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Kinetic Investigation of the Reactions Between Triphenylphosphine, Dialkyl Acetylenedicarboxilates and NH-Acid, such as 5,6-Dimethyl Benzimidazole by the UV Spectrophotometry Technique

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The work was undertaken to carry out kinetic studies of the reactions between triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of NH-acid, such as 5,6-dimethyl benzimidazole. To determine the kinetic parameters of the reactions, they were monitored by UV spectrophotometery. The second order fits were automatically drawn by the software associated with the UV instrument at an appropriate wavelength. The values of the second order rate constant (k_2) were automatically 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 the Arrhenius equation. This provided the relevant plots to calculate the activation energy of all reactions. Furthermore, useful information was obtained from studies of the effect of solvent, the structure of the reactants (different alkyl groups within the dialkyl acetylenedicarboxylates) and, also, the concentration of the reactants on the rate of the reactions.

INTRODUCTION

Phosphorous ylides are reactive systems, which take part in many important 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 acetylendicarboxylates, in the presence of CH, SH or NH-acids [13-25]. A facile synthesis of the reaction between triphenylphosphine 1, dialkyl acetylendicarboxylates 2 and 5,6-dimethyl benzimidazole (as NH-acid) has been reported previously [26] but, the kinetic studies of these reactions have not yet been investigated. In order to gain further insight into the reaction kinetic, a kinetic study of the mentioned reactions was undertaken using the UV spectrophotometer 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 results from the initial addition of triphenylphosphine to the acetylenic ester 2 (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) (see Schemes 1 and 2).

EXPERIMENTAL PROCEDURES

Chemicals and apparatus used: dialkyl acetylenedicarboxylates, triphenylphosphine and benzimidazole derivatives were purchased from Fulka (Buchs, Switzerland) and used without further purification. All extra pure solvents, including the 1,2-dichloroethane and ethyl acetate, were also obtained from Merk (Darmstadt, Germany). A Cary UV/Vis spectrophotometer, model Bio-300, with a 10 mm light-path black quartz

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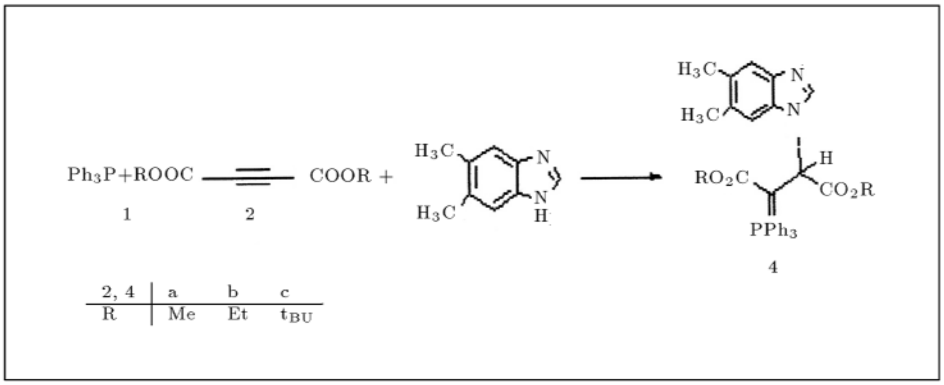
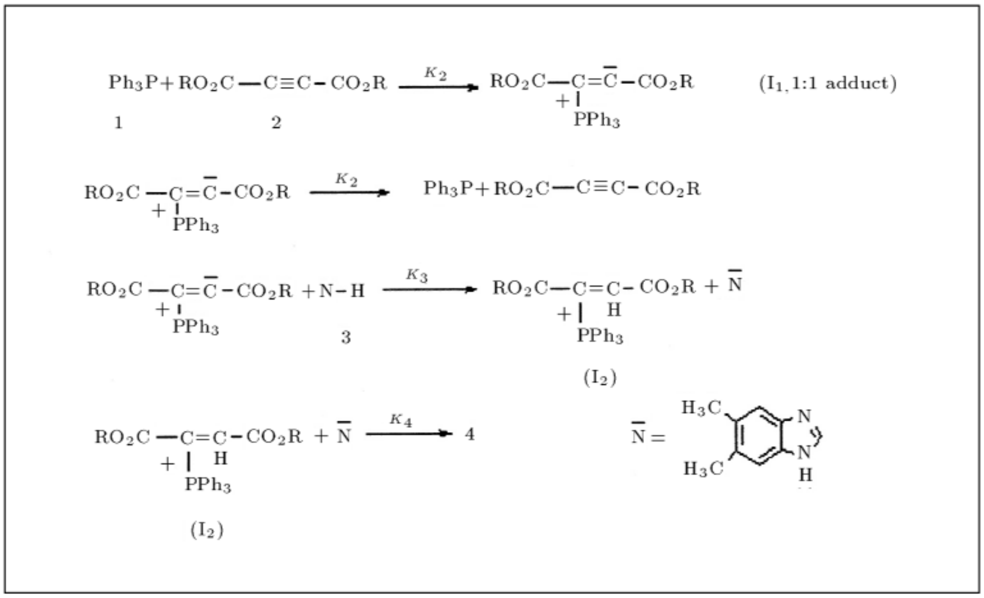


Scheme 1. The reaction between triphenyl phosphine 1, dialkyl acatylenedicarboxylate 2 and 5,6-dimethyl benzimidazole 3 for generation of stable phosphorus ylids 4.



Scheme 2. Mechanism proposed for the reaction between 1, 2 and 3 on the basis of literatures for generation of phosphorus ylides 4.

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, a $3\times 10^{\ 3}$ M solution of compounds 1, 2c and 3 was prepared in 1,2-dichloroethane as solvent. Approximately 3 mL aliquot from each reactant was pipetted into a 10 mm light path quartz spectrophotometer cell, which was then placed in the UV spectrophotometer. The relevant spectra were recorded over the wavelength ranges of 190-400 nm. Figures 1 to 3 show the ultraviolet spectra of compounds 1, 2c and 3, respectively. In the second experiment, first, 1 mL aliquot from the $3 \times 10^{\ 3}$ 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 $3 \times 10^{\ 3}$ M solution of reactant 2c was added to the mixture. The reaction was monitored by recording scans of the entire spectra every 13 min over the whole reaction time at the ambient temperature. The ultraviolet spectra shown in Figure 4 are typical. As can be seen from this figure, the appropriate wavelength can be chosen as 330 nm (corresponding mainly to the compound 4c (product), as shown in Figure 4). At this wavelength, compounds 1, 2c and 3 have relatively no absorbance value. This provided a good opportunity to fully investigate the kinetics of the reaction between triphenylphosphine 1, di-tert-butyl acetylenedicarboxylate 2c and 5,6-dimethyl benzimidazole 3 at 330 nm in the presence of 1,2-dichloroethane 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 concentration ranges ($2 \times 10^{4}\text{M} \leq \text{M}_{4c} \leq 10^{3}\text{M}$) to check a linear relationship between absorbance values and concentrations. Therefore, the UV/Vis experiments may be carried out over these concentration ranges. With respect to the obtained concentration ranges and identification of the suitable wavelength in preliminary investigations, it seems that practical conditions have been found to allow an investigation of the kinetics of the reaction between compounds 1, 2c and 3 by the UV/Vis spectrophotometry technique. This will be discussed according to the following procedure.

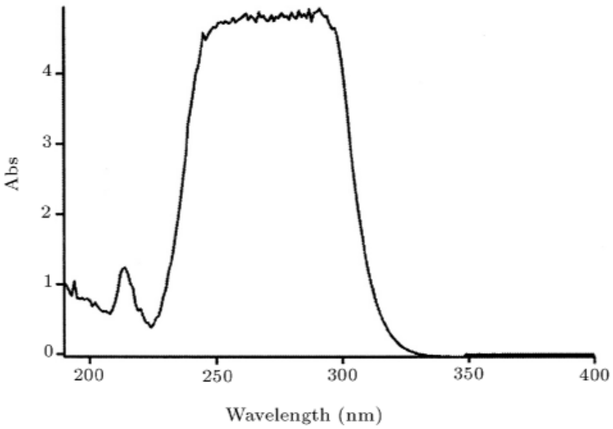


Figure 1. The UV spectrum of 10 ^{3} M triphenylphosphine 1 in 1,2-dichloroethane.

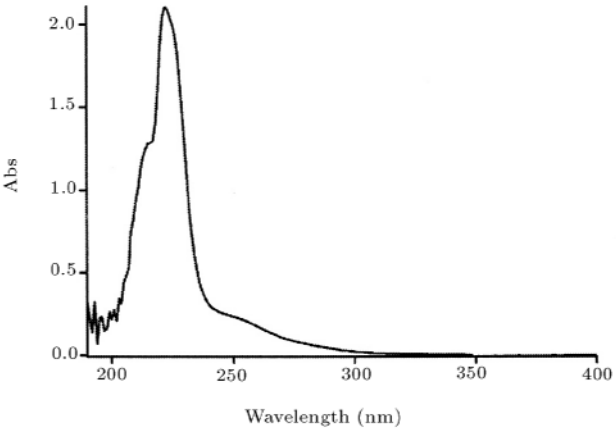


Figure 2. The UV spectrum of 10 ^{3} M di-tert-butyl acetylenedicarboxylate 2c in 1,2-dichloroethane.

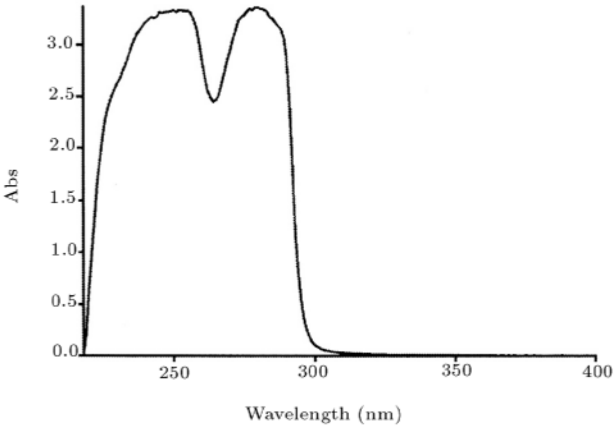


Figure 3. The UV spectrum of 10 ^{3} M 5,6-dimethyl benzimidazole 3 in 1,2-dichloroethane.

For each kinetic experiment, first, 1 mL aliquot from each freshly made solution of 3×10^{3} M compounds 1 and 3 in 1,2-dichloroethane were pipetted into a quartz cell, then, 1 mL aliquot of 3×10^{3} M solution of reactant 2c was added to the mixture. The cuvette was then place in the UV spectrophotometer, keeping the temperature at 5.0°C. The wavelength chosen was 330 nm, as described previously, and the reaction kinetics were followed via UV absorbance against time measurement. Figure 5 illustrates the expanded section wavelength regions (295-390 nm) of the UV spectra of the reaction mixture as the reaction proceeds. Also, Figure 6 shows the absorbance change versus time for the 1:1:1 addition reaction between compounds 1, 2c and 3. The infinity absorbance (A_{∞}) i.e., the absorbance at reaction completion, can be obtained from Figure 6 at $t = 160$ 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 Figure 7.

Thus, the reaction between compounds 1, 2c and 3 follows a second-order kinetic. The second order rate constant (k_2) is then automatically calculated, using a standard equation within the program at 5.0°C, which is reported in Table 1. It is necessary to remember that all kinetic studies, under the same concentration of each reactant as mentioned previously, were also carried out in a series of separate experiments with 4×10^{3} M and 2×10^{3} M, respectively. As expected, the second order rate constant was independent of the concentrations and its value was the same as the

Table 1. The values of second order rate constants for the reaction between compounds 1, 2c and 3 at 330 nm and different temperatures in 1,2-dichloroethane.

t/°C	k_2.M^{1}.min^{1}
5.0	59.1
10.0	73.3
15.0	87.9
20.0	112.6

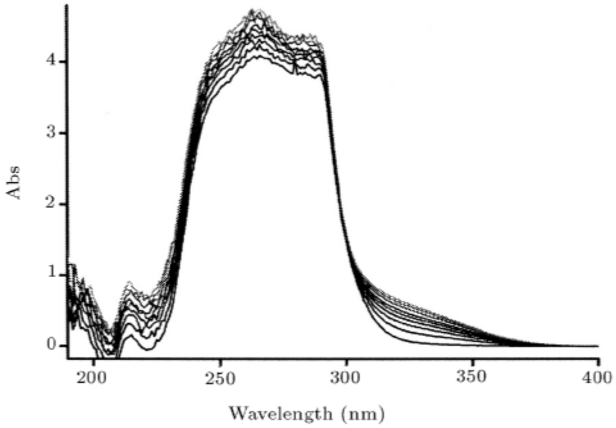


Figure 4. The UV spectra of the reaction between 1, 2c and 3 with concentration 10 ^{3} M of each compound as reaction proceeds in 1,2-dichloroethane with 10 mm light-path cell.

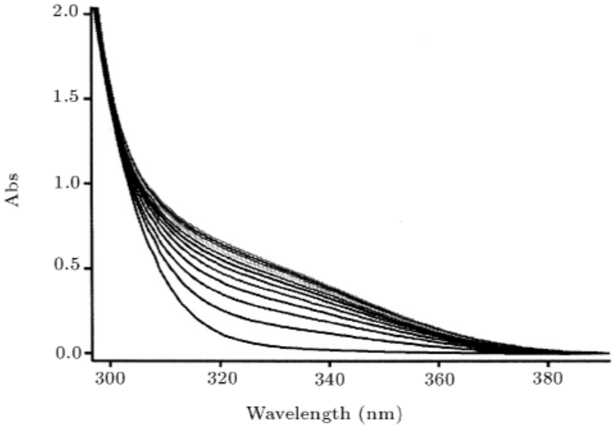


Figure 5. The expanded section wavelengths range (290-385 nm) of UV spectra of reaction mixture of compounds 1, 2c and 3 as reaction proceeds in 1,2-dichloroethane.

previous experiment. In addition, the overall order of the reaction was also 2.

RESULT AND DISCUSSION

Effect of Temperature

As can be seen from Table 1, the rate of reaction is accelerated when the reaction is followed at a higher temperature. In the temperature range studied, the dependence of the second-order rate constant (ln k_2) of the reaction on the reciprocal temperature is consistent with the Arrhenius equation. This behavior is shown in Figure 8. The activation energy of the reaction (29.8 kJ/mol) was obtained from the slope of this figure.

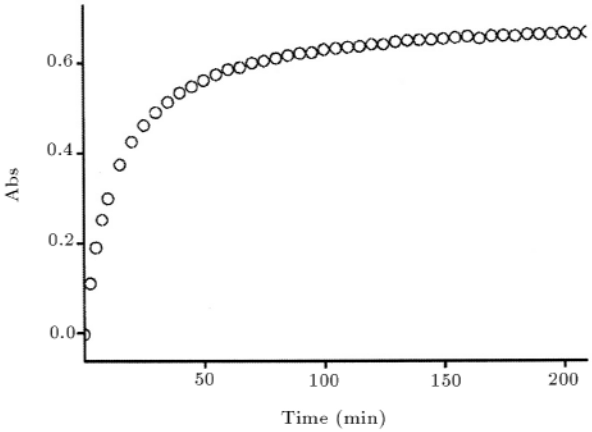


Figure 6. Experimental absorbance change (dotted line) against time at 330 nm for the reaction between compounds 1, 2c and 3 at 330 nm and 5.0°C in 1,2-dichloroethane.

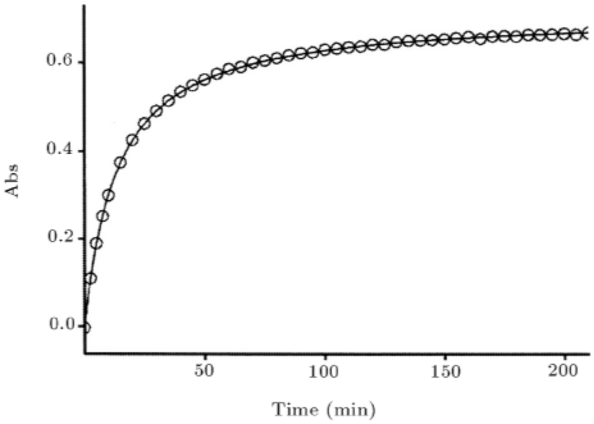


Figure 7. Second order fit curve (full line) accompanied by the original experimental curve (dotted line) for the reaction between 1, 2c and 3 at 330 nm and 5.0°C in 1,2-dichloroethane.

EFFECT OF SOLVENTS

To determine the effect of change in the solvent environment on the rate of reaction, it was necessary to arrange various experiments with different solvent polarity under the same conditions as the previous experiment. For this purpose, ethyl acetate was chosen as a suitable solvent, which could not only dissolve all compounds (1, 2c and 3), but also, does not react with them. In a series of separate experiments, it was cleared that all compounds 1, 2c and 3 do not interact with solvents that have, approximately, a dielectric constant in the range between 1.8-30 debye ($1.8 \leq \varepsilon \leq 30$), so, ethyl acetate, with a dielectric constant of 6, was chosen as a suitable solvent for this purpose. The effects of solvents on the rate constant are given in Table 2.

As can be seen from this table, the rate of reaction in each solvent was increased at a higher

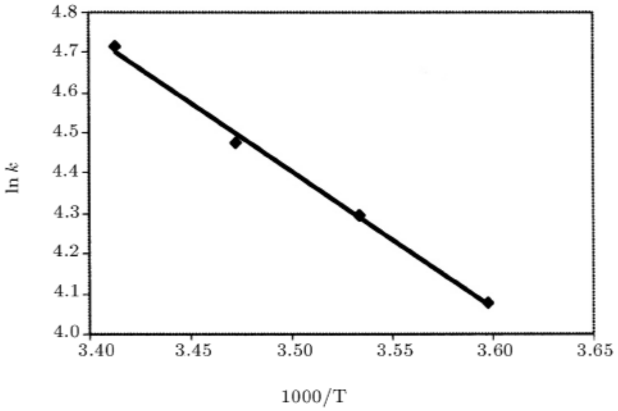


Figure 8. Dependence of second order rate constant (ln k_2) on reciprocal temperature for the reaction between compounds 1, 2c and 3 measured at wavelength 330 nm in 1,2-dichloroethane as solvent in accordance with the Arrhenius equation.

Table 2. The values of second order rate constant for the reaction between compounds 1, 2c and 3 in the presence of solvents such as 1,2-dichloroethane and ethyl acetate at all temperatures investigated.

Solvent	ε	$\mathbf{k_2}$**.M^{-1}.min^{-1}**			
		5.0°C	10.0°C	15.0°C	20.0°C
1,2-dichloroethane	10	59.1	73.3	87.9	112.6
Ethyl acetate	6	34.3	49.7	60.8	75.7

temperature. In addition, the rate of reaction between 1, 2c and 3 was accelerated in a high dielectric constant environment (1,2-dichloroethane), in comparison with a low dielectric constant environment (ethyl acetate) at all temperatures investigated.

Effect of Concentration

To determine the reaction order, with respect to triphenylphosphine 1 and dialkyl acetylene-dicarboxylate 2 (in fact 2c), in a series of other separate experiments, all kinetic studies were carried out in the presence of excess3. Under this condition, the rate equation may, therefore, be expressed as:

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

or:

$$\ln k_{\text{obs}} = \ln k_2 + \gamma \ln[3], \tag{1}$$

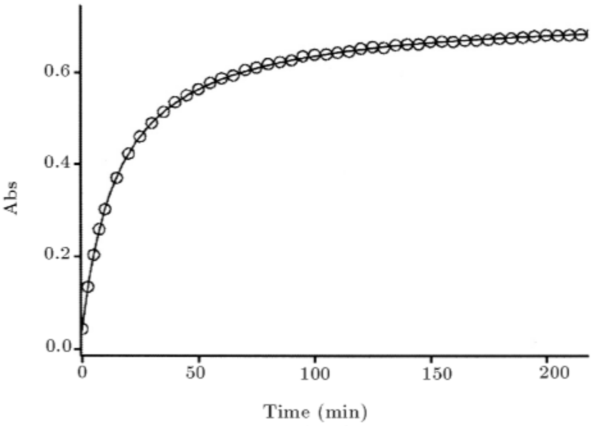


Figure 9. Pseudo second order fit curve (full line) for the reaction between 1 and 2c in the presence of excess 3 (3×10^{-2} M) at 368 nm and 5.0°C in 1,2-dichloroethane.

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 368 nm, which exactly fits the experimental curve (dotted line) (Figure 9). The value of the rate constant was the same as that of the previous experiment (3×10^{-3} M). Repeat experiments with 5×10^{-2} M and 7×10^{-2} M of 3 were separately undertaken with the same fit curve and rate constant. In fact, the experimental data indicated that the 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, therefore, appears that the reaction is zero and second order, with respect to 3 (NH-acid) and the sum of 1 and 2 ($\alpha + \beta = 2$), respectively. To determine the reaction order, with respect to triphenylphosphine 1, a separate experiment was performed in the presence of an excess of 1:

$$\text{rate} = k'_{\text{obs}}[3]^{\gamma}[2]^{\beta}, \qquad k'_{\text{obs}} = k_2[1]^{\alpha}. \tag{2}$$

The original experimental absorbance versus time data provides a first order fit curve at 368 nm, which exactly fits the experimental curve (dotted line), as shown in Figure 10. As a result of this, since $\gamma = 0$ (was determined in a previous experiment), it is reasonable to accept that the reaction is first order with respect to

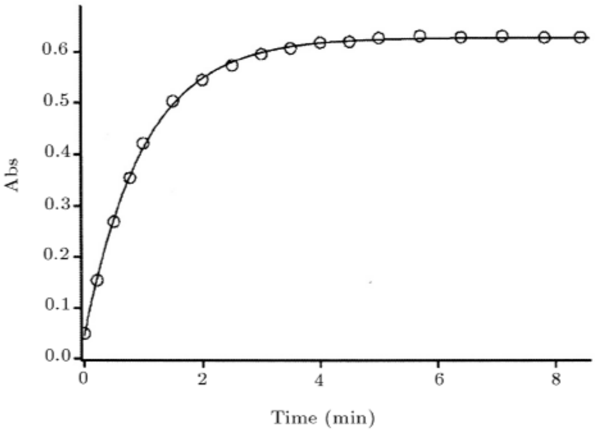


Figure 10. Pseudo first order fit curve (full line) for the reaction between 2c and 3 in the presence of excess 1 (3×10^{-2} M) at 368 nm and 5.0°C in 1,2-dichloroethane.

2 ($\beta = 1$). Due to the overall order of the reaction being 2 ($\alpha+\beta+\gamma = 2$), it is obvious that $\alpha = 1$ and the order of dialkyl acetylenedicarboxylates 2 must be equal to 1. Based on the above results, the simplified Scheme for the proposed reaction mechanism [1-20] as a possible explanation is shown in Scheme 2. 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 of the law can be expressed as follows:

$$\text{rate} = k_3[I_1][3]. \tag{3}$$

The steady state assumption can be employed for $[I_1]$, which is generated by the 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, as follows:

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

Because it is 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 low becomes:

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

The final equation indicated that the overall order of the reaction is 3, which is not compatible with the experimental overall order of the reaction (=2). In addition, according to this equation, the order of the reaction, with respect to 5,6-dimethyl benzimidazole 3, is one, whereas it was practically obtained equal to zero. For this reason, it therefore appeared that the third step is presumably, the fast step, if one assumes that the fourth step (rate constant k_4) is the rate determining step for the proposed mechanism. In this case, there are two species of ion to consider in the rate determining step, namely phosphonium ion (I_2) and benzimidazole ion (N). The phosphonium and benzimidazole ions, as seen in Scheme 2, have full positive and negative charges and form very powerful ion dipole bonds to the ethyl acetate as a solvent (high dielectric constant) in the reaction mechanism. But, the formation of a transition state of reaction between two ions carries a dispersed change which here, is divided between the attacking benzimidazole and the phosphonium ions. Bonding of the solvent (ethyl acetate) to this dispersed charge is much weaker than to the concentrated charge of benzimidazole and phosphonium ions. The solvent thus stabilizes the species ions more than it does the transition state and, therefore, E_a is raised, which slows down the reaction. But, conversely, ethyl acetate practically speeds up the reaction. For this reason, the fourth step, which is independent of a change in the solvent medium, could not be presented as the rate determining step. Furthermore, the rate law of the formation of product (IV) for the proposed reaction mechanism, with an application of steady state assumption, can be expressed by:

$$\text{rate} = \frac{k_2 k_3[1][2][3]}{k_{\ 2} + k_3[3]}, \tag{4}$$

this equation is independent of the rate constant of the fourth step (k_4) and confirms why the fourth step would not be affected by a change in the solvent medium. In addition, it was earlier suggested that kinetic studies of the phenomena of ionic species are so fast [36,37]. If the first step (rate constant k_2) is to be the rate determining step, in this case, two reactants (triphenylphosphine 1 and dialkyl acetylenedicarboxylate 2), as seen in Scheme 2, would 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, here, is divided between the attacking 1 and 2. The bonding of solvent to this dispersed charge is much stronger than to the reactants with a lack of 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. From the experimental result, it is found that solvents with a high dielectric constant exert a powerful effect on the rate of reaction (in fact, the first step is with rate constant k_2 of the proposed mechanism) but, is opposite to the solvent with low dielectric constant (1,2-dichloroethane). The result of the current work (effect of solvent and concentration of compounds, in particular the concentration of NH-acid) altogether provided useful evidence for steps 1 (k_2), 3 (k_3) and 4 (k_4) of the reaction between triphenylphosphine 1, dialkyl acetylenedicarboxylate 2 and 5,6-dimethyl benzimidazole 3. According to the above discussion, the two steps involving 3 and 4 are not the determining steps, although these effects together are compatible with the first step (k_2) of the proposed mechanism and would allow for being the rate determining step. However, a good kinetic description of the 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 (Scheme 2) is a simplified version of Scheme 2, which is given by:

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

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

$$\frac{d[I_1]}{dt} = k_2[1][2] \quad k\ _2[I_1] \quad k_3[I_1][3],$$

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

To obtain a suitable expression for $[I_2]$ to put into Equation 5, one 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 one can obtain expressions for $[I_2]$ and $[I_1]$ as follows:

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

$$\frac{d[I_1]}{dt} = 0, \qquad [I_1] = \frac{k_2[1][2]}{k\ _2 + k_3[3]}. \tag{7}$$

One can now replace $[I_1]$ in Equation 6:

$$[I_2] = \frac{k_2k_3[1][2][3]}{k_4[N\ \ ][k\ _2 + k_3[3]]}.$$

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

$$\text{rate} = \frac{k_2k_3k_4[1][2][3][N\ \ ]}{k_4[N\ \ ][k\ _2 + k_3[3]]}. \tag{8}$$

Experimental data indicated that Steps 3 and 4, i.e. k_3 and k_4, are fast, but, in contrast, Step 2, i.e. k_2, is slow and it is, therefore, reasonable to make the following assumption:

$$k_3[3] >> k\ _2.$$

So, the rate equation becomes:

$$\text{rate} = k_3[1][3].$$

This equation, which was obtained from the mechanism scheme (shown in Scheme 2) by applying the steady-state approximation, is compatible with the results obtained by the UV spectrophotometery.

Table 3. The values of second order rate constant for the reaction between 1, 2b and 3 in the presence of solvents such as 1,2-dichloroethane and ethyl acetate, respectively at all temperatures investigated.

Solvent	ε	k_2.M ^{1}.min ^{1}			
		5.0°C	10.0°C	15.0°C	20.0°C
1,2-dichloroethane	10	459.0	603.1	632.8	717.9
Ethyl acetate	6	200.7	286.1	349.3	435.2

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 3 and 4, 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, are shown in Figures 11 and 12 at 5.0°C, respectively.

As can be seen from Tables 3 and 4, the behavior of diethyl acetylenedicarboxylate 2b and dimethyl acetylenedicarboxylate 2a is the same as that of di-tert-

Table 4. The values of second order rate constant for the reaction between 1, 2a and 3 in the presence of solvents such as 1,2-dichloroethane and ethyl acetate, respectively at all temperatures investigated.

Solvent	ε	k_2.M ^{1}.min ^{1}			
		5.0°C	10.0°C	15.0°C	20.0°C
1,2-dichloroethane	10	644.1	894.5	965.4	1098.5
Ethyl acetate	6	373.0	434.3	537.3	621.2

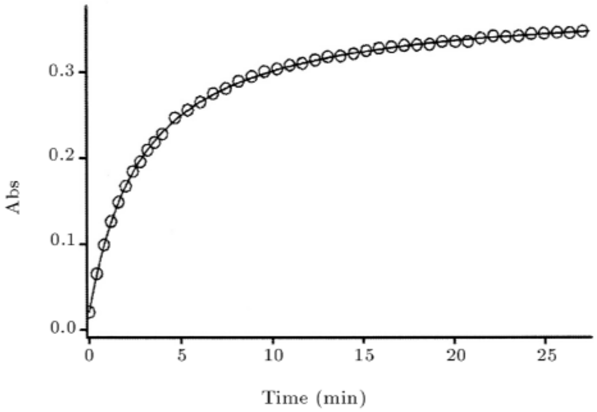


Figure 11. Second order fit curve (full line) accompanied by the original experimental curve (dotted line) for the reaction between compounds 1, 2b and 3 at 330 nm in 1,2-dichloroethane.

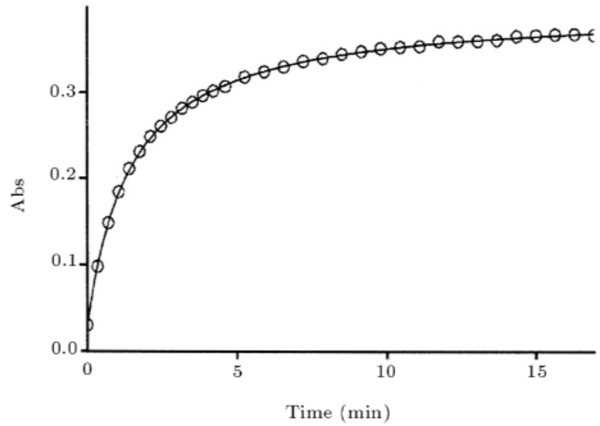


Figure 12. Second order fit curve (full line) accompanied by the original experimental curve (dotted line) for the reaction between compounds 1, 2a and 3 at 330 nm in 1,2-dichloroethane.

butylacetylenedicarboxylate 2c (Table 2), with respect to the reaction with triphenylphosphine 1 and 5,6-dimethyl benzimidazole 3. The rates of both recent reactions were also accelerated in a high dielectric constant environment and high temperature. Nevertheless their rate under the same conditions, is approximately 6 to 8 time greater than the reaction with di-tert-butylacetylenedicarboxylate 2c. It seems that the steric factor and bulky groups within the structure of dialky acetylenedicarboxylate would tend to reduce the rate of the overall reactions. These results are illustrated in Table 5 for three reactions at appropriate wavelengths and at different tempratures in the presence of a solvent such as 1,2-dichloroethane. As a result of this, it appears that the dialkyl acetylenedicarboxylates participate in the rate determining step of the reaction (rate constant k_2) and their structures (steric and inductive factors) affect the rate of this step. In the case of dimetyl acetylenedicarboxylate 2a, the less steric and, also the less inductive effects of dimethyl groups both together exert a powerful effect on the rate of the reaction.

These observations are also obtained for ethyl acetate (Tables 2 to 4).

Table 5. The effect of alkyl groups within the structure of dialkyl acetylenedicarboxylates on the rate of reactions between compounds (1, 2a and 3), (1, 2b and 3) and also (1, 2c and 3) in 1,2-dichloroethane.

Reactions	**2**	k_2.M ^{1}.min ^{1}			
		5.0°C	10.0°C	15.0°C	20.0°C
1,2 and 3	2a	644.1	894.5	965.4	1098.5
	2b	459.0	603.1	632.8	717.9
	2c	59.1	73.3	87.9	112.6

CONCLUSIONS

Kinetic investigation of the reactions between triphenylphosphin and dialkyl acetylenedicaroxylates, with 2-methyl benzimidazole, was undertaken using the UV spectrophotometery. The results can be summarized as follows:

1. The appropriate wavelengths and concentrations were successfully determined to follow the kinetic investigations;
2. The overall order of all three reactions followed a second-order kinetic and order of reaction, with respect to triphenylphosphine, dialkyl acetylenedicarboxylate and 2-methyl benzimidazole, which were obtained at 1,1 and zero, respectively;
3. The values of the 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;
4. The rate of the three reactions was accelerated at high temperature. Under the same conditions, the activation energy of the reaction with di-tert-butylacetylenedicarboxylate (29.8 kJ/mol) was higher than the two reactions which were followed by the diethyl acetylenedicarboxylate (18.9 kJ/mol) and dimethyl acetylenedicarboxylate (16.6 kJ/mol);
5. The rate of the reactions was increased in the media of higher dielectric constant solvent. This can be related to differences in the stabilization of the reactants and the activated complex in the transition state by the solvent;
6. More steric factor and bulky alkyl groups, accompanied by its more inductive effect within the structure of dialkyl acetylenedicarboxylate, would tend to reduce the rate of the overall reactions;
7. With respect to the experimental data, the first step of the proposed mechanism was recognized as a rate determining step (k_2), which was confirmed, based upon the steady state approximation.

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