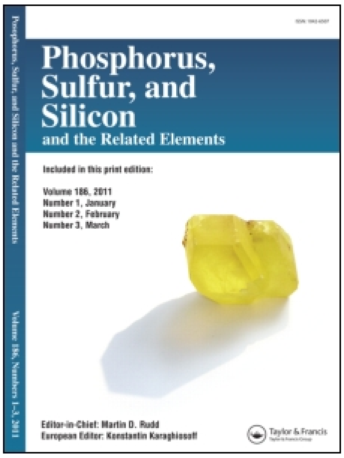

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Kinetic Investigation of the Reaction between Triphenylphosphine, Dialkyl Acetylenedicarboxylate, and Carbazole by the UV Spectrophotometry Technique

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Kinetic Investigation of the Reaction between Triphenylphosphine, Dialkyl Acetylenedicarboxylate, and Carbazole by the UV Spectrophotometry Technique

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The major objectives of the work undertaken were to carry out kinetic studies of the reaction between triphenylphosphine and dialkyl acetylenedicarboxylate in the presence of strong NH-acids, such as carbazole. To determine the kinetic parameters of the reaction, it was monitored by the UV spectrophotometer technique. The values of the second order rate constant (k_2) were automatically calculated using standard equations within the program when the second order fits of the mentioned reactions were automatically drawn by the software associated with a Cary UV spectrophotometer model Bio-300 at an appropriate wavelength. At the temperature range studied, the dependence of the second order rate constant (Ln k) 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 and different alkyl groups within the dialkyl acetylenedicarboxylates on the rate of reactions.

Keywords Acetylenic ester; carbazole; kinetic parameters; NH-acid; phosphorus ylide; triphenylphosphine; UV spectrophotometry technique

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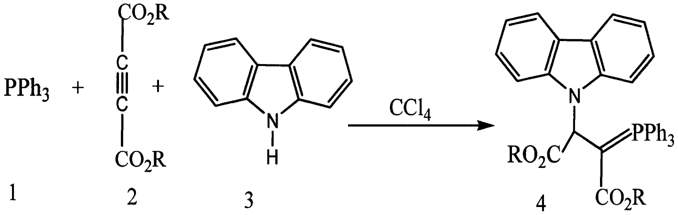
INTRODUCTION

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 strong CH, SH, or NH-acids.[12–19] A facile synthesis of the reaction between triphenylphosphine **1**, dialkyl acetylenedicarboxylates **2**, and carbazole **3** (as an NH-acid) has been earlier reported[20] (see Scheme 1) but the kinetic study of this reaction has not been investigated previously. In order to gain further insight into the reaction mechanism, a kinetic study of the mentioned reactions was undertaken by a UV spectrophotometer technique. Numerous kinetic investigations over a large area of different reactions have been previously reported using the UV instrument.[21–24] Before the beginning of the experiments, 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, 1 × 10^{-3} M solutions of compounds **1**, **2c**, and **3** in carbon tetrachloride have been prepared. 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 240–400 nm.



R	2	4
Me	a	a
Et	b	b
Bu^t	c	c

SCHEME 1 The reaction between triphenylphosphine **1**, dialkyl acetylenedicarboxylate **2**, and carbazole **3** for generation of stable phosphorus ylides **4**.

Figures 1, 2 and 3 show the ultraviolet spectra of compounds **1**, **2c**, and **3**, respectively. In the second experiment, first 1 mL aliquot from the 3 × 10^{-3}M solutions of compounds **1**, and **3** was 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

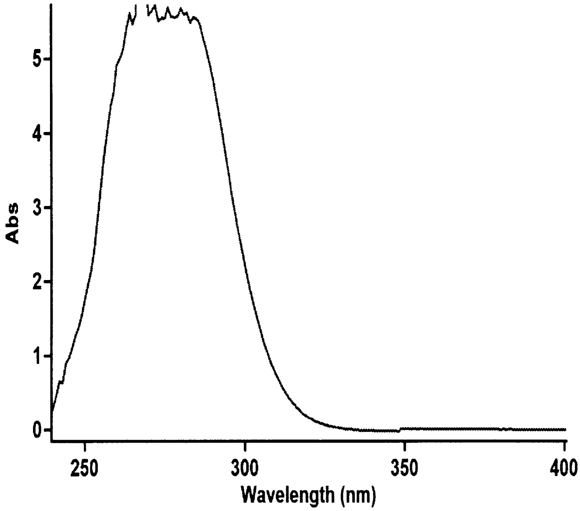


FIGURE 1 The UV spectrum of 10^{-3} M triphenylphosphine **1** in dried carbon tetrachloride with a 10 mm light-path cell.

added to the mixture (It is important to remember that in the present work the concentration of each reactant in the quartz spectrophotometer cell is a third (i.e. $1/3 \times 3 \times 10^{-3}$ M) of the initial concentration (3×10^{-3} M)).

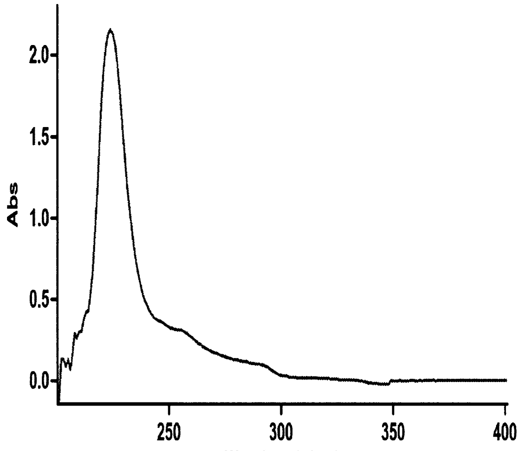


FIGURE 2 The UV spectrum of 10^{-3} M di-tert-butylacetylenedicarboxylate **2c** in dried carbon tetrachloride with a 10 mm light-path cell.

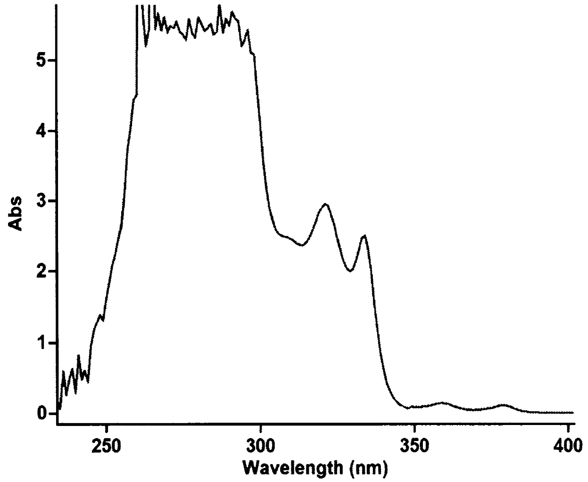


FIGURE 3 The UV spectrum of 10^{-3} M carbazole **3** in dried carbon tetrachloride with a 10 mm light-path cell.

Hence, for the second experiment with a UV instrument, the concentration of each compound in the quartz spectrophotometer cell was consistent with the concentration of each compound that was previously used for the experiment (described in first work). The quartz cell was placed in the UV spectrophotometer, and the reaction was monitored by recording scans of the entire spectra every 4 min over the whole reaction time at ambient temperature. The ultra-violet spectra shown in Figure 4 are typical. As can be seen from Figure 4, the appropriate wavelength can be chosen at 355 nm (corresponding mainly to compound **4c** (product) as shown in Figure 4). At this wavelength, compounds **1**, **2c**, and **3** have relatively no absorbance value. This provided good opportunity in order to fully investigate the kinetic of the reaction between triphenylphosphine **1**, di-tert-butyl acetylenedicarboxylate **2c**, and carbazole **3** at 355 nm in the presence of carbon tetrachloride as a 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 $\leq M_{4c} \leq 2 \times 10^{-4}$M) to check a linear relationship between absorbance values and concentrations at 355 nm. Figure 5 shows a linear relationship between concentration and absorbance at 355 nm for the UV/Vis spectra of compound **4c** in carbon tetrachloride. 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

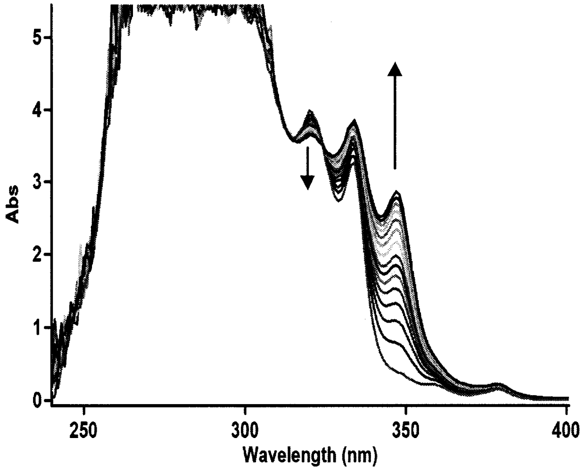


FIGURE 4 The UV spectra of the reaction between 10^{-3} M of each compounds **1**, **2c**, and **3** as reaction proceeds over 120 min in dried carbon tetrachloride with a 10 mm light-path cell.

practical conditions have been found to allow an investigation of the kinetics of reaction between triphenylphosphie **1**, di-tert-butylacetylene dicarboxylte **2c**, and carbazole **3** by the UV/Vis spectrophotometer technique. This will be discussed in the next section.

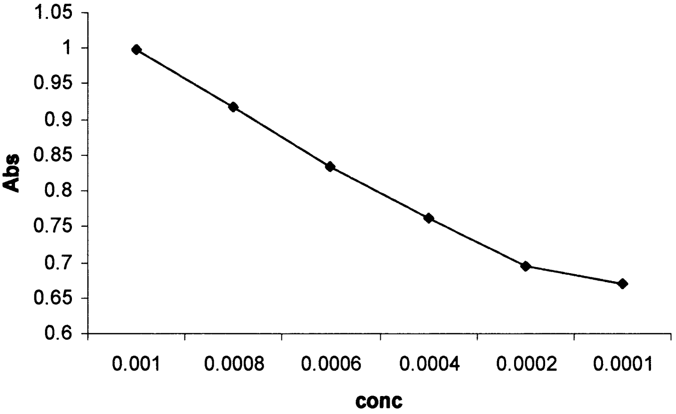


FIGURE 5 A linear relationship between concentrations and absorbance values at 355 nm for compound **4c** when dried CCl_4 was used as solvent in the UV/Vis experiment.

EXPERIMENTAL PROCEDURES

Chemicals and apparatus used are as follows: dialkyl acetylenedicarboxylates, triphenylphosphine, and carbazole were purchased from Fulka (Buchs, Switzerland) and used without further purifications. All extra pure solvents including the carbon tetrachloride, ethyl acetate, and 1,2 dichloroethan were 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 current work.

Methods

For each kinetic experiment, first 1 mL aliquot from freshly made solution of 3×10^{-3}M compounds **1** and **3** in dried carbon tetrachloride 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 5°C. Because the reaction was followed at 5°C, in order to avoid condensation of moisture on the quartz cuvette windows, it was necessary to exclude air from the whole of the spectrophotometer sample housing. This was achieved by a vigorously flowing stream of dry argon. The wavelength chosen was 355 nm as described previously, and the reaction kinetics were followed via UV absorbance against time measurement every 4 min over a period of 60 min. Because all solutions were made outside the cell housing of UV equipment and were then transferred for the UV kinetic experiment, there was a delay of about 3 seconds before reaction monitoring began. Therefore, zero time for all kinetic traces was not absolutely zero. This had no effect on the result obtained because the reaction was slow, and so this initial delay was insignificant. Figure 6 shows the absorbance change versus time at wavelength 355 nm for the 1:1:1 addition reaction between compounds **1**, **2c**, and **3** at 5°C. Also Figure 7 illustrates the expanded section wavelengths (310–400 nm) of UV spectra of the reaction mixture as reaction proceeds. If the reaction was complete over the 300 min, infinity absorbance (A_∞) that is the absorbance at reaction completion, can be obtained from Figure **6** at t = 300 min. Using this value, a second-order fit for the mentioned reaction was drawn automatically by the software[25] associated with the UV instrument at 355 nm. The Cary-300 UV/Vis spectrophotometer software contains a curve fitting program which uses the chosen value of infinity absorbance (A_∞) to generate the absorbance curve (full line) assuming first order kinetic and using the original experimental absorbance curve (dotted line) versus time as shown in Figure 8.

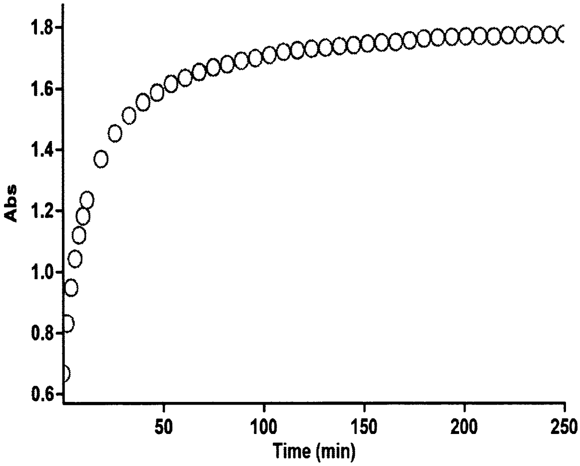


FIGURE 6 Experimental absorbance change (dotted line) against time at **355** nm for the reaction between compounds **1**, **2c**, and **3** over the 250 min at 5°C.

Assuming that the curve fitting is first order, a good fit indicates that the chosen value is sound. In the case of Figure 8, there is a poor agreement between the original experimental curves (dotted line) and first order fit curve (full line), so the reaction between compounds **1**, **2c**, and **3** did not follow first-order kinetic.

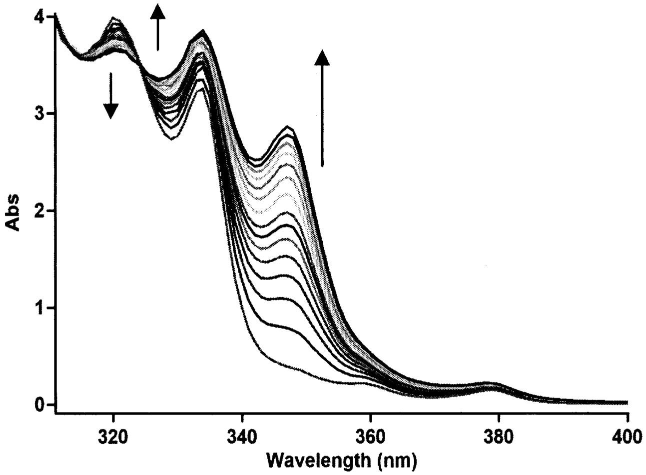


FIGURE 7 The expanded section wavelength (310–400 nm) of UV spectra of reaction mixture of compounds **1**, **2c**, and **3** as reaction proceeds in carbon tetrachloride.

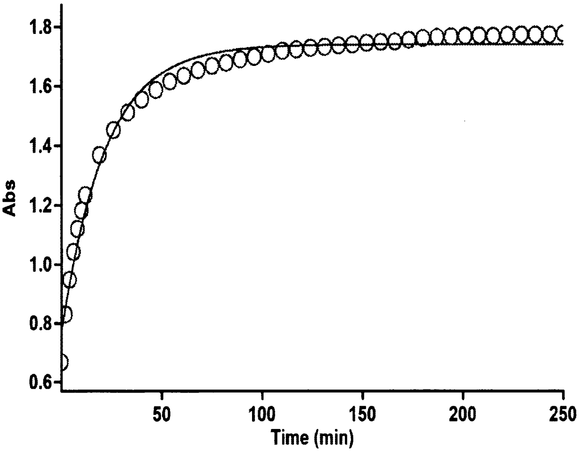


FIGURE 8 First-order fit curve (full line) accompanied by the original experimental curve (dotted line) for the reaction between compounds **1**, **2c**, and **3** at 355 nm and 5°C in carbon tetrachloride.

Assuming second-order kinetic and using the original experimental absorbance versus time data provides a second-order fit curve (full line) at 355 nm, which exactly fits the experimental curve (dotted line) as shown in Figure 9. Thus, the reaction between triphenylphosphine **1**,

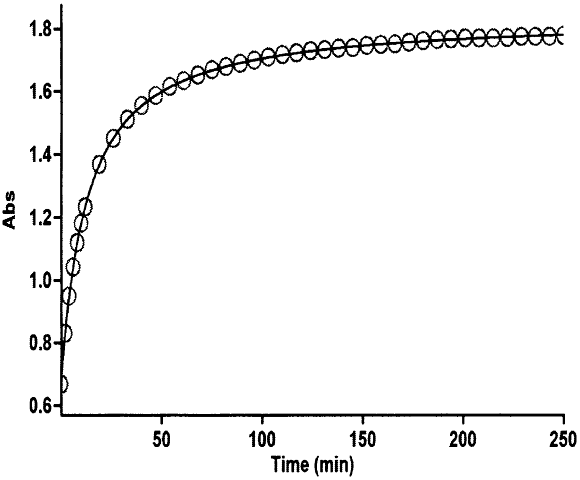


FIGURE 9 Second-order fit curve (full line) accompanied by the original experimental curve (dotted line) for the reaction between compounds **1**, **2c**, and **3** at 355 nm and 5°C in carbon tetrachloride.

TABLE I The Values of Second-Order Rate Constants for the Reaction Between Compounds 1, 2c, and 3 at 355 nm and Different Temperatures in Carbon Tetrachloride

t/°C	$k/M^{-1}\ min^{-1}$
−5	45.82
0	62.05
5	78.37
10	122.46

di-tert-butylacetylene dicarboxylate **2c**, and **3** follows a second-order kinetic. The second-order rate constant (k_2) is then automatically calculated using a standard equation[25] within the program at 5°C. It is reported in Table I at 355 nm wavelength.

RESULT AND DISCUSSION

Effect of Temperature

As can be seen from Table I, 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 of the mentioned reaction on reciprocal temperature is consistent with the Arrhenius equation. This behavior is shown in Figure 10. The activation energy of reaction (2.64 kJ/mol) was obtained from the slop of this figure.

Effect of Solvents

The effect of solvents on the rate constant is given in Table II. 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 triphenylphosphine **1**, di-tert-butylacetylenedicarboxylate **2c**, and carbazole **3** was accelerate in a high dielectric constant environment (both ethyl acetate and 1,2 dichloroethan) in comparison with a low dielectric constant environment (carbon tetrachloride) at all temperatures investigated.

FURTHER KINETIC INVESTIGATIONS

To confirm the previously discussed observations, further experiments were performed with diethyl acetylene dicarboxylate **2b** and dimethyl

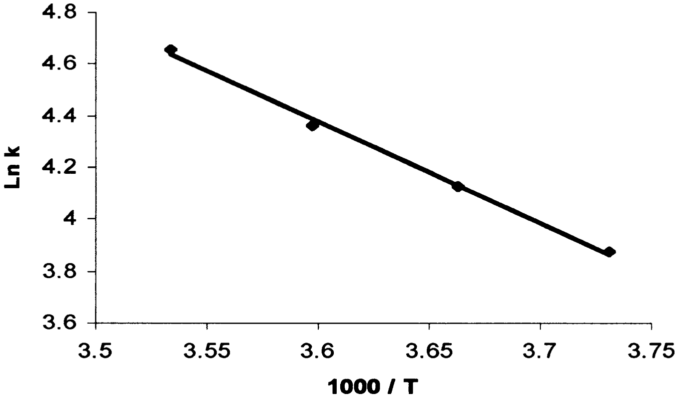


FIGURE 10 Dependence of second-order rate constant (Ln k) on reciprocal temperature for the reaction between compounds **1, 2c**, and **3** measured at wavelength 355 nm in CCl_4 in accordance with Arrhenius equation.

acetylenedicarboxylate **2a**, respectively. The values of the second-order rate constant (k_2) for the reactions between **1**, **2b**, and **3** and also **1, 2a**, and **3** are reported in Tables III and IV respectively, for all solvents and temperatures investigated.

As can bee seen from Tables III and IV, the behavior of diethyl acetylenedicarboxylate **2b** and dimethyl acetylenedicarboxylate **2a** are the same as the di-tert-butyl acetylenedicarboxylate **2c** (Table II) with respect to the reaction with triphenylphosphine **1** and carbazole **3**. The rate of both recent reactions were also accelerated in a high dielectric constant environment and high temperature; nevertheless, the rate of them are approximately 5 to 10 times greater than the reaction with di-tert- butyl acetylenedicarboxylate **2c**. It seems that steric and bulky groups within the structure of dialky acetylenedicarboxylate would tend to reduce the rate of overall reaction. These results are illustrated

TABLE II The Values of Second-Order Rate Constant for the Reaction Between Compounds 1, 2c, and 3 in the Presence of Solvents Such as CCl_4, Ethyl Acetate 1, and 2 Dichloroethan, Respectively, at all Temperatures Investigated

Solvent	ε	k_2/M^{-1} min^{-1} (5°C)	k_2/M^{-1} min^{-1} (0°C)	k_2/M^{-1} min^{-1} (5°C)	k_2/M^{-1} min^{-1} (10°C)
CCl_4	2.02	45.82	61.05	78.37	122.46
Ethyl acetate	6.02	85.72	104.58	127.93	164.32
1,2 dichloroethan	10.03	122.96	158.72	191.01	212.76

TABLE III The Values of Second-Order Rate Constant for the Reaction Between 1, 2b, and 3 in the presence of Solvents Such as, CCl_4, Ethyl Acetate, and 1,2 Dichloroethan, Respectively, at All Temperatures Investigated

Solvent	ε	$k_2/M^{-1}\ min^{-1}$ (−5°C)	$k_2/M^{-1}\ min^{-1}$ (0°C)	$k_2/M^{-1}\ min^{-1}$ (5°C)	$k_2/M^{-1}\ min^{-1}$ (10°C)
CCl_4	2.02	359.36	419.54	510.36	626.42
Ethyl acetate	6.02	370.74	442.23	535.73	654.18
1,2 dichloroethan	10.03	474.63	554.07	659.13	779.75

TABLE IV The Values of Second-Order Rate Constant for the Reaction Between 1, 2b, and 3 in the Presence of Solvents Such as CCl_4, Ethyl Acetate, 1,2 Dichloroethan, Respectively, at All Temperatures Investigated

Solvent	ε	$k_2/M^{-1}\ min^{-1}$ (−55°C)	$k_2/M^{-1}\ min^{-1}$ (0°C)	$k_2/M^{-1}\ min^{-1}$ (5°C)	$k_2/M^{-1}\ min^{-1}$ (10°C)
CCl_4	2.02	447.47	586.38	648.19	799.12
Ethyl acetate	6.02	661.44	780.95	887.17	1005.14
1,2 dichloroethan	10.03	791.33	1003.18	1209.32	1521.5

TABLE V The Effect of Alkyl Groups Within the Structure of Dialkyl Acetylenedicarboxylate on the Rate of Reactions Between Compounds (1, 2a, and 3), (1, 2b, and 3) and Also (1, 2c, and 3) in Carbon Tetrachloride

					$k_2/M^{-1}\ min^{-1}$			
R	Compound	Product	Solvent	λ/nm	−5°C	0°C	5°C	10°C
Methyl	2a	4a	CCl_4	355	447.47	586.38	648.19	799.12
Ethyl	2b	4b	CCl_4	355	359.36	419.54	510.36	626.42
Bu^t	2c	4c	CCI_4	355	45.82	61.05	78.37	122.46

TABLE VI The Effect of Alkyl Groups Within the Structure of Dialkyl Acetylenedicarboxylate on the Rate of Reactions Between Compounds (1, 2a, and 3), (1, 2b, and 3) and also (1, 2c, and 3) in Ethyl Acetate

					$k_2/M^{-1}\ min^{-1}$			
R	Compound	Product	Solvent	λ/nm	−5°C	0°C	5°C	10°C
Methyl	2a	4a	Ethyl acetate	346	661.44	780.95	887.17	1005.04
Ethyl	2b	4b	Ethyl acetate	346	370.74	442.23	535.73	654.18
Bu^t	2c	4c	Ethyl acetate	350	85.72	104.58	127.93	164.32

TABLE VII The Effect of Alkyl Groups Within the Structure of Dialkyl Acetylenedicarboxylate on the Rate of Reactions Between Compounds (1, 2a, and 3), (1, 2b, and 3) and also (1, 2c, and 3) in 1,2 Dichloroethan

					k_2/M^{-1} min^{-1}			
R	Compound	Product	Solvent	λ /nm	−5°C	0°C	5°C	10°C
Methyl	2a	4a	1,2 dichloroethan	348	791.33	1003.18	1209.32	1521.50
Ethyl	2b	4b	1,2 dichloroethan	348	474.63	554.07	659.13	779.75
Bu^t	2c	4c	1,2 dichloroethan	350	122.96	158.72	191.01	212.76

in Table V for three reactions at appropriate wavelength and −5°C, 0°C, 5°C, and 10°C in the presence of solvent such as carbon tetrachloride.

This observation is also reported for ethyl acetate and 1,2 dichloroethan in Tables VI and VII, respectively.

CONCLUSIONS

Kinetic investigation of the reaction between triphenylphosphin, dialkyl acetylenedicaroxylate, and carbzole was undertaken by the UV spectrophotometery. The results can be summarized as follows:

1. The appropriate wavelengths and concentrations were successfully determined to follow kinetic investigations.
2. All reactions followed a second-order kinetic.
3. The rate of three reactions were accelerated at a higher temperature.
4. The values of a 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, the activation energy of the reaction with di-tert-butyl acetylenedicarboxylate (2.64 kJ/mol) was higher than the two reactions that were followed by the diethyl acetylenedicarboxylate (1.548 kJ/mol) and dimethyl acetylenedicarboxylate (1.529 kJ/mol).
6. The rate of reactions was increased in a media of higher dielectric constant solvent. This can be related to differences in stabilization of the reactants and the activated complex in a transition state by a solvent.
7. The steric and bulky alkyl groups within the structure of dialkyl acetylenedicarboxylate would tend to reduce the rate of overall reactions.

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