

Kinetic spectrophotometric method for the reaction mechanism study of the stable 1,5-diionic organophosphorus formation in the presence carbazole

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Abstract: Kinetic studies were carried out on the reaction between triphenylphosphine and acetylenedicarboxylic acid in the presence of carbazole. In order to determine the kinetic parameters, the reaction was monitored based on a global kinetic analysis methodology using the UV-vis spectrophotometry technique. The second order fits were automatically drawn and the values were calculated with the standard equations and associated program of the apparatus. Dependence of the second order rate constant ($\ln k_2$) on reciprocal temperature was in agreement with the Arrhenius equation. Furthermore, the useful information was obtained from the studies of solvent effects and concentration of the reactants on the rate of reaction. The proposed mechanism was confirmed according to the steady-state approximation and the first step (k_2) of reaction was recognized as a rate-determining step on the basis of experimental data.

Keywords: Kinetics, Mechanism, UV spectrophotometry, 1,5-Diionic organophosphorus.

Introduction

Trivalent phosphorus compound is known to be a nucleophile, whereas it behaves as an electron donor toward good electron acceptor either in the ground or excited state [1, 2]. In recent years there has been an increasing interest in the synthesis of organophosphorus compounds, that is, those bearing a carbon atom bound directly to a phosphorus atom [3-15]. This interest has resulted from the recognition of the value of such compounds in a variety of biological, industrial and chemical synthetic uses [3-5]. A number of reactions have been observed which involve 1,4-diionic phosphorus compounds as elusive transient species [8-10]. In all of this reaction in which this diionic system is postulated, the betaines cannot be isolated but appears to occur as an intermediate on the pathway to an observed product. Researchers have recently described the synthesis of stable diionic compounds from the reaction between triphenylphosphine and electron-deficient acetylenic

esters in the presence of NH, OH, SH, CH-acids [11-28]. The synthesis of the reaction between triphenylphosphine **1**, acetylenedicarboxylic acid (ADA) **2** and carbazole **3** for preparation of the crystalline and stable 1,5-diionic organophosphorus compound was reported (Figure 1) [29]. In this work, we describe kinetic results along with detailed mechanistic studies of this reaction in various solvents based on a global kinetic analysis methodology using the UV-vis spectrophotometry apparatus.

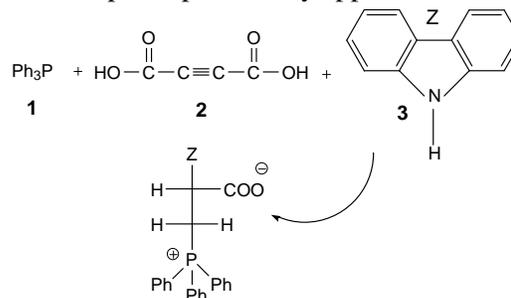


Figure 1: The overall reaction between triphenylphosphine **1**, acetylenedicarboxylic acid (ADA) **2** and carbazole (N-H

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heterocyclic) **3** for preparation of the crystalline and stable 1,5-diionic organophosphorus compound

Results and discussion

In order to following the kinetic of the reaction in the appropriate wavelength, in the first experiment, solutions of compounds **1**, **2** and **3** ($3 \times 10^{-3} \text{ M}$) were prepared in CH_2Cl_2 . Approximately 3 mL aliquot from each reactant was pipetted into a 10 mm light path quartz spectrophotometer cell and the relevant spectra were recorded over the wavelength range 200-600 nm. Figures 2, 3 and 4 show the UV spectra of compounds **1**, **2** and **3** respectively. In the second experiment, 1 mL aliquots from the $3 \times 10^{-3} \text{ M}$ solutions of compounds **1** and **3** were first pipetted into a quartz spectrophotometer cell (TPP and carbazole haven't any interaction with together), then 1 mL aliquot of $3 \times 10^{-3} \text{ M}$ solution of reactant **2** was added to the mixture, The reaction monitored by recording scans of the entire spectra every 10 min over the whole reaction time at the ambient temperature. From the typical UV spectrum as Figure 5, the appropriate wavelengths were found to be 358 and 378 nm (corresponding to the carbazole **3** spectrum) as shown in Figure 4. At these wavelengths, compounds **1** and **2** have relatively no absorbance value. This provided a good opportunity to investigate the kinetic of the reaction between triphenylphosphine **1** and acetylenedicarboxylic acid **2** in the presence of carbazole **3** at 358 and 378 nm in CH_2Cl_2 . Since the spectrophotometer cell of the UV equipment had a 10 mm light-path cuvette, the UV-Vis spectra of compound **3** was measured over the concentrations range ($3 \times 10^{-4} \text{ M} \leq M_{\text{carbazole}} \leq 6 \times 10^{-3} \text{ M}$) to check a linear relationship between absorbance values and concentrations as shown in Figure 6.

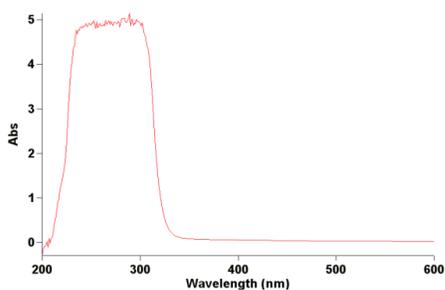


Figure 2: The UV spectrum of triphenylphosphine **1** ($3 \times 10^{-3} \text{ M}$) in CH_2Cl_2

Therefore, the UV-Vis experiments can be carried out over this concentrations range. With respect to this concentrations range and identification of suitable wavelengths in preliminary investigations, it seems that practical conditions have been found that allow an

investigation of the kinetics of the reaction between compounds **1**, **2** and **3** using the UV-Vis spectrophotometry. The following procedure was employed:

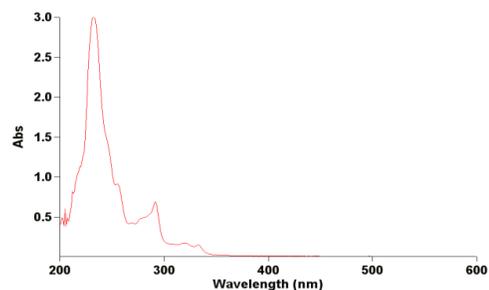


Figure 3: The UV spectrum of acetylenedicarboxylic acid (ADA) **2** ($3 \times 10^{-3} \text{ M}$) in CH_2Cl_2

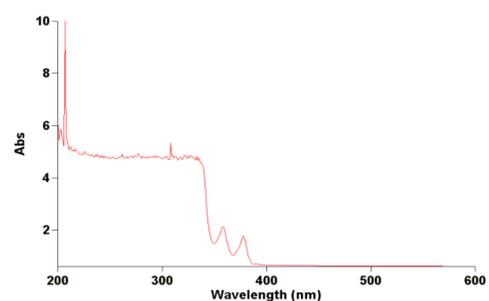


Figure 4: The UV spectrum of carbazole **3** ($3 \times 10^{-3} \text{ M}$) in CH_2Cl_2

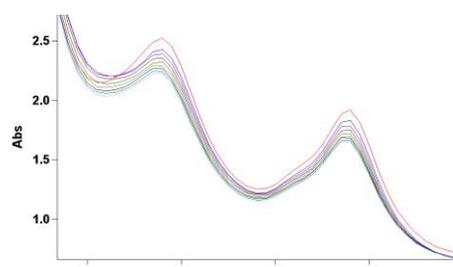


Figure 5: The UV spectra of the reaction between **1**, **2** and **3** ($3 \times 10^{-3} \text{ M}$) in CH_2Cl_2

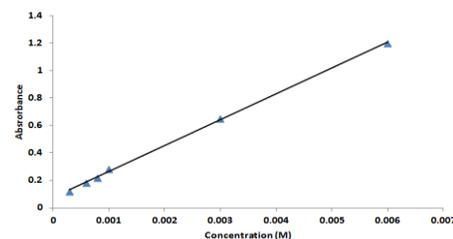


Figure 6: A linear relationship between concentrations and absorbance values at 378 nm for carbazole in CH_2Cl_2 by the UV-vis spectrophotometer

For each kinetic experiment, first 1 mL aliquots from each freshly made solution of $3 \times 10^{-3} \text{ M}$ compounds **1** and **3** in CH_2Cl_2 were pipetted into a quartz cell, then a

1 mL aliquot of 3×10^{-3} M solution of reactant **2** was added to the mixture, keeping the temperature at 25 °C, and the reaction kinetics were followed plotting UV absorbance against time. Figure 7 shows the absorbance change versus time for the 1:1:1 addition reaction between compounds **1**, **2** and **3**. The infinity absorbance (A_{∞}) that is the absorbance at reaction completion, can be obtained from Figure 7 at $t = 130$ min. With respect to this value, zero, first, second and etc. curve fitting could be automatically drawn for the reaction using the software associated with the UV instrument. Using the original experimental absorbance versus time data provided a second order fit curve (solid line) at 358 and 378 nm that exactly fits the experimental curve (dotted line) as shown in Figure 7.

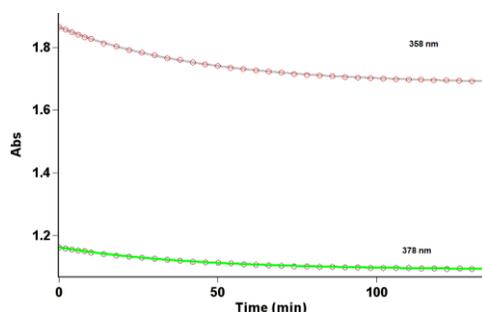
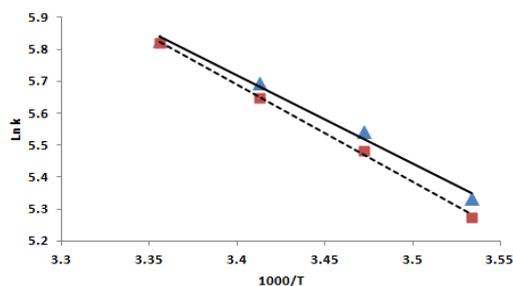


Figure 7: Experimental absorbance change (dotted line) accompanied with the second order fit curve (full line) against time at 358 and 378 nm for the reaction between **1**, **2** and **3** in CH_2Cl_2 at 25 °C

Therefore, the reaction between compounds **1**, **2** and **3** follows second-order kinetics. The second order rate constant (k_2) is then automatically calculated using the

Table 1. Values of overall second order rate constants for the reaction between **1**, **2** and **3** in the presence of different solvents at all temperatures investigated at 358 and 378 nm

λ (nm)	Solvent	ϵ	k_2 ($\text{M}^{-1} \cdot \text{min}^{-1}$)/ S.D			
			25.0 °C	20.0 °C	15.0 °C	10.0 °C
378	dichloromethane	10.3	$328.9/1.3 \times 10^{-2}$	$296.7/1.2 \times 10^{-2}$	$255.1/0.9 \times 10^{-2}$	$197.1/1.3 \times 10^{-2}$
378	ethylacetate	6.0	$302.8/1.1 \times 10^{-2}$	$264.5/1.4 \times 10^{-2}$	$218.0/1.9 \times 10^{-2}$	$177.2/1.0 \times 10^{-2}$
378	carbon tetrachloride	2.2	$299.5/2.6 \times 10^{-2}$	$251.3/1.5 \times 10^{-2}$	$212.6/1.5 \times 10^{-2}$	$148.7/1.4 \times 10^{-2}$
358	dichloromethane	10.3	$336.4/2.4 \times 10^{-2}$	$283.9/1.7 \times 10^{-2}$	$255.6/1.3 \times 10^{-2}$	$164.3/1.3 \times 10^{-2}$
358	ethylacetate	6.0	$317.2/2.3 \times 10^{-2}$	$275.1/2.4 \times 10^{-2}$	$214.8/1.5 \times 10^{-2}$	$152.5/0.8 \times 10^{-2}$
358	carbon tetrachloride	2.2	$305.4/1.6 \times 10^{-2}$	$256.6/1.4 \times 10^{-2}$	$211.4/1.0 \times 10^{-2}$	$137.8/1.9 \times 10^{-2}$



standard equation within the program at 25 °C. All kinetic studies under same concentration of each reactant as mentioned previously were also carried out in a series of separate experiment with 6×10^{-3} M and 1×10^{-3} M respectively. As expected, the second order rate constant was independent of concentrations and its value was same as previous experiment. In addition, the overall order of reaction was also 2.

Effect of solvents and temperature:

To determine the effect of change in temperature and solvent environment on the rate of reaction, it was necessary to carry out various experiments using the different temperature and solvent polarities but under same condition as the previous experiment. Dichloromethane ($\epsilon = 10.3$ at 25 °C), CCl_4 ($\epsilon = 2.2$ at 20 °C) and ethyl acetate ($\epsilon = 6$ at 25 °C) were chosen as suitable solvents, because these solvents dissolved reactants but did not react with them. The effects of solvents and temperatures on the rate constant are given in Table 1. This shows that the rate of reaction in each solvent was increased at higher temperature. In addition, the rate of reaction was accelerated with increasing the dielectric constant amount of solvents (Table 1). In the temperature range studied, the dependence of the second-order rate constant ($\text{Ln } k_2$) of the reactions on reciprocal temperature is consistent with the Arrhenius equation. This behavior is shown in Figure 8. The obtained activation energies of the reaction were 25.2 kJ/mol and 22.8 kJ/mol at 358 and 378 nm in CH_2Cl_2 , respectively.

Figure 8: Dependence of second order rate constant ($\text{Ln } k_2$) on reciprocal temperature for the reaction at 378 nm (solid line) and 358 nm (dash line) according with Arrhenius equation in CH_2Cl_2 .

Plausible mechanism:

To determine reaction order with respect to triphenylphosphine **1** and acetylenedicarboxylic acid **2**, in a series of other separate experiments, all kinetic studies were carried out in the presence of excess **3**.

Under this condition the rate equation may therefore be expressed as:

$$\text{rate}_{obs} = k_2 [3]^\gamma \quad \text{or} \quad \text{Ln} k_{obs} = \text{Ln} k_2 + \gamma \text{Ln}[3] \quad (\text{I})$$

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 378 and 358 nm which exactly fits the experimental curve. The value of rate constant was same with that of the previous experiment (3×10^{-3} M). Repeating the experiments with 6×10^{-2} M and 9×10^{-3} M of **3** gave separately the same fit curve and rate constant. In fact, the experimental data indicated 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 reaction order with respect to acetylenedicarboxylic acid **2**, a separate experiment was performed in the presence of excess of **1**.

$$\text{rate} = k'_{obs} [3]^\gamma [2]^\beta, \quad k'_{obs} = k_2 [1]^\alpha \quad (\text{II})$$

The original experimental absorbance versus time data is shown in Figure 9. These data provide a pseudo

first order fit curve at 378 nm. As a result, since $\gamma = 0$ (as determined in previous experiment), it is reasonable to accept that the reaction is first order with respect to compound **2** ($\beta = 1$). Because the overall order of reaction is two ($\alpha + \beta + \gamma = 2$) it is obvious that $\alpha = 1$ and the order of triphenylphosphine **1** must be equal to one. Based on the above results, a simplified plausible mechanism for the proposed reaction mechanism (Figure 10) is shown in Figure 11.

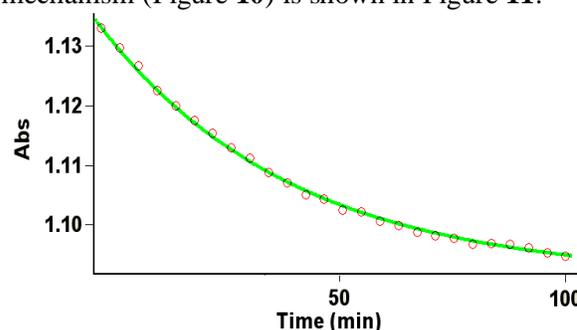


Figure 9: Pseudo first order fit curve (solid line) for the reaction in the presence of excess **1** (3×10^{-2} M) at 378 nm and 25 °C in CH_2Cl_2 .

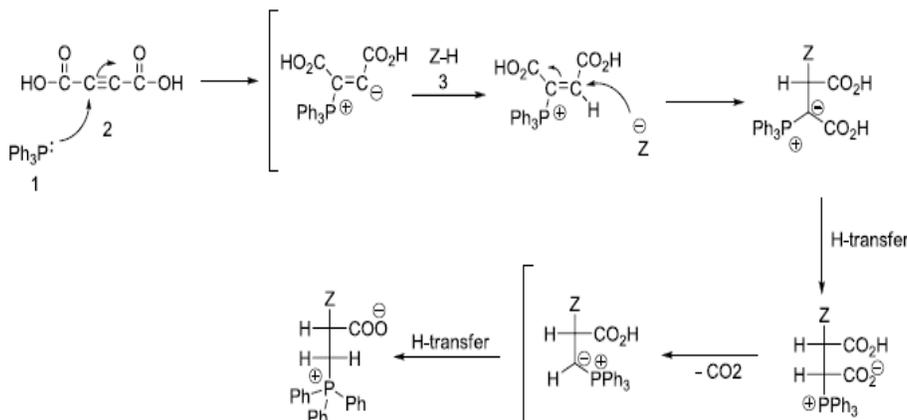


Figure 10: Proposed mechanism for the reaction between **1**, **2** and **3** for generation of stable 1,5-diionic organophosphorus compound

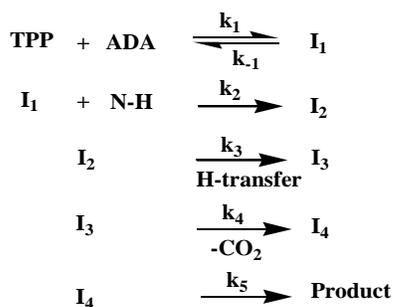


Figure 11: The simplified scheme for the plausible mechanism

At first, the rate law is written using final step for formation of the product.

$$\text{Rate} = k_5 [\text{I}_4] \quad (1)$$

We can apply the steady-state approximation to $[\text{I}_4]$, $[\text{I}_3]$, $[\text{I}_2]$ and $[\text{I}_1]$. To obtain a suitable expression for $[\text{I}_4]$, $[\text{I}_3]$, $[\text{I}_2]$ and $[\text{I}_1]$ we can assume that, after an initial brief period, the concentration of $[\text{I}_4]$, $[\text{I}_3]$, $[\text{I}_2]$ and $[\text{I}_1]$ achieve a steady state with their rates of formation and rates of disappearance becoming balanced.

Therefore $\frac{d[\text{I}_4]}{dt}$, $\frac{d[\text{I}_3]}{dt}$, $\frac{d[\text{I}_2]}{dt}$ and $\frac{d[\text{I}_1]}{dt}$ are zero and we can obtain expressions for intermediates as follows:

$$\frac{d[\text{I}_4]}{dt} = k_4 [\text{I}_3] - k_5 [\text{I}_4] = 0, \quad [\text{I}_4] = \frac{k_4 [\text{I}_3]}{k_5} \quad (2)$$

$$\begin{aligned} \frac{d[I_3]}{dt} &= k_3[I_2] - k_4[I_3] = 0, & [I_3] &= \frac{k_3[I_2]}{k_4} \\ (3) \quad \frac{d[I_2]}{dt} &= k_2[I_1][N-H] - k_3[I_2] = 0, & [I_2] &= \frac{k_2[I_1][N-H]}{k_3} \\ (4) \quad \frac{d[I_1]}{dt} &= k_1[TPP][ADA] - k_{-1}[I_1] - k_2[I_1][N-H] = 0 \\ [I_1] &= \frac{k_1[TPP][ADA]}{k_{-1} + k_2[N-H]} \end{aligned} \quad (5)$$

The value of (3) can be replaced in equation (2) to yield equation (6):

$$[I_4] = \frac{k_5[I_2]}{k_5} \quad (6)$$

And with the replacement of equation (4) in (6) the following equation is obtained:

$$[I_4] = \frac{k_2[I_1][N-H]}{k_5} \quad (7)$$

By substituting (5) in (7), equation (8) is yielded:

$$[I_4] = \frac{k_1 k_2 [TPP][ADA][N-H]}{k_5(k_{-1} + k_2[N-H])} \quad (8)$$

Now the value of (8) can be replaced in equation (1) to yield equation (9).

$$\text{Rate} = \frac{k_1 k_2 [TPP][ADA][N-H]}{(k_{-1} + k_2[N-H])} \quad (9)$$

Since experimental data were indicated that steps 3 (k_3), 4 (k_4) and 5 (k_5) are fast but step 1 (k_1) is slow, it is therefore reasonable to make the following assumption:

$$k_1 \ll k_2[N-H]$$

so the rate equation becomes:

$$\text{Rate} = k_1[TPP][ADA] \quad (10)$$

This equation which was obtained from a mechanistic scheme (shown in Figure 11) by applying the steady-state approximation is compatible with the results obtained by UV spectrophotometer. With respect to the equation (10) that is overall reaction rate (Figure 1), the activation parameters involving ΔG^\ddagger , ΔS^\ddagger and ΔH^\ddagger could be now calculated for the first step (rate-determining step), as an elementary reaction, on the basis of Eyring equation. The results are reported in Table 2.

Table 2: The activation parameters involving ΔG^\ddagger , ΔS^\ddagger and ΔH^\ddagger for the reaction between **1**, **2** and **3** at 25 °C, and 378 and 358 nm in C₂H₂Cl₂.

Reaction	λ (nm)	ΔG^\ddagger (kJ.mol ⁻¹)	ΔH^\ddagger (kJ.mol ⁻¹)	ΔS^\ddagger (kJ.mol ⁻¹ .K ⁻¹)
1, 2 and 3	378	58.46	20.32	-0.128
1, 2 and 3	358	58.48	22.72	-0.120

Conclusion

Kinetics investigation of the reaction between triphenylphosphine and acetylenedicarboxylic acid with carbazole was undertaken using the UV-vis spectrophotometry. The results can be summarized as follows:

1. The appropriate wavelengths and concentrations were determined in order to follow the reaction kinetics.

2. The overall reaction order followed second-order kinetics and the reaction orders with respect to triphenylphosphine, acetylenedicarboxylic acid and carbazole were one, one and zero respectively.

3. The value of the second-order rate constants for reaction was calculated automatically with respect to the standard equation using the software associated with the Cary-300 UV instrument.

4. The rate of reaction was accelerated 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.

5. 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.

Experimental

Triphenylphosphine, acetylenedicarboxylic acid and carbazole were purchased from Fluka, Merck and Acros companies and used without further purification. All extra pure solvents including the carbon tetrachloride, dichloromethane and ethylacetate also obtained from Merk (Darmstadt, Germany). The reaction is followed using the monitoring absorbance changes of products with time on a Varian (Model Cary Bio-300) UV-vis spectrophotometer with a 10 mm light-path cell. The temperature of reaction is maintained to within ± 0.1 °C at various temperatures by circulating water bath.

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