian Chemical Society, Vol. 3, No. 3, September 2006, pp. 223-232.

JOURNAL OF THE
Iranian
Chemical Society

UV Spectrophotometric Study of the Kinetics and Mechanism of the Reactions between Triphenylphosphine, Dialkyl Acetylenedicarboxylates and NH-Acid

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(Received 15 March 2006, Accepted 16 April 2006)

To determine the kinetic parameters of the reactions between triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of an NH-acid, such as 2,3-di-hydroxybenzaldehyde, the reactions were monitored by UV spectrophotometry. The second order fits were automatically drawn and the values of the second order rate constants (k_2) were calculated using standard equations as part of the program. The dependence of the second order rate constant (lnk_2) on the reciprocal temperature was in agreement with the Arrhenius equation, in the temperature range studied, providing the relevant plots to calculate the activation energy of all reactions. Furthermore, we evaluated the effects of solvent, structure of different alkyl groups within the dialkyl acetylenedicarboxylates, and their concentration on the rates of reactions. The proposed mechanism was confirmed by experimental results and steady-state approximation. The first step (k_2) of the reaction was recognized as the rate determining step on the basis of experimental data.

Keywords: Phosphorus ylide, NH-acid, UV spectrophotometry, Kinetic parameters, Rate constant

INTRODUCTION

Phosphorus ylides are reactive systems that 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 and dialkyl acetylene-dicarboxylates, 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 2,3-di-hydroxybenzaldehyde **3** (an NH-acid) has been reported [26], however, 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 using UV spectrophotometry. We also go on to investigate subsequent protonation of the 1:1 adduct by the NH-acid **3** (rate constant k_3) to form phosphoranes **4** (rate constant k_4, Schemes 1 and 2), since well established chemistry of trivalent phosphorus nucleophiles [1-6] shows 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).

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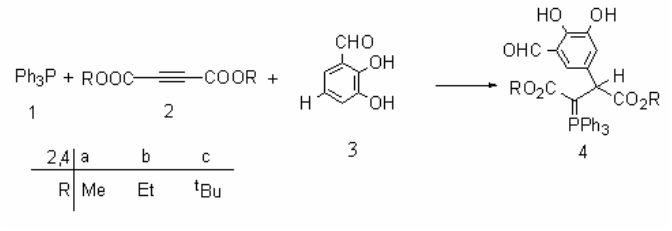
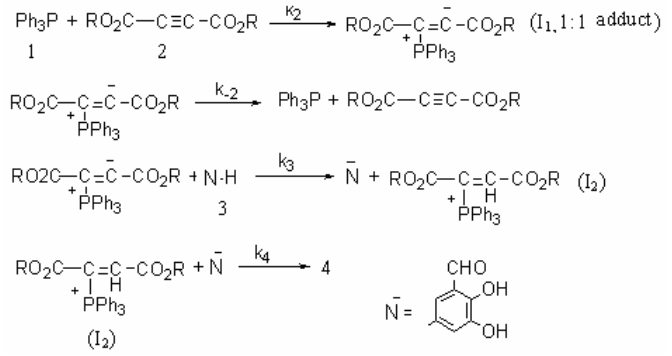
EXPERIMENTAL

Chemicals and Apparatus

Dialkyl acetylenedicarboxylates, triphenylphosphine, 2,3-di-hydroxybenzaldehyde were purchased from Fluka (Buchs, Switzerland) and used without further purification. All extra pure solvents, including *n*-hexane and ethyl acetate, were obtained from Merck (Darmstadt, Germany). A Cary 300 Bio UV-Vis spectrophotometer with a 10 mm light-path quartz



Scheme 1. The reaction between triphenylphosphine **1**, dialkylacetylenedicarboxylate **2** (**2a**, **2b** or **2c**) and NH-acid **3** for the generation of stable phosphorus ylides **4** (**4a**, **4b** or **4c**).



Scheme 2. Proposed mechanism for the reaction between **1**, **2** (**2a**, **2b** or **2c**) and **3** based on previous reports [13-26] for the generation of phosohorus ylides **4** (**4a**, **4b** or **4c**).

spectrophotometer cell, was employed throughout the current work.

Methods

To find the appropriate wavelength to follow the kinetic study of the reaction, solutions of compounds **1**, **2c**, and **3** (3×10^{-3} M) were prepared in *n*-hexane. Aliquots (3 ml) from each reactant were pipetted into the quartz spectrophotometer cell and the relevant spectra were recorded over the wavelength range of 190-400 nm.

In the second experiment, first 1 ml aliquots from the solutions (3×10^{-3} M) of compounds **1** and **3** were pipetted into the spectrophotometer cell (because there is no reaction between them), and 1 ml of a solution of reactant **2c** (3×10^{-3} M) was added to the mixture. The reaction was monitored by recording scans of the entire spectra every 10 min over the whole reaction time at ambient temperature.

The optimal wavelength for the investigation of the kinetics of the reaction between triphenylphosphine **1**, di-*tert*-butyl acetylenedicarboxylate **2c** and 2,3-di-hydroxy-benzaldehyde **3** was 410 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 **4c** was measured over a concentration range of 2×10^{-4} M $\leq M_{\mathbf{4c}} \leq 10^{-3}$ M to check for linear relationships between absorbance values and concentrations. This concentration range and wavelength were used for the investigation of kinetics of the reaction between compounds **1**, **2c**, and **3**.

For each kinetic experiment, 1 ml aliquot from each freshly made solution of compounds **1** and **3** (3×10^{-3} M) in *n*-hexane were pipetted into the quartz cell, then 1 ml of reactant **2c** (3×10^{-3} M) was added to the mixture, keeping the temperature at 10.0 ºC. The reaction kinetics were followed *via* UV absorbance over time.

The infinity absorbance (A_∞), the absorbance at reaction completion were determined, from which zero and first or second order curve fits were automatically drawn for the reaction by the software [27] associated with the UV instrument (Marquardt non-linear fit technique. The second-order rate constant (k_2) was then automatically calculated using the standard equation [27] within the program at 10.0 ºC. To determine the reaction order with respect to triphenylphosphine **1** and dialkyl acetylenedicarboxylate **2** (**2c**), in a series of separate experiments**,** all kinetic studies were carried out with a concentration of 5×10^{-3} M and 7×10^{-3} M, respectively, with an excess of compound **3**. As expected, the second order rate constant was independent of concentration and its value was the same as the previous experiment. In addition, the overall order of reaction was also 2.

RESULTS AND DISCUSSION

Figures 1, 2 and 3 show the ultraviolet spectra of compounds **1**, **2c** and **3**, respectively. The ultra-violet spectra shown in Fig. 4 are typical. The optimal wavelength was 410 nm, corresponding to compound **4c** (product) as shown in Fig. 4. At this wavelength, compounds **1**, **2c**, and **3** have relatively

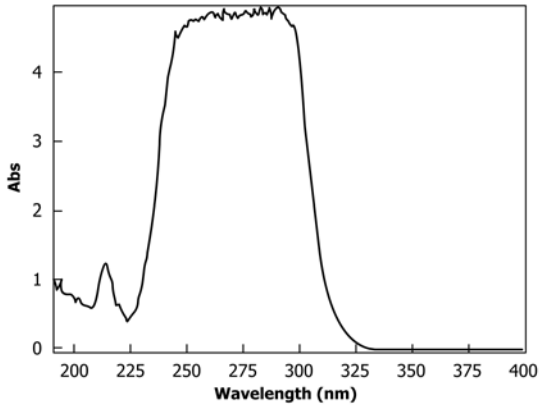


Fig. 1. The UV spectrum of triphenyl-phosphine **1** (10^{-3} M) in *n*-hexane.

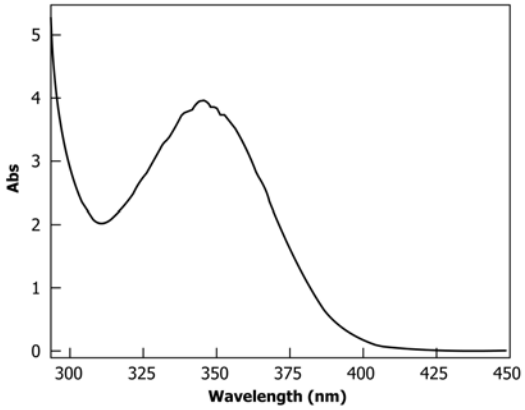


Fig. 3. The UV spectrum of 2,3 di-hydroxybenzaldehyde **3** (10^{-3} M) in *n*-hexane.

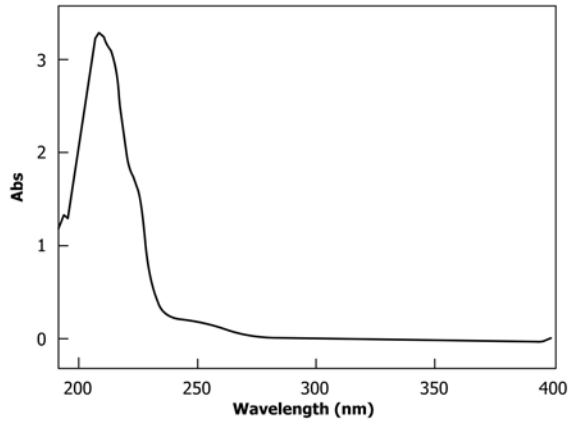


Fig. 2. The UV spectrum of 10^{-3} M di-*tert*-butylacetylene-dicarboxylate **2c** in *n*-hexane.

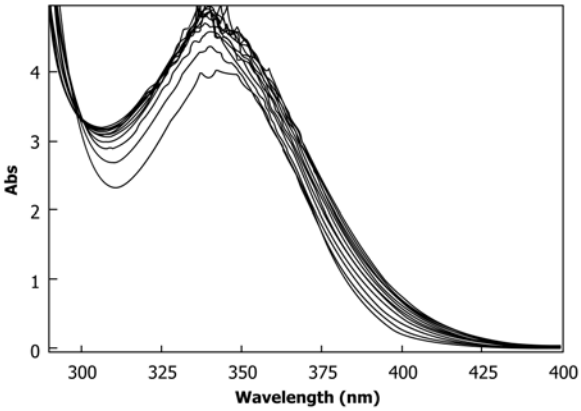


Fig. 4. The UV spectra of the reaction between **1**, **2c**, and **3** (10^{-3} M) in *n*-hexane.

no absorbance value. Figure 5 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. 5 at t = 122 min. In this case, using the original experimental absorbance *vs*. time data provided a second order curve fit (full line) at 410 nm, which exactly fits the experimental curve (dotted line) as shown in Fig. 6. Thus the reaction between compounds **1**, **2c**, and **3** follows second-order kinetics.

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 temperatures and solvent polarities under the same conditions as the kinetics experiment. For this purpose, ethyl acetate, with a dielectric constant of six, was chosen as a suitable solvent which not only dissolves all compounds used, 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 temperatures. In addition, the rate of reaction between **1**, **2c**, and **3** was accelerated in ethyl acetate, with a higher dielectric constant than *n*-hexane, at all temperatures investigated. In the

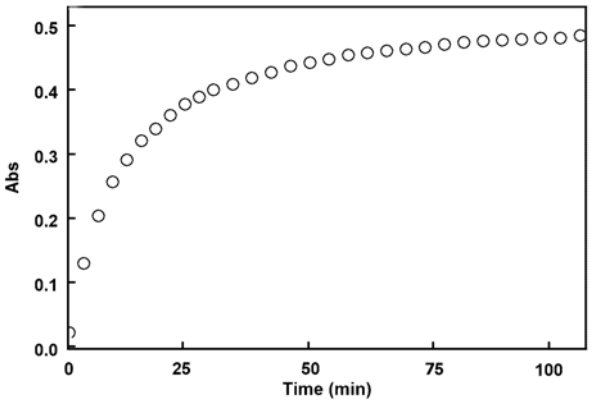


Fig. 5. The experimental absorbance change (dotted line) against time for the reaction between compounds **1**, **2c**, and **3** at 410 nm and 10.0 ºC in *n*-hexane.

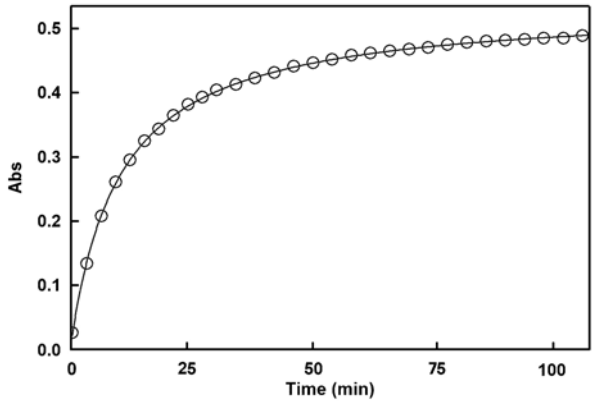


Fig. 6. Second order curve fit (full line) accompanied by the original experimental curve (dotted line) for the reaction between **1**, **2c**, and **3** at 410 nm and 10.0 ºC in *n*-hexane.

Table 1. 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})			
		10.0 ºC	15.0 ºC	20.0 ºC	25.0 ºC
n-hexane	2	64.5	76.1	89.1	105.8
Ethyl acetat	6	90.4	101.7	125.0	137.2

temperature range studied, the second-order equation rate constant (lnk_2) of the reactions was inversely proportional to the temperature, which is consistent with the Arrhenius equation. This behavior is shown in Fig. 7. The activation energy of the reaction between **1**, **2c**, and **3** was obtained (22.9 kJ mol^{-1}) from the slope in this figure.

EFFECT OF CONCENTRATION

To determine reaction order with respect to triphenylphosphine **1** and dialkylacetylenedicarboxylate **2** (**2c**), in a separate series of experiments**,** all kinetic studies were carried out in the presence of an excess of compound **3**. Under these conditions, the rate equation may therefore be expressed as:

$$\text{rate} = k_{obs}\,[1]^{\alpha}\,[2]^{\beta},\ k_{obs} = k_2\,[3]^{\gamma}$$
$$\text{or } lnk_{obs} = lnk_2 + \gamma\, ln[3] \qquad (1)$$

in this case using the increased concentration of compound **3** (3×10^{-2} M of instead of 3×10^{-3} M) and the original experimental absorbance *vs*. time data (Fig. 8) provides a second order curve fit (full line) against time at 410 nm, which exactly fits the experimental curve (Fig. 9). The value of rate constant was the same as that of the previous experiment (3×10^{-3} M). Repeat experiments with higher concentrations of **3** (5×10^{-2} M and 7×10^{-2} M) separately led to same curve fit and rate constant. In fact, the experimental data indicated that observed the pseudo second order rate constant (k_{obs}) is equal to the second order rate constant (k_2), which is possible when γ is zero in equation (1). Therefore, it appears that the reaction is

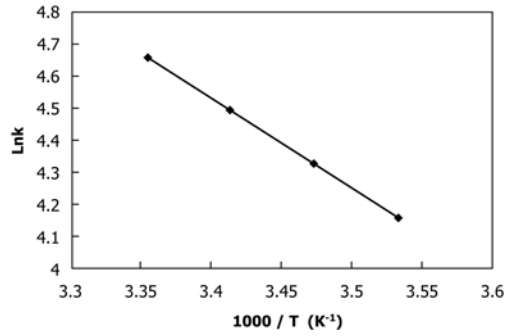


Fig. 7. Dependence of second order rate constant (lnk_2) on reciprocal temperature for the reaction between compounds **1, 2c**, and **3** measured at wavelength 410 nm in *n*-hexane in accordance with Arrhenius equation.

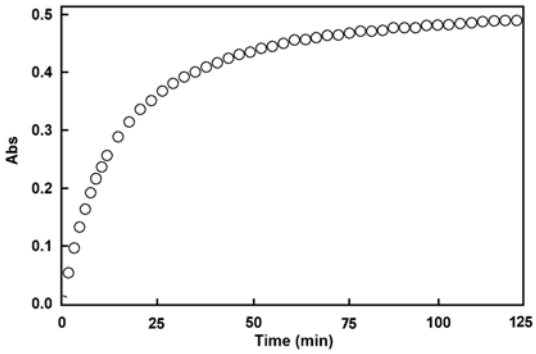


Fig. 8. The experimental absorbance change *vs*. time for the reaction between **1** and **2c** with an excess of **3** (10^{-2} M) at 410 nm and 10.0 °C in *n*-hexane.

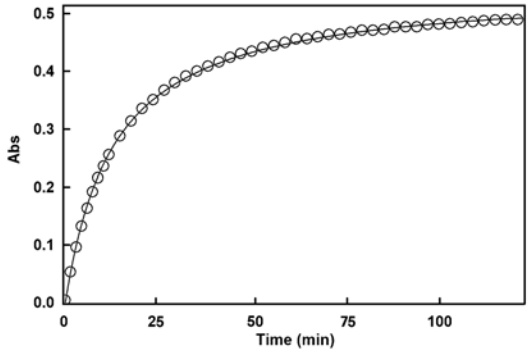


Fig. 9. Pseudo second order curve fit (full line) for the reaction between **1** and **2c** in the presence of excess **3** (10^{-2} M) at 410 nm and 10.0 °C in *n*-hexane.

zero and second order with respect to **3** (NH-acid) and the sum of **1** and **2** (**2c**) ($\alpha + \beta = 2$), respectively.

To determine the reaction order with respect to dialkyl acetylenedicarboxylate **2** (**2c**), a separate experiment was performed in the presence of an excess of **1** (rate $= k'_{obs}[3]^{\gamma}[2]^{\beta}$, $k'_{obs} = k_2[1]^{\alpha}$ (II)). The original experimental absorbance *vs*. time data is shown in Fig. 10. This provides a pseudo first order curve fit (full line) at 410 nm which exactly fits the experimental curve (dotted line) as shown in Fig. 11. As a result, since $\gamma = 0$ (determined in previous experiment), it is reasonable to accept that the reaction is first order with respect to compound **2** (**2c**) ($\beta = 1$). Since 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 (Scheme 2) as a possible explanation is shown in Scheme 3 The experimental results indicate the possibility that the third step (rate constant k_3) is 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:

$$\text{rate} = k_3 [I_1][3] \qquad (2)$$

The steady-state assumption can be employed for $[I_1]$, which generates following equation,

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

The value of $[I_1]$ can be replaced in equation (2) to obtain:

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

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

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

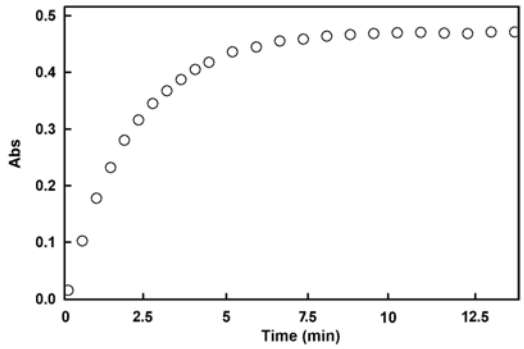


Fig. 10. The experimental absorbance change *vs*. time for the reaction between **2c** and **3** with an excess of **1** (10^{-2} M) at 410 nm and 10.0 °C in *n*-hexane.

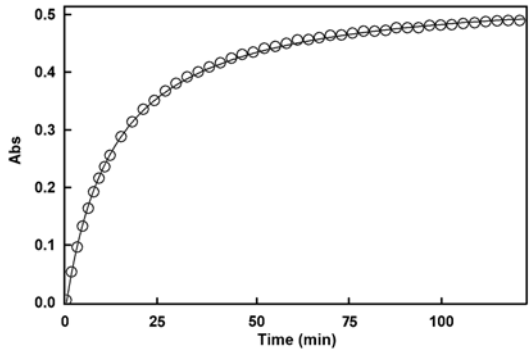


Fig. 11. Pseudo first order curve fit (full line) for the reaction between **2c** and **3** with an excess of **1** (10^{-2} M) at 410 nm and 10.0 °C in *n*-hexane.

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

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

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

$$I_2 + N^- \xrightarrow{k_4} 4 \text{ (product, ylide)}$$

Scheme 3. The simplified pathway for the proposed reaction mechanism.

The final equation indicates that the calculated overall order of reaction is 3, which is not compatible with experimental overall order of reaction of 2. In addition, according to this equation, order of reaction with respect to 2,3-di-hydroxy-benzaldehyde **3** is one whereas it was practically obtained as zero. For this reason, it appears that the third step is presumably a fast step. If we assume that fourth step (rate constant k_4) is the rate determining step for the proposed mechanism, there are two ion species to consider in the rate determining step, namely phosphonium ion (I_2) and N^-. The phosphonium and N^- ions, as we see in Scheme 2, have full positive and negative charges and form very powerful ion dipole bonds to the ethyl acetate as a solvent with a high dielectric constant in the reaction mechanism. However, the formation of a transition state of reaction between two ions carries a dispersed charge, which here is divided between the attacking N^- and the phosphonium ions. Bonding of the solvent (ethyl acetate) to this dispersed charge is much weaker than to the concentrated charge of the N^- and phosphonium ions. The solvent thus stabilizes the species ions more than it does the transition state, and therefore E_a is increases, which slows down the reaction. Conversely, ethyl acetate practically speeds 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 the proposed reaction mechanism can be expressed:

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

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

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

This equation is independent of the rate constant of the fourth step (k_4), which is why the fourth step would not be affected by a change in the solvent medium. Additionally, it has already been suggested that kinetic studies show the phenomena of ionic species to be this fast [28-29]. If the first step (rate constant k_2) is the rate determining step, two reactants (triphenylphosphine **1** and dialkyl acetylene-dicarboxylate **2** (**2c**)) (Scheme 2) have no charge and could not form powerful ion-dipole bonds with ethyl acetate as a solvent in the reaction medium. However, the transition state carries a dispersed charge, which here is divided between the attacking

1 and **2**. Bonding of the 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, thereby speeding up the reaction. From the experimental result, solvents with high dielectric constants exert a power full effect on the rate of reaction (the first step with rate constant k_2 of the proposed mechanism), but the opposite is true for solvents with low dielectric constants (such as *n*-hexane).

For all reactions between triphenylphosphine **1**, **2** (**2a**, **2b** or **2c**) and **3**, the two steps involving compounds 3 and 4 (k_3 and k_4, respectively) are not rate determining steps, according to the results of the effect of solvent and concentration of compounds. However, these effects are compatible with first step (k_2) of the proposed mechanism, allowing step 1 to be the rate determining step. Furthermore, a good kinetic description of experimental results 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 (Scheme 3) is given by:

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

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 equation (4) we can assume that, after an initial brief period, the concentration of $[I_1]$ and $[I_2]$ achieve a steady state, with a balance in their rates of formation and rates of disappearance. Therefore $d[I_1]/dt$ and $d[I_2]/dt$ are zero and we can obtain expressions for $[I_2]$ and $[I_1]$ as follows:

$$\frac{d[I_2]}{dt}=0 \qquad [I_2]=\frac{k_3[I_1][3]}{k_4[N^-]} \quad (5)$$

$$\frac{d[I_1]}{dt}=0 \qquad [I_1]=\frac{k_2[1][2]}{k_{-2}+k_3[3]} \quad (6)$$

We can now replace $[I_1]$ in equation (5) to generate the following 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 equation (4) to obtain the rate equation (7) for the proposed mechanism:

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

or $$rate=\frac{k_2\,k_3[1][2][3]}{\left[k_{-2}+k_3[3]\right]} \quad (7)$$

Experimental data indicate that steps 3 (k_3) and 4 (k_4) are fast, in contrast to step 1 (k_2). Therefore, it is reasonable to make the following assumption:

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

Then, the rate equation becomes:

$$\text{rate} = k_2[1][2] \quad (8)$$

By applying the steady-state approximation, this equation, which was obtained from the mechanistic scheme shown in Scheme 3, is compatible with the results obtained by UV spectrophotometry.

Effect of Structure of Dialkyl Acetylenedicarboxylates

To confirm the above observations, further experiments were performed with diethyl acetylenedicarboxylate **2b** and dimethyl acetylenedicarboxylate **2a**. 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 curve fits (full line) at 410 nm for both reactions are shown in Figs. 12 and 13.

As can be seen from the Tables 2 and 3, the behavior of

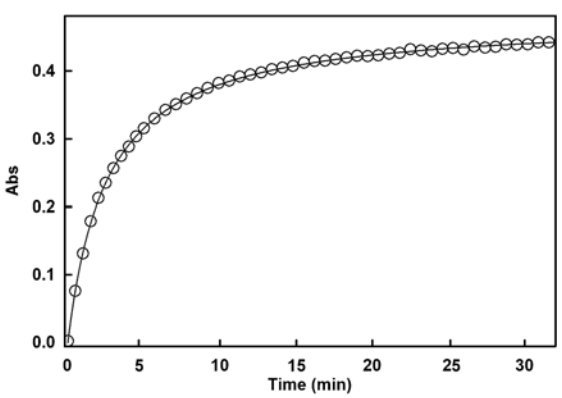


Fig. 12. Second order curve fit (full line) accompanied by the original experimental curve (dotted line) for the reaction between **1**, **2b**, and **3** at 410 nm and 10.0 °C in *n*-hexane.

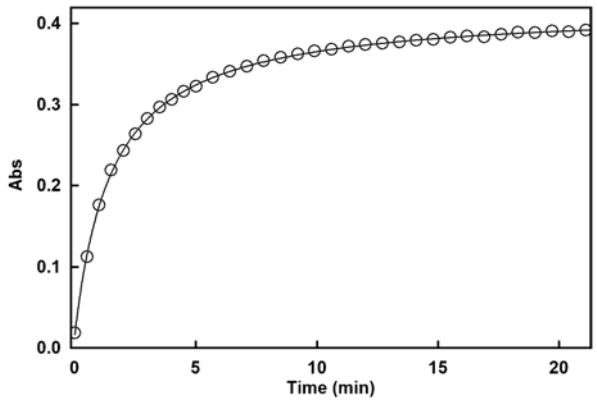


Fig. 13. Second order curve fit (full line) accompanied by the original experimental curve (dotted line) for the reaction between **1**, **2a** and **3** at 410 nm and 10.0 °C in *n*-hexane.

Table 2. Second Order Rate Constants for the Reaction between **1**, **2b**, and **3** in Different Solvents and at Different Temperatures

		K_2 (M^{-1} min^{-i})			
Solvent	ε	10.0 ºC	15.0 ºC	20.0 ºC	25.0 ºC
n-hexane	2	250.4	278.2	321.0	371.6
Ethyl acetate	6	363.7	410.2	454.7	523.8

Table 3. Second Order Rate Constants for the Reaction between **1**, **2a**, and **3** in Different Solvents and at Different Temperatures

		K_2 (M^{-1} min^{-i})			
Solvent	ε	10.0 ºC	15.0 ºC	20.0 ºC	25.0 ºC
n-hexane	2	501.1	545.4	620.7	682.6
Ethyl acetate	6	530.3	582.1	647.4	730.5

diethyl acetylenedicarboxylate **2b** and dimethyl acetylenedicarboxylate **2a** are the same as that of di-*tert*-butyl acetylenedicarboxylate **2c** with respect to the reaction with **1** and **3**. Although the rates of both of these reactions were accelerated in solvents with high dielectric constants and high temperature, their rates are approximately 4 to 6 times 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 tend to reduce the overall rate of reaction (see equation 8). In the case of dimethyl acetylenedicarboxylate **2a**, less steric and less inductive effects

of dimethyl groups exert a powerful effect on the rate of reaction.

CONCLUSIONS

In summary, the overall order of the three reactions followed second-order kinetics and the order of reaction with respect to triphenylphosphine, dialkyl acetylenedicarboxylate and 2,3-di-hydroxybenzaldehyde were 1, 1 and zero, respectively. The higher reaction rates in a solvent with a higher dielectric constant are related to differences in the solvent's stabilization of the reactants and the activated complex in transition state. The rates of all reactions were accelerated at higher temperatures. The activation energy of the reaction with di-*tert*-butylacetylenedicarboxylate **2c** (22.9 kJ mol^{-1}) was higher than those of the two reactions involving diethyl acetylenedicarboxylate **2b** (14.8 kJ mol^{-1}) and dimethyl acetylenedicarboxylate **2a** (18.5 kJ mol^{-1}) in *n*-hexane. The more steric factor in bulky alkyl groups accompanied by its more inductive effect within the structure of dialkyl acetylenedicarboxylate reduces the overall rate of reactions. According to the experimental data, the first step of the proposed mechanism was recognized as a rate determining step (k_2) and the reaction mechanism was confirmed by experimental results and the steady-state approximation.

ACKNOWLEDGMENTS

The authors sincerely thank the University of Sistan & Baluchestan for providing financial support for this work.

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