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Spectrophotometric Kinetic Studies of the Reaction between Triphenylphosphine, Dialkyl Acetylenedicarboxylates and NH-Acids

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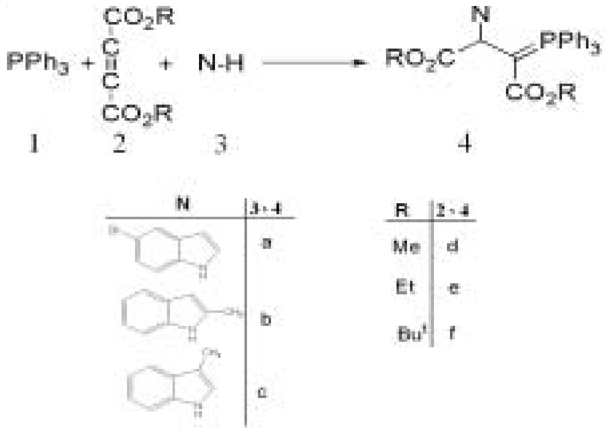
The major objective of the work undertaken were to carry out kinetic studies of the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of indole derivatives (as a NH-acid). To determine the kinetic parameters of the reaction, it was monitored by UV spectrophotometer. The second order fits were automatically drawn by the software associated with a Cary UV spectrophotometer model Bio-300 at 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) on reciprocal temperature was in agreement with Arrhenius equation. This provide the relevant plots to calculate the activation energy of all reactions. Furthermore useful information was obtained from studies of the effect of solvent and different alkyl groups within the dialkyl acetylenedicarboxylates on the rate of reactions.

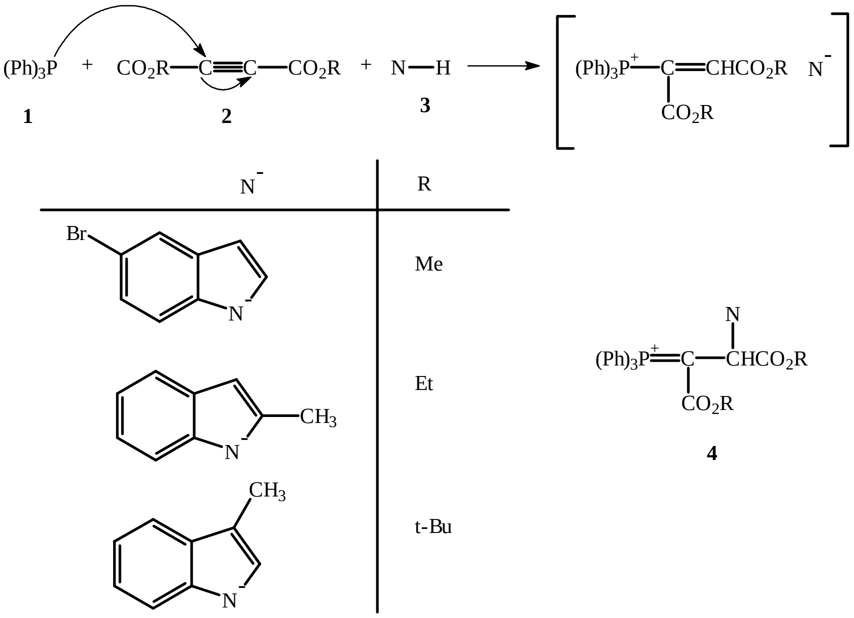
Key Words: Phosphorus ylide, NH-acid, Triphenylphosphine, Kinetic parameters, Acetylenic ester, UV spectrophotometry.

INTRODUCTION

Phosphorus ylides are reactive systems, which take part in many valuable reactions of organic syntheses[1-11]. These are most often obtained in excellent yields from the 1:1:1 addition reaction between triphenylphosphine, dialkyl acetylenedicarboxylates, in the presence of CH, SH or NH-acids[12-19]. A facile synthesis of the reaction between triphenylphosphine **1**, dialkyl acetylene dicarboxylates **2** and indole derivatives **3** (as a NH-acid) has been earlier reported[20] (**Scheme-1**) but the kinetic study of this reaction has not been investigated earlier. In order to gain further insight into the reaction mechanism, a kinetic study of the mentioned reactions was undertaken by UV spectrophotometery technique. On the basis of well established chemistry of trivalent phosphorus nucleophiles, 1-5,[20-25] it is reasonable to assume that phosphorus ylide 4 results from initial addition of triphenylphosphine **1** to the acetylenic ester **2** and subsequent protonation of the 1:1 adduct by the NH-acid to form phosphoranes (**Scheme-2**). In past several kinetic investigations area of different reactions have been previously reported using the UV instrument[26-32].



Scheme-1 Reaction between triphenylphosphine **1**, dialkyl acetylenedicarboxylates **2** and indole derivatives **3** for generation of stable phosphorus ylides **4**.



Scheme-2 Mechanism proposed for reaction between **1**, **2** and **3** on the basis of report of the Literatures1-5,[20-25] for generate of stable phosphorus ylides **4**.

EXPERIMENTAL

Dialkyl acetylenedicarboxylates, triphenylphosphine and 5-bromo indole, 2-methyl indole or 3-methyl indole were purchased from Fulka (Buchs, Switzerland) and used without further purifications. All extra pure solvents including ethyl acetate and 1,2-dichloroethane also obtained from Merk (Darmstadt, Germany). A Cary UV/vis spectrophotometer model Bio-300 with a 10 mm light-path black quartz spectrophotometer cell was employed throughout the present work.

Before starting the experiments, it was necessary to find the appropriate wavelength in order to follow kinetic study of the reaction. For this purpose, in the first experiment, 1×10^{-3} M solutions of compounds **1**, **2f** and **3a** have been 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 and then was placed in the UV spectrometer. The relevant spectra were recorded over the wavelengths range 190-400 nm. Figs. 1-3 show the ultraviolet spectra of compounds **1**, **2f** and **3a**, respectively.

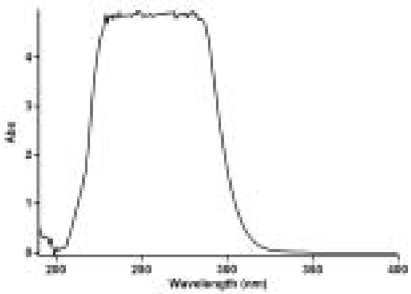


Fig. 1. The UV spectrum of 10^{-3} M triphenylphosphine (**1**) in dried 1,2-dichloroethane

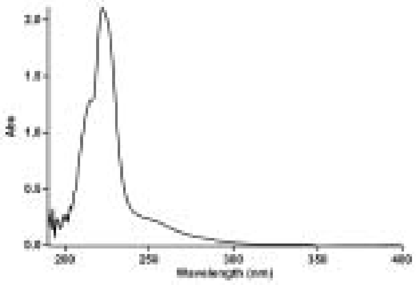


Fig. 2. The UV spectrum of 10^{-3} M di-*tert*-butylacetylenedicarboxylate (**2c**) in dried 1,2-dichloroethane

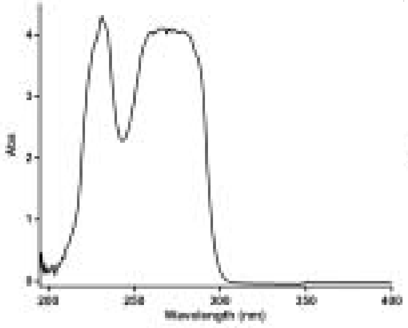


Fig. 3. The UV spectrum of 10^{-3} M 5-bromo indole (**3a**) in dried 1,2-dichloroethane

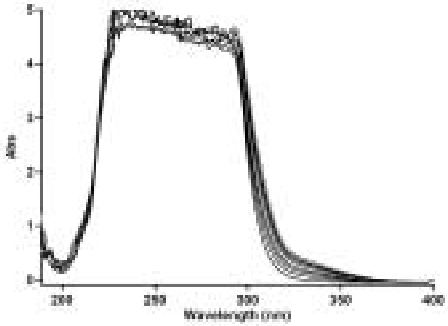


Fig. 4. The UV spectra of the reaction between 10^{-3} M of each compounds **1**, **2f** and **3a** as reaction proceeds in dried 1,2-dichloroethane

In the second experiment, first 1mL aliquot from the 3×10^{-3} M solutions of compound **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 **2c** was added to the mixture. The quartz cell was placed in the UV spectrophotometer and the reaction monitored by recording scans of the entire spectra every 15 min over the whole reaction time at ambient temperature. The ultra-violet spectra shown in Fig. 4 are typical. As can be seen from this Figure, the appropriate wavelength can be chosen 330 nm (corresponding mainly to compound **4c** (product) as shown in Fig. 4). At this wavelength, compounds **1**, **2c** 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-butylacetylenedicarboxylate **2c** and 5-bromo indole **3a** 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 in a 10 mm light-path cuvette over the concentrations range (10^{-3} M $\leq M_{4c} \leq 2\times10^{-4}$ M) to check a linear relationship between absorbance values and concentrations at 330 nm. Fig. 5 shows a linear relationship between concentration and absorbance at 330 nm for the UV/Vis spectra of compound **4c** in 1,2-dichloroethane. Therefore, the UV/Vis experiments may be carried out over this concentrations range. With respect to the obtained concentrations range and identification of suitable wavelength in preliminary investigations it seems that practical conditions have been found to allow an investigation of the kinetic of reaction between compounds **1**, **2c** and **3a** by the UV/Vis spectrophotometry technique.

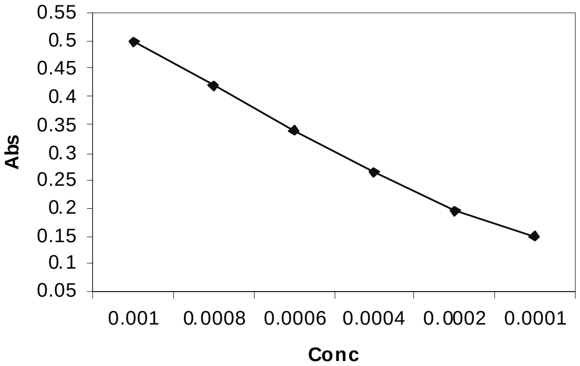


Fig. 5. A linear relationship between concentrations and absorbance values at 330 nm for compound 4af over concentration range (10^{-3} M $\leq M_{4c} \leq 2\times10^{-4}$ M) when dried 1, 2-dichloroethane was used as solvent in the UV/vis experiment

For each kinetic experiment, first 1 mL aliquot from freshly made solution of 3×10^{-3} M compounds **1** and **3a** in dried 1,2-dichloroethane was 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 10ºC. The wavelength chosen was 330 nm as described previously. Fig.6 illustrates the expanded wavelengths (300-385 nm) of UV spectra of reaction mixture as reaction proceeds. Fig. 7 shows the absorbance change *vs.* time at wavelength 330 nm for the 1:1:1 addition reaction between compounds **1**, **2c** and **3** at 10ºC. The infinity absorbance (A_∞) that is the absorbance at reaction completion, can be obtained from Fig. 6 at t = 260 min. With respect to this value, zero and first or second curve fitting could be automatically drawn for the mentioned reaction by the software[33] associated with the UV instrument at 330 nm. In this case using the original experimental absorbance *vs.* time data provided a second order fit curve (full line) at 330 nm which exactly fits the experimental curve (dotted line) as shown in Fig.8. Thus the reaction between compounds **1**, **2c** and **3** follows second-order kinetic.

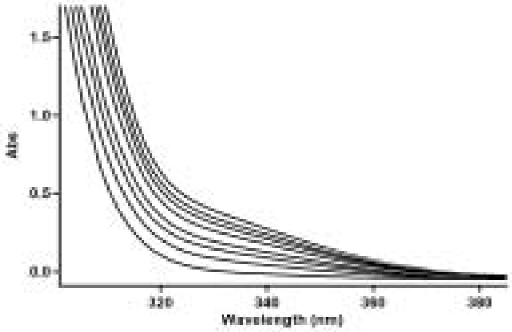


Fig. 6. The expanded section wavelengths range (300-385 nm) of UV spectra of reaction mixture of compounds **1**, **2c** and **3** as reaction proceeds in 1,2-dichloroethane

Fig. 7. Experimental absorbance change (dotted line) against time at 330 nm for the reaction between compounds **1**, **2f** and **3a** over 110 min at 0ºC in 1,2-dichloroethane

Fig. 8. Second order fit curve (full line) accompanied by the original experimental curve (dotted line) for the reaction between **1**, **2f** and **3a** at 330 nm and 0ºC in 1,2-dichloroethane

The second order rate constant (k_2) is then automatically calculated using standard equation within the program at 10ºC. It is reported in Table-1 at 330 nm wavelength.

TABLE-1
VALUES OF SECOND ORDER RATE CONSTANTS FOR THE REACTION BETWEEN COMPOUNDS **1**, **2c** AND **3** AT 330 nm AND DIFFERENT TEMPERATURE IN 1,2-DICHLOROETHANE

Temp. (ºC)	k/m.min
0.0	41.9
5.0	59.8
10.0	77.2
15.0	99.1

RESULTS AND DISCUSSION

Effect of temperature: As can be seen from the Table-1, the rate of reaction is accelerated when the reaction is followed at higher temperature. In the temperature range studied, the dependence of the second-order rate constant of the mentioned reaction on reciprocal temperature is consistent with the Arrhenius equation. This behavior is shown in Fig. 9. The activation energy of reaction (37.1 kJ/mol) was obtained from the slop.

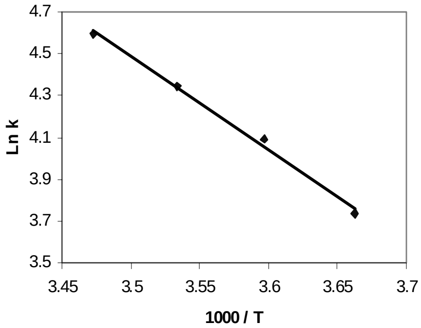


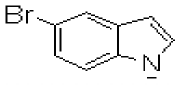
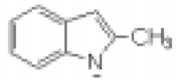
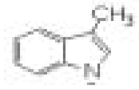
Fig. 9. Dependence of second order rate constant (ln k) on reciprocal temperature for the reaction between compounds **1**, **2c** and **3** measured at wavelength 330 nm in 1,2-dichloroethane in accordance with Arrhenious equation

Effect of solvents and structure of NH-acids: To determine the effect of change in solvent environment on the rate of reaction, it was necessary to arrange various experiments with different solvent polarity. For this purpose, ethyl acetate was chosen as suitable solvents which not only could be dissolved all compounds but also does not react with them. In a series of separate experiments which have been previously achieved it was cleared that all compounds **1**, **2** and **3** does not interact with solvents which have approximately dielectric constant in the range between 1.8-20 debye ($1.8 < \varepsilon < 20$) so ethyl acetate with 6.02 dielectric constant were chosen as suitable solvents for this purpose. The effects of solvents on the rate constant of reactions (**1**, **2c** and **3**) are given in Table-2. As can be seen from this table, the rate of reaction in each solvent was increased with increasing temperature. In addition, the rate of reaction between **1**, **2c** and indole derivatives **3** was accelerate in a high dielectric constant environment (1,2-dichloroethane) in comparison with a low dielectric constant environment (ethyl acetate) at all temperature investigated. Finally, when the reaction was followed in the presence of 2-methyl indole and 3-bromo indole under the same conditions, the rate of reactions were increased in comparison with 5-bromo indole respectively. The results are only reported for 1,2-dichloroethane at 0, 5, 10 and 15ºC, respectively in Table-3. This behaviour would be observed in ethyl acetate and all temperatures investigated (Table-2).

TABLE-2
THE VALUES OF SECOND ORDER RATE CONSTANT FOR THE THREE REACTIONS (1, 2f AND 3a), (**1**, **2c** AND **3b**) AND (**1**, **2f** AND **3c**) IN THE PRESENCE OF DIFFERENT SOLVENTS AT ALL TEMPERATURES INVESTIGATED

3	Solvent	ε	k_2/M.min			
			0ºC	5ºC	10ºC	15ºC
3a	1,2-Dichloroethane	10.03	41.9	59.8	77.2	99.1
	ethyl acetate	6.02	32.3	48.6	64.8	82.5
3b	1,2-Dichloroethane	10.03	51.5	63.1	82.3	117.7
	ethyl acetate	6.02	37.1	52.3	71.4	95.6
3c	1,2-Dichloroethane	10.03	128.1	137.2	151.7	181.4
	ethyl acetate	6.02	51.8	69.9	95.7	119.1

TABLE-3
THE VALUES OF SECOND ORDER RATE CONSTANTS FOR THE REACTIONS BETWEEN COMPOUNDS (**1**, **2f** AND **3a**), (**1**, **2f** AND **3b**) AND (**1**, **2f** AND **3c**) IN 1,2-DICHLOROETHANE AT DIFFERENT TEMPERATURES

3	NH-acid	k_2/M.min			
3a		41.9	59.8	77.2	99.1
3b		51.5	63.1	82.3	117.7
3c		66.1	81.7	91.7	122.8

Further kinetic investigations: To confirm the above observations, further experiments were performed with diethyl acetylenedicarboxylate **2e** and dimethyl acetylenedicarboxylate **2d**, respectively. The values of the second-order rate constant (k_2) for the reactions between (1, 2e and 3) and (1, 2d and 3) are reported in Tables 4 and 5, respectively for all solvents

TABLE-4
THE VALUES OF SECOND ORDER RATE CONSTANT FOR THE REACTION BETWEEN **1**, **2e** AND **3** IN THE PRESENCE OF SOLVENTS SUCH AS ETHYL ACETATE AND 1,2-DICHLOROETHANE RESPECTIVELY AT ALL TEMPERATURES INVESTIGATED

3	Solvent	ε	k_2/M.min			
			0ºC	5ºC	10ºC	15ºC
3a	1,2-Dichloroethane	10.03	397.2	479.8	590.9	716.1
	ethyl acetate	6.02	630.0	742.4	913.9	1062.6
3b	1,2-Dichloroethane	10.03	426.5	472.1	534.5	631.8
	ethyl acetate	6.02	452.1	495.3	625.0	748.3
3c	1,2-Dichloroethane	10.03	436.08	467.81	546.22	636.05
	ethyl acetate	6.02	476.01	498.03	573.29	682.11

TABLE-5
THE VALUES OF SECOND ORDER RATE CONSTANT FOR THE REACTION BETWEEN **1**, **2d** AND **3** IN THE PRESENCE OF SOLVENTS SUCH AS ETHYL ACETATE AND 1,2-DICHLOROETHANE RESPECTIVELY AT ALL TEMPERATURES INVESTIGATED

3	Solvent	ε	k_2/M.min			
			0ºC	5ºC	10ºC	15ºC
3a	1,2-Dichloroethane	10.03	440.7	502.1	584.0	707.1
	ethyl acetate	6.02	361.3	440.3	517.5	615.4
3b	1,2-Dichloroethane	10.03	560.2	662.3	784.9	920.1
	ethyl acetate	6.02	420.0	502.1	584.0	591.8
3c	1,2-Dichloroethane	10.03	601.2	698.3	721.2	844.8
	ethyl acetate	6.02	474.0	567.7	672.1	803.9

TABLE-6
THE EFFECT OF ALKYL GROUPS WITHIN THE STRUCTURE OF DIALKYL ACETYLENEDICARBOXYLATES ON THE RATE OF REACTIONS BETWEEN COMPOUNDS (**1**, **2d** AND **3**), (**1**, **2e** AND **3**) AND ALSO (**1**, **2f** AND **3**) IN 1,2-DICHLOROETHANE

Reaction	2	k_2/M.min			
		0ºC	5ºC	10ºC	15ºC
1, **2** and **3a**	2d	842.8	899.2	1023.2	1142.0
	2e	596.5	636.5	685.7	742.9
	2f	71.6	89.7	107.4	136.4
1, **2** and **3a**	2d	522.0	582.0	666.0	753.7
	2e	438.4	488.3	569.9	668.0
	2f	66.1	81.7	91.7	112.8
1, **2** and **3a**	2d	746.7	789.2	847.8	988.0
	2e	488.0	522.4	579.3	697.0
	2f	69.2	59.8	100.3	128.1

and temperature investigated. Second order fit curve (full line) accompanied by the original experimental curve (dotted line) for the reaction between compounds (1, 2e and 3a) and (1, 2d and 3a) are illustrated in Figures 10 and 11, respectively.

As can bee seen from the Tables 4 and 5 the rate of both recent reactions were also accelerated in high dielectric constant environment and high temperature, nevertheless the rate of them are approximately 7 to 10 time greater than the reaction with di-tert-butylacetylenedicarboxylate **2c**. It seems that steric and bulky groups within the structure of dialky acetylenedicarboxylate would tend to reduce the rate of overall reactions. These results are illustrated in Table-6 for three reactions at appropriate wavelength and 0.0ºC, 5.0ºC, 10.0ºC and 15.0ºC in the presence of solvent such as 1,2-dichloroethane.

This observation are also obtained for ethyl acetate (Tables 2-4).

Conclusion

Kinetic investigation of the reaction between triphenylphosphin, dialkyl acetylenedicaroxylates and 5-bromoindole, 2-methyl indole or 3-methyl indole was undertaken by UV spectrophotometry. The results can be summarized as follow: 1) The appropriate wavelengths and concentrations were successfully determined to follow kinetic investigations, 2) All reactions followed second-order kinetic, 3) The rate of three reactions were accelerate at high temperature, 4) The values of second-order rate constant of all reactions were automatically calculated with respect to the standard equation within the software associated with Cary-300 UV equipment, 5) Under the same conditions, activation energy of the reaction with di-tert-butylacetylene-dicarboxylate (37.1 kJ/mol) was higher than the two reactions which were followed by the diethyl acetylenedicarboxylate (25.8 kJ/mol) and dimethyl acetylenedicarboxylate (20.5 kJ/mol), 6) The rate of 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 and 7) The steric and bulky alkyl groups within the structure of dialkyl acetylenedicarboxylate would tend to reduce rate of overall reactions.

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