Mechanism investigation of stable phosphorus ylides derived from 4-nitro aniline and different dialkyl acetyeledicarbixylates: A kinetic study

**Mohammad Zakarianejad[1], Sayyed Mostafa Habibi-Khorassani[2]*,
Batoul Makiabadi[3], Hojjat Ghasempour[4]**

[1]Department of Chemistry, Payam Noor University, Tehran, (IRAN)
[2]Department of Chemistry, The University of Sistan and Baluchestan, Zahedan, (IRAN)
[3]Department of Chemical Engineering, Sirjan University of Technology, Sirjan, (IRAN)
[4]Department of Chemistry, Bardsir Branch, Islamic Azad University, Bardsir, (IRAN)
E-mail : khorassani_habibi@yahoo.com

ABSTRACT

Kinetic studies were made of the reactions between triphenylphosphine 1, dialkyl acetylenedicarboxylates 2 in the presence of NH-acid, such as 4-nitro aniline (as a protic/nucleophilic reagent) 3. 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 automatically calculated using standard equations within the program. All reactions repeated at different temperature range, the dependence of the second order rate constant (ln k_2) and (ln k_2/T) on reciprocal temperature was in a good agreement with Arrhenius and Eyring equations. This provided the relevant plots to calculate the activation parameters (Ea, $\Delta H^\#$, $\Delta S^\#$ and $\Delta G^\#$) of all reactions. Furthermore, useful information were obtained from studies of the effect of solvent, structure of reactants (dialkyl acetylenedicarboxylates) and also concentration of reactants on the reaction rates. Proposed mechanism was confirmed according to the obtained results and steady state approximation, first and third steps (k_2, k_3) of all reactions was recognized as a rate determining and fast steps, respectively on the basis of experimental data.
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KEYWORDS

Stable phosphorus ylides;
Dialkyl cetylenedicarboxylates;
NH-acid;
Heterocyclic compounds;
Kinetic studies.

INTRODUCTION

The synthesis of phosphorus ylides is important in organic chemistry because of the applications in the synthesis of organic products[1-5] especially synthesis of naturally occurring products with biological and phar-macological activity[6-13] These are most often obtained in excellent yields from the 1:1:1 addition reaction between triphenylphosphine, dialkyl acetylendicarboxylates, in the presence of CH, SH, NH or OH-acid. Phosphorus ylides are usually prepared by deprotonation of phosphonium salts which can

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be prepared most often by the reaction of triphenylphosphine and an alkyl halide[1]. In recent years a three component method has been developed for the synthesis of organophosphorus compounds using a novel approach employing vinylphosphonium salts[7-9]. This method is successful for the preparation of 1,4-diionic organophosphorus compounds[10,11]. A facile synthesis of the reaction between triphenylphosphine 1, dialkyl acetylenedicarboxilate 2 and 4-nitro aniline 3 (as a NH-acid) has been reported earlier[14] but the kinetic studies of this reaction has not been investigated yet. In order to gain further insight into the reaction mechanism, a kinetic study of the reaction between triphenylphosphine 1, dialkyl acetylendicarboxylates 2 and 4-nitro aniline 3 as NH-acid was undertaken by the UV spectrophotometer technique. On the basis of the well established chemistry of trivalent phosphorus nucleophiles, 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). To gain further insight into the reaction mechanism between triphenylphosphin 1, dialkyl acetylenedicarboxylates 2 and 4-nitro aniline 3 (as a NH- heterocyclic compound) for generation of phosphorus ylids 4a-c (Figure 1), a kinetic study of the reactions was undertaken by UV spectrophotometeric technique.

$$PPh_3 + RO_2C-C\equiv C-CO_2R + Z\text{-}H \longrightarrow$$
$$1 \qquad\qquad 2 \qquad\qquad\qquad 3$$

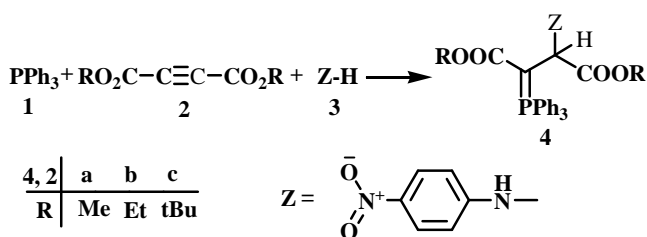| 4, 2	a	b	c
R	Me	Et	tBu

$$Z = $$

Figure 1 : The reaction between triphenylphosphine 1, dialkyl acetylenedicarboxylate 2 (2a, 2b or 2c) and 4-nitro aniline 3 for generation of stable phosphorus ylides 4 (4a, 4b or 4c).

EXPERIMENTAL

Chemicals and apparatus used

Dialkyl acetylenedicarboxylates, triphenylphosphine and 4-nitro aniline were purchased from Fluka (Buchs, Switzerland) and used without further purifications. All extra pure solvents including the ethyl acetate and 1,2-dichloromethane also obtained from Merck (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

To find the appropriate wavelength to follow the kinetic study of the reaction, in the first experiment, 3×10^{-3} M solution of compounds 1, 2c and 3 was prepared in 1,2-dichloroethane as solvent. The relevant spectra of each compound were recorded over the wavelength range 190-400 nm. Figures 2, 3 and 4 show the ultra-violet spectra of compounds 1, 2c and 3 respectively. In a second experiment, a 1mL aliquot from the 3×10^{-3} M solutions of each compound of 1 and 3 was pipetted first into a quartz spectrophotometer cell (as there is no reaction between them), later 1ml aliquot of the 3×10^{-3} M solution of reactant 2c was added to the mixture and the reaction monitored by recording scans of the entire spectra every 10 min over the whole reaction time at ambient temperature. The ultra-violet spectra shown in Figure 5 are typical. From this, the appropriate wavelength was found to be 300 nm (corresponding mainly to triphenylphosphine 1). Since at this wavelength, compounds 4, 2c and 3 have relatively no absorbance value, so provided the opportunity to fully investigate the kinetics of the reaction between triphenylphosphine 1, di-*tert*-butyl acetylenedicarboxylate 2c and 4-nitro aniline 3.

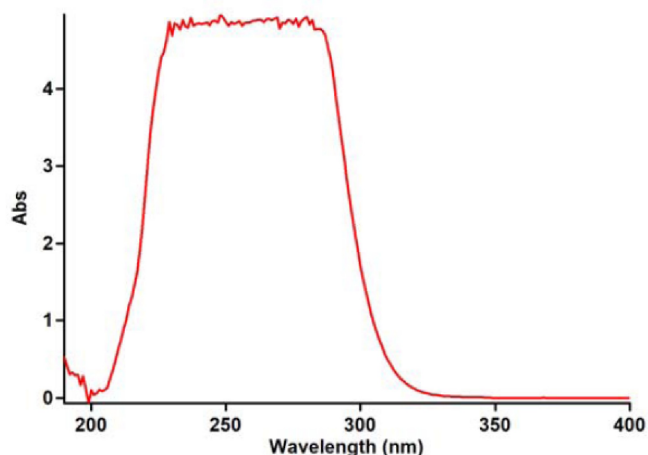The reaction kinetics was followed by plotting UV

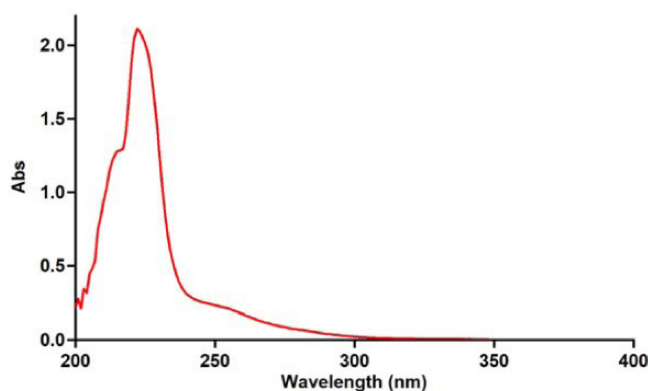**Figure 2 : The UV spectrum of 10^{-3}M triphenyphosphine 1 in 1,2-dichloroethane.**

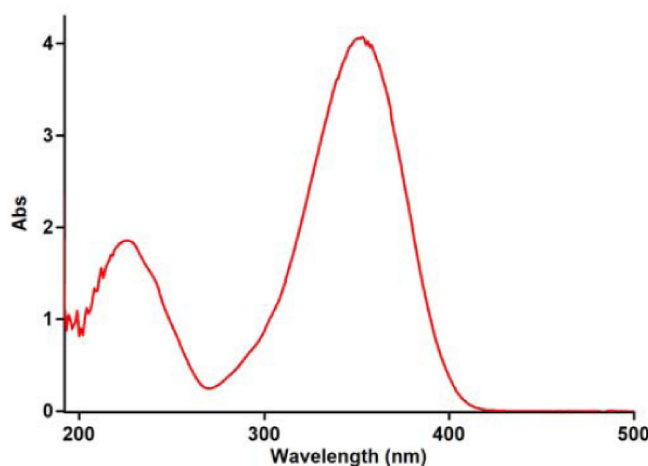**Figure 3 : The UV spectrum of 10^{-3}M di-*tert*-butyl acetylenedicarboxylate 2c in 1,2-dichloroethane.**

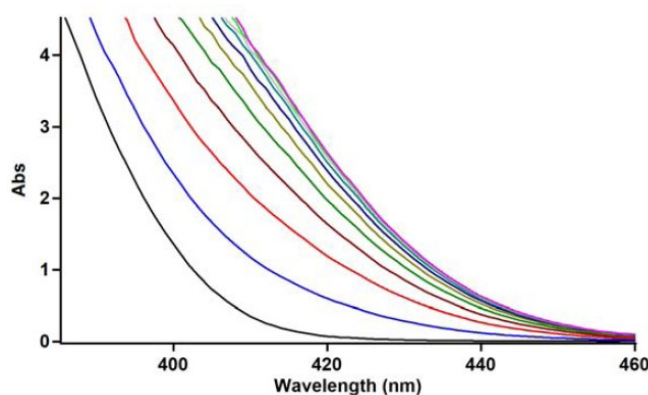**Figure 4 : The UV spectrum of 10^{-3}M 4-nitro aniline 3 in 1,2-dichloroethane.**

Figure 5 : The UV spectra of the reaction between 1, 2c and 3 with 10^{-3}M concentration of each compound as reaction proceeds in 1,2-dichloroethane.

absorbance against time 12.0ºC. Figure 6 shows the absorbance change (dotted line) versus time for the 1:1:1 addition reaction between compounds 1, 2c and 3 at 12.0ºC. The infinity absorbance (A$_\infty$) that is the absorbance at reaction completion, can be obtained from

Figure 6 at t =78 min. With respect to this value, zero, first or second curve fitting could be drawn automatically for the reaction by the software[15] associated with the UV instrument. Using the original experimental absorbance versus time data provided a second-order fit curve (solid line) that fits exactly the experimental curve (dotted line) as shown in Figure 7. Thus, the reaction between triphenylphosphine 1, di-*tert*-butyl acetylenedicarboxylate 2c and 3 follows second-order kinetics. The second-order rate constant (k_2) is then automatically calculated using a standard equation within the program at 12.0ºC is reported in TABLE 1. Furthermore, kinetic studies were carried out using the same concentration of each reactant in the continuation of experiments with concentrations of 5×10^{-3}M and 7×10^{-3}M respectively. As expected, the second-order rate constant was independent of concentration and its value was the same as in the previous experiment. In addition, the overall order of reaction was also 2.
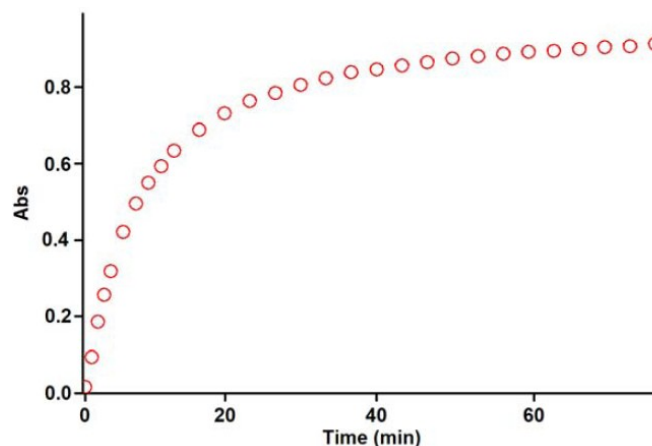

Figure 6 : The experimental absorbance changes (dotted line) against time at 300 nm for the reaction between compounds 1, 2c and 3 at 12.0 ºC in 1,2-dichloroethane.

RESULTS AND DISCUSSION

Effect of solvent and temperature

To determine the effect of change in temperature and solvent environment on the rate of reaction, it was elected to perform various experiments at different temperatures and solvent polarities but otherwise under the same conditions as for the previous experiment. For this purpose, 1,2-dichloromethane with dielectric constant 9 was chosen as a suitable solvent since it is not
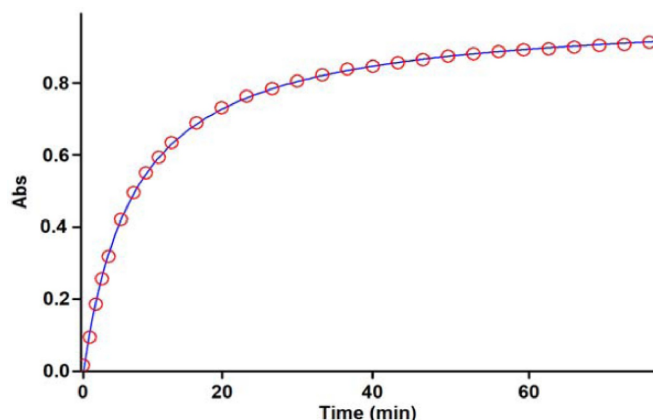
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Figure 7 : Second order fit curve (solid line) accompanied by the original experimental curve (dotted line) for the reaction between compounds 1, 2c and 3 at 300 nm and 12.0ºC in 1,2-dichloroethane.

Figure 8 : Dependence of second order rate constant (ln k_2) on reciprocal temperature for the reaction between compounds 1, 2c and 3 measured at wavelength 300 nm in ethyl acetate.

TABLE 1 : Values of overall second order rate constant for all reactions (1, 2c and 3), (1, 2b and 3) and (1, 2a and 3) in the presence of solvents such as ethyl acetate and 1,2-dichloromethane, respectively, at all temperatures investigated.

Reaction	Solvent	$k_2.M^{-1}.min^{-1}$			
		12.0ºC	17.0ºC	22.0ºC	27.0ºC
1, 2c and 3	ethyl acetate	76.1	105.3	143.2	168.6
	1,2-dichloromethane	109.1	131.5	159.6	189.2
1, 2b and 3	ethyl acetate	411.1	532.3	615.4	696.7
	1,2-dichloromethane	631.2	677.8	753.1	878.3
1, 2a and 3	ethyl acetate	615.2	714.4	845.6	984.7
	1,2-dichloromethane	782.3	826.2	898.1	1005.5

only could be dissolved all compounds but also did not react with them. The results show that the rate of reaction in each case was increased at higher temperatures. In addition, the rate of reaction between 1, 2c and 3 was accelerated in a higher dielectric constant environment (1,2-dichloromethane) in comparison with a lower dielectric constant environment (ethyl acetate) 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 is consistent with the Arrhenius equation, giving activation energy of reaction from the slope of Figure 8.

Effect of concentration

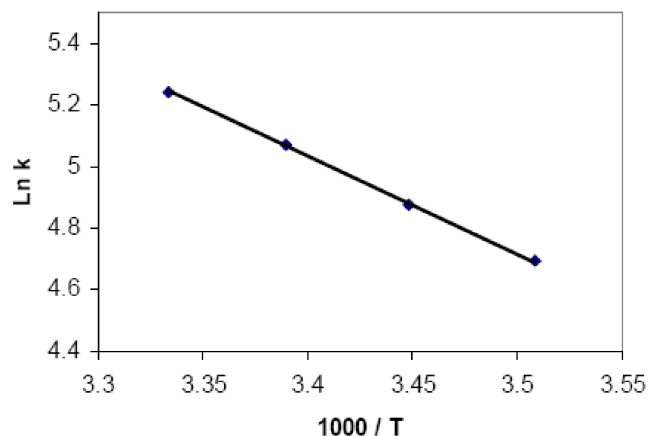To determine reaction order with respect to triphenylphosphine 1 and dialkyl acetylenedicarboxylate 2 (2c), in the continuation of experiments, all kinetic studies were carried out in the presence of excess 3. Under this condition, the rate equation may therefore be expressed as:

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

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 (solid line) against time at 300 nm which exactly fits the experimental curve. The value of rate constant was the same as that of obtained from the previous experiment (3×10^{-3} M). Repetition of the experiments with 5×10^{-2} M and 7×10^{-2} M of 3 gave, separately, the same fit curve and rate constant. In fact, the experimental data indicated that the observed pseudo second order rate constant (k_{obs}) was equal to the second order rate constant (k_2), this is possible when γ is zero in equation (1). It is appears, therefore, that the reaction is 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 triphenylphosphine 1, the continuation of experiment was performed in the presence of excess 2 (2c) (rate $_= k'_{obs}$ $[3]^\gamma [1]^\alpha$, $k'_{obs} = k_2 [2]^\beta$ (2)). The original experimental absorbance versus time data provides a pseudo-first-order fit curve at 300 nm, which exactly fits the experimental curve (dotted line) as shown in Figure 9.

As a result, since $\gamma = 0$ (as determined previously), it is reasonable to accept that the reaction is first order with respect to compound 1 ($\alpha = 1$). Because the overall order of reaction is 2 ($\alpha + \beta + \gamma = 2$), it is obvious
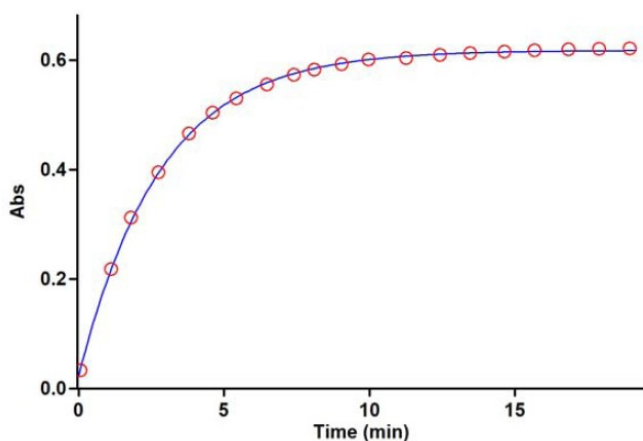
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Figure 9 : Pseudo first order fit curve (solid line) for the reaction between 1 and 3 in the presence of excess 2 (2c) (10^{-2}M) at 300 nm and 12.0°C in ethyl acetate.

that β=1 and the order of dialkyl acetylenedicarboxylate 2 (2c) must be equal to 1. This observation was also obtained for reactions between (1, 2b and 3) and (1, 2a and 3). Based on the above results, a simplified proposed reaction mechanism is shown in Figure 10.
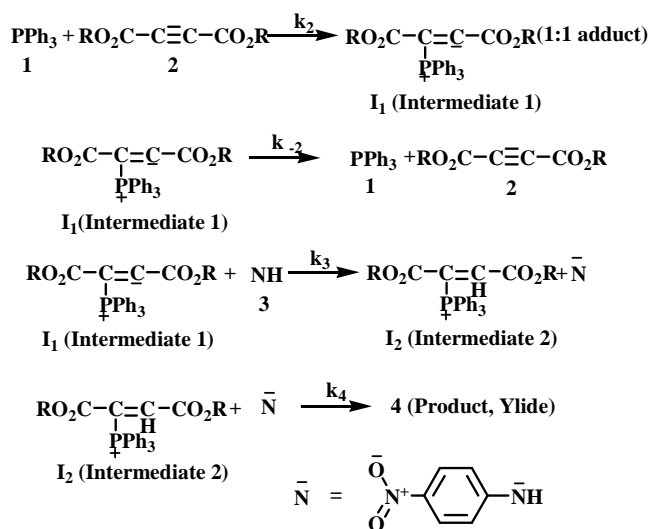

Figure 10 : Proposed mechanism for the reaction between 1, 2(2a, 2b or 2c) and 3 for generation of phosphorus ylides 4a-c.

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

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

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 (3) to obtain this equation:

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

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

The final equation is indicates that overall order of reaction is three which is not compatible with experimental overall order of reaction (=two). In addition, according to this equation, the order of reaction with respect to 4-nitro aniline 3 is one, whereas it was actually shown to be equal to zero. For this reason, it appeared that the third step is fast. If we assume that the fourth step (rate constant k_4) is the rate-determining step for the proposed mechanism, in this case, there are two ionic species to consider in the rate determining step, namely phosphonium ion (I_2) and 4-nitro aniline ion (Z^-). The phosphonium and 4-nitro aniline ions, as we see in Figure 10, have full positive and negative charges and form very powerful ion-dipole bonds to the 1,2-dichloromethane, the high dielectric constant solvent. However, the transition state for the reaction between two ions carries a dispersed charge, which here is divided between the attacking 4-nitro aniline and the phosphonium ions. Bonding of solvent (1,2-dichloromethane) to this dispersed charge would be much weaker than to the concentrated charge of 4-nitro aniline and phosphonium ions. The solvent thus stabilize the species ions more than it would the transition state, and therefore E_a would be higher, slowing down the reaction. However, in practice, 1,2-dichloromethane speeds up the reaction and for this reason, the fourth step, which is independent of the change in the solvent medium, could not be 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: $\text{rate} = k_4[I_2][Z^-]$

By application of steady state for $[I_2]$ and $[Z^-]$, and replacement of their values in the above equation, the

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following 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 for the fourth step (k_4) and shows why the fourth step would not be affected by a change in the solvent medium. In addition, it has been suggested earlier that the kinetics of ionic species' phenomena (e.g. the fourth step) are very fast[16]. If the first step (rate constant k_2) were the rate determining step, in this case, two reactants (triphenylphosphine 1 and dialkyl acetylenedicarboxylate 2), as we see in Figure 10, have no charge and could not form strong ion-dipole bonds to the high dielectric constant solvent, 1,2-dichloromethane. However, the transition state carries a dispersed charge which here is divided between the attacking 1 and 2 and, hence, bonding of solvent to this dispersed charge is much stronger than 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 speeds up the reaction. Our experimental results show that the solvent with higher dielectric constant exerts a power full effect on the rate of reaction (in fact, the first step has rate constant k_2 in the proposed mechanism) but the opposite occurs with the solvent of lower dielectric constant, (see TABLE 1,). The results of the current work (effects of solvent and concentration of compounds) have provided useful evidence for steps 1 (k_2), 3 (k_3) and 4 (k_4) of the reactions between triphenylphosphine 1, dialkyl acetylenedicarboxylate 2 (2a, 2b or 2c) and 4-nitro aniline 3. Two steps involving 3 and 4 are not determining, although the discussed effects, taken altogether, are compatible with first step (k_2) of the proposed mechanism and would allow it to be the rate-determining step. However, a good kinetic description of the experimental result using a mechanistic scheme based upon the steady state approximation is frequently taken as evidence of its validity. By application of this, the rate formation of product 4 from the reaction mechanism (Figure 10) is given by:

$$\frac{d[4]}{dt} = \frac{d[\text{ylide}]}{dt} = \text{rate} = k_4 [I_2][Z^-] \qquad (5)$$

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

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

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

To obtain a suitable expression for $[I_2]$ to put into equation (5) 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:

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

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

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

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

The value of $[I_2]$ can be put into equation (5) to obtain the rate equation (8) for proposed mechanism:

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

Since experimental data were indicated that steps 3 (k_3) and 4 (k_4) are fast but step 1 (k_2) is slow, it is therefore reasonable to make the following assumption: $k_3 [3] \gg k_{-2}$

So the rate equation becomes:

$$\text{rate} = k_2 [1][2] \qquad (9)$$

This equation which was obtained from a mechanistic scheme (shown in Figure 10) by applying the steady-state approximation is compatible with the results obtained by UV spectrophotometery. With respect to the equation (9) that is overall reaction rate, the activation parameters involving $\Delta G^{\#}$, $\Delta S^{\#}$ and $\Delta H^{\#}$ could be now calculated for the first step (rate determining step), as an elementary reaction, on the basis of Eyring

TABLE 2 : The activation parameters involving $\Delta G^{\#}$, $\Delta S^{\#}$ and $\Delta H^{\#}$ for the reactions between (1, 2c and 3), (1, 2b and 3) and (1, 2a and 3) in 1,2-dichloroethane

Reaction	$\Delta G^{\#}$ (kJ.mol^{-1})	$\Delta H^{\#}$ (kJ.mol^{-1})	$\Delta S^{\#}$(J.mol^{-1}.K^{-1})
1, 2c and 3	105.2	21.6	-330.7
1, 2b and 3	101.0	10.8	-320.1
1, 2a and 3	100.5	7.1	-290.2

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equation. The results are reported in TABLE 2.

Further kinetic investigations

To confirm the above observations, further experiments were performed with diethyl acetylenedicarboxylate 2b and dimethyl acetylenedicarboxylate 2a, respectively, under the same conditions used in the previous experiments. 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 TABLE 1 for all solvents and temperatures investigated. The original experimental absorbance curves (dotted line) accompanied by the second order fit curves (solid line), which exactly fit experimental curves (dotted line) confirm the previous observations again for both reactions at 12.0ºC and 300 nm. As can be seen from TABLE 1 the behavior of diethyl acetylenedicarboxylate 2b and dimethyl acetylenedicarboxylate 2a is the same as for the di-*tert*-butyl acetylenedicarboxylate 2c with respect to the reaction with triphenylphosphine 1 and 4-nitro aniline 3. The rate of the former reactions was also accelerated in a higher dielectric constant environment and with higher temperatures, however, these rates under the same condition are approximately 5.3 to 10.6 times more than for the reaction with di-*tert*-butyl acetylenedicarboxylate 2c (see TABLE 1). It seems that both inductive and steric factors for the bulky alkyl groups in 2c tend to reduce the overall reaction rate (see equation 9). In the case of dimetyl acetylenedicarboxylate 2a, the lower steric and inductive effects of the dimethyl groups exert a powerful effect on the rate of reaction.

CONCLUSION

Kinetic investigation of recent reactions was undertaken using UV spectrophotometry. The results can be summarized as follow: (1) the appropriate wavelengths and concentrations were determined to follow the reaction kinetics. (2) The overall reaction order followed second-order kinetics and the reaction orders with respect to triphenylphosphine, dialkyl acetylenedicarboxylate and 4-nitro aniline were one, one and zero respectively. (3) The values of the second-order rate constants of all reactions were calcu-

lated successfully at all solvents and tempratures investigated (4). The rates of all reactions were accelerated at higher temperatures. Under the same conditions, the activation energy for the reaction with di-*tert*-butyl acetylenedicarboxylate 2c (26.3 kJ/mol) was higher than that for the both reactions which were followed by the diethyl acetylenedicarboxylate 2b (15.5 kJ/mol) and dimethyl acetylenedicarboxylate 2a (11.8 kJ/mol) in 1,2-dichloroethane (5) The rates of all reactions were increased in solvents of higher dielectric constant and this can be related to differences in stabilization by the solvent of the reactants and the activated complex in the transition state. (6) Increased steric bulk in the alkyl groups of the dialkyl acetylenedicarboxylates, accompanied by the correspondingly greater inductive effect, reduced the overall reaction rate. (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. (8) Also, the third step was identified as a fast step (k_3). (9) The activation parameters involving $\Delta G^{\#}$, $\Delta S^{\#}$ and $\Delta H^{\#}$ were reported for three reactions.

ACKNOWLEDGMENTS

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