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Effect of Medium on the Kinetics of Stereoselective Synthesis of a Highly Functionalized Cyclopropanesame

F. Mahmoudi, M. Shahraki* and S.M. Habibi-Khorassani

Department of Chemistry, Faculty of Science, University of Sistan and Baluchestan, Zahedan, Iran, P. O. Box: 98135-674

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The effect of different media on the kinetics and mechanism of formation of diethyl (1S,2S)-3,3-dibenzoylcyclopropane-1,2-dicarboxylate was investigated. The reaction was accelerated with changing the medium from non-ionic to ionic. Among the selected ionic salts, NaCl was the best salt to increase the reaction rate of the titled synthesis about 2.5 fold (k_{obs} = 1.295 M^{-1} min^{-1} against k_{obs} = 3.105 M^{-1} min^{-1}). The incremental effect of ionic salts was found to be in this order: NaCl > NaBr > KBr > KCl. Isokinetic plots for the reaction in the presence of different salts were obtained and a linear relationship, which indicated an identical mechanism for all reactions, was found. Moreover, the effect of cationic, nonionic, and anionic surfactants on the reaction rate was evaluated. Substantial reduction on the reaction rate and change in the mechanism was observed with the addition of an anionic surfactant such as sodium dodecyl sulfate. The values of activation parameters were also estimated ($\Delta H^{\ddagger}$ = 80.1 ± 0.6 kJ mol^{-1}, $\Delta S^{\ddagger}$ = 23.9 ± 2.0 J mol^{-1} K^{-1}, and $\Delta G^{\ddagger}$ = 72.9 ± 1.1 kJ mol^{-1}); the positive value of $\Delta H^{\ddagger}$ confirmed the endothermic process, and the entropy value referred to an associative mechanism.

Keywords: Kinetics, Mechanism, Cyclopropanes, Ionic strength, Surfactant

INTRODUCTION

Cyclopropane derivatives are used in a variety of pharmaceutical and biological compounds [1,2]. From the past, methods for the preparation of these compounds have been developed due to their unique properties and effects of different substituents were examined [3-5]. Several achievements of stereoselective synthesis have been reported for various catalytic and reaction conditions [6,7]. Maghsoodlou and coworkers have reported a highly stereoselective synthesis of trans-cyclopropanes through the reaction between acetylenic esters and C-H acids in the presence of catalyst [8]. We have previously investigated the kinetics and mechanism of the reaction between alkyl acetylenedicarboxylates and C-H with N-H acids in the presence of triphenylarsine (TPA) and triphenylphosphine (TPP) by UV-Vis spectrophotometry and stopped-flow technique [9-12]. There, the effect of various factors such as temperature, structure, and solvent on the kinetics and mechanism was studied. It was found that the change of the structure from triphenylarsine to triphenylphosphine not only produces different products but also leads to different kinetics and mechanisms. The rate law was found to be dependent on the concentration of alkyl acetylenedicarboxylates and TPP and independent of the concentration of the C-H acids, while TPA played a catalytic role and the rate law depended on the concentrations of both alkyl acetylenedicarboxylates and C-H acids. The zwitterionic intermediate generated in the first step of the mechanism was more stable due to the polar interactions in solvents with larger dielectric constant; the speed of the first step is faster than the second step. On the other hand, the transfer rate of the proton from N-H or C-H acids to the zwitterionic intermediate is accelerated in the presence of a solvent such as methanol with less steric effect leading to an increase in the reaction rate. The third step of the reaction involved two ionic components and

*Corresponding author. E-mail: mehdishahraki@chem.usb.ac.ir

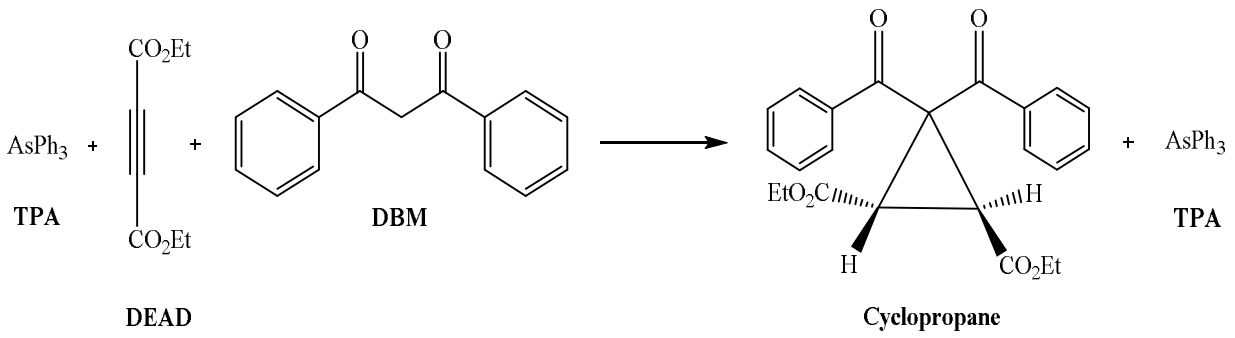


Fig. 1. The reaction between diethyl acetylendicarboxylate and dibenzoylmethane in the presence of triphenylarsine for the generation of diethyl (1S,2S)-3,3-dibenzoylcyclopropane-1,2-dicarboxylate.

showed a change in rate in polar liquid solvents. Due to the nature of the intermediates and more comprehensive information on the reaction mechanism, the effect of media was more closely examined to facile the method of synthesis of the relevant products. For this purpose, the effects of salts and micelles on the reaction between diethyl acetylendicarboxylate (DEAD) and dibenzoylmethane (DBM) in the presence of triphenylarsine (TPA) were studied and kinetic changes and mechanism were analyzed (Fig. 1).

EXPERIMENTAL

Materials

The reagents dimethyl acetylendicarboxylate (98%), diethyl acetylendicarboxylate (99%), dibenzoylmethane (98%), and triphenylarsine (97%) were obtained from Sigma-Aldrich, and methanol (99.5%) and ethanol (99.5%) the solvents were obtained from Merck (Darmstadt, Germany) and used without further purification. The salts NaCl (99.5%), NaBr (99%), KBr (99%), and KCl (99%) were purchased from Sigma-Aldrich, and the surfactants sodium dodecyl sulfate (99%), N-dodecyl pyridinium chloride (98%), and Triton X-100 (98%) used were purchased from Fluka (Buchs, Switzerland). The rate of reaction was followed by monitoring absorbance changes with time on a Varian (Model Cary Bio-300) UV-Vis spectrophotometer with a 10 mm light path cell. The temperature of the reaction is maintained to within ±0.1 °C circulating water bath.

Experimental Procedure

The reactions in different media were started with 1.00×10^{-2} M of DEAD and 1.00×10^{-2} M of DBM in the presence of 5.00×10^{-2} M of TPA at various temperatures in methanol as solvent. The absorbance of the product was obtained as a function of wavelength at 460 nm against time. Since the reactants and intermediates had no significant absorbance at 460 nm, this wavelength provided an opportunity to investigate the kinetics of the reaction [13]. The experimental curve was fitted by the fitting curve and the desired rate constants using the standard equations in the program were automatically computed [14]. Details of the kinetic calculations and mechanism, along with the diagrams and relevant data without applying salts and surfactants effects, are provided in the Supplementary Materials File.

RESULTS AND DISCUSSION

Effect of Ionic Strength

Several factors increase the reaction rate such as raising the temperature or changing the solvent but all of these cannot always be accomplished. Salt added to the solution changes the ionic strength of the medium which depending on the reaction mechanism increase or decrease the reaction rate. When ionic species react in solution, their charges result in electrostatic forces that affect the kinetics of the reactions. The effect of ionic strength on the reaction rate is referred to as the kinetic salt effect, which is the effect of primary and secondary salt, and can be interpreted by

Debye-Huckel equation [15]. When primary and secondary salt effects are operative in the same direction, either significant acceleration or significant inhibition takes place. In the reaction stated, ionic intermediates were proposed in the reaction path, hence, addition of salt to the reaction mixture can create more uniform and stabile solution. To this end, the inorganic salts such as NaCl, NaBr, KBr and KCl were selected. To determine the optimum concentration of the salts, values of rate constant (k_{obs}) at 300.15 K were measured at several concentrations and 1.00×10^{-2} M is selected to perform the experiments.

The linear relation between the activation enthalpies ($\Delta H^{\ddagger}$) and activation entropies ($\Delta S^{\ddagger}$) in a series of reactions, which are sufficiently similar in R-squared value, it may be expected that same mechanism operates along the series and this is called the isokinetic relationship. The following equation demonstrates this relationship:

$$\Delta H^{\neq} = \beta \Delta S^{\neq} + \Delta H^{\circ} \quad (1)$$

The slope β has the temperature dimension and is known as the isokinetic temperature or as the compensation temperature, and represents a temperature at which all reactions of the series should proceed at the same rate. This temperature is a characteristic of the process. At this temperature, $\Delta G^{\ddagger}$ is identical and equal to $\Delta H^{\ddagger}$. In addition, at isokinetic temperature, the enthalpy and entropy variations fully compensate one another. Equation (3) can be derived from Eqs. (1) and (2):

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \quad (2)$$

$$\Delta G^{\neq} = (\beta - T)\Delta S^{\neq} + \Delta H^{\circ} \quad (3)$$

The values of activation parameters for all the reactions are computed and presented in Table 2. On the basis of data in Table 2, Fig. 2 indicates that the same mechanism exists for all reactions in the presence of different salts, so that it can be defined as a general mechanism for these reactions. At temperature T = β, $\Delta G^{\ddagger}$ is equal to $\Delta H^{\ddagger}$, hence, from the interaction point of each plot, Fig. 2, the ΔH° value was calculated at 65.0 kJ mol^{-1}, the details + are available in supplementary materials file).

The careful examination of the mechanism shows that the interaction of intermediates with ions and solvents in all steps is worth paying close attention (Supplementary Materials File). The stabilizing or destabilizing effect of I_3 in the reaction path can affect the rate of reaction. According to the results, k_{obs} is directly related to k_1, k_2 and k_4 ($k_{obs} = k_1k_2k_4[TPA]/k_{-1}k_{-3}$). As shown in the mechanism, the product in the first equilibrium step is charged and salt effect can stabilize the product more than the reactants; according to the Le Chatlier's principle, the amount of I_1 increases in the medium and consequently k_1 enhances [19,20]. In $step_2$ like $step_1$, the products are more polar (charged) than reactants. The ionic medium is also more favorable for stabilizing the products than the reactants in this step, so increasing of the value of k_2 is more acceptable. With the look at the contribution of various rate constants (k_1, k_2 and k_4) in k_{obs}, k_4, surely will be affected by ions, because of its important role in the RDS. In $step_4$ (rate constant k_4), I_3 is directly converted to the product through the concerted reaction. In fact, I_4 is not formed in the reaction media. Therefore, cyclopropane and TPA as the final products of $step_4$ have no charges in the reaction media. Hence, the ionic strength of added salt is more consistent with the fully charged reactant (I_3). So, k_4 may decrease. Since k_{obs} is directly related to k_1, k_2 and k_4, the reaction rate can increase due to k_1 and k_2 and also subsequently by k_4. There seems to be a counterbalance between physical ionic strength and chemical salts causing an increase in the reaction rate, because different salts with same or nearly same ionic strength have different effects on the reaction rate.

Effect of Surfactants

Effects of micelles on the reaction can be attributed to their hydrophobic and electrostatic interactions with reactants [21]. In this study, the effect of surfactant on the reaction rate is evaluated using anionic (sodium dodecyl sulfate, SDS), cationic (N-dodecyl pyridinium chloride), and nonionic (Triton X-100) surfactants. Addition of N-dodecyl pyridinium chloride and Triton X-100 did not exhibit any significant change in the rate constant. When SDS was added to the reaction mixture (TPA, DEAD and DBM) near to its critical micelle concentration (CMC = 0.0081) [22] at 300.15 K in methanol, the reaction rate decreased. Figure 3 shows that the UV-Vis spectrum of

Table 1. Values of k_{obs} (M^{-1} min^{-1}) for the Reaction between DEAD, and DBM with TPA in the Presence of Different Salts (1.00×10^{-2} M) at Diverse Temperatures in Methanol

Salt	290.15 K	295.15 K	300.15 K	305.15 K
NaCl	1.011 (0.026)[a]	1.820 (0.033)	3.105 (0.053)	5.032 (0.052)
NaBr	1.000 (0.021)	1.693 (0.031)	2.607 (0.058)	5.188 (0.052)
KBr	0.880 (0.022)	1.485 (0.029)	2.807 (0.038)	4.305 (0.039)
KCl	0.610 (0.020)	1.059 (0.025)	1.724 (0.037)	3.271 (0.040)
Without salt[b]	0.401 (0.019)	0.706 (0.024)	1.295 (0.027)	2.127 (0.041)

[a]Standard deviation (SD). [b]See supplementary materials file for more information.

Table 2. Values of Activation Parameters for the Reaction between DEAD, and DBM with TPA in the Presence of Different Salts (1.00×10^{-2} M) at 300.15 K and in Methanol

Salt	$\Delta G^{\ddagger}$ (kJ mol^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})	E_a (kJ mol^{-1})
Without salt[a]	72.9 ± 1.1	80.1 ± 0.6	23.9 ± 2.0	82.6
KCl	72.0 ± 2.4	78.8 ± 1.2	22.6 ± 4.2	81.2
KBr	71.0 ± 2.4	77.0 ± 1.2	19.8 ± 4.1	79.5
NaBr	70.8 ± 3.9	76.5 ± 1.9	18.7 ± 6.6	78.9
NaCl	70.7 ± 1.0	76.3 ± 0.5	18.5 ± 1.8	78.7

[a]See supplementary materials file for more information.

the reaction has three parts, part A: ascending, part B: descending, and part C: smooth ascending. It is presumed that part A is related to the reaction between TPA and DEAD for the formation of an intermediate I_1 and subsequently protonation process of I_1 for the generation of I_2 ($step_1$ and $step_2$ of the proposed mechanism), part B belongs to the reaction between I_2 and SDS ($step_3$), and finally part C can be attributed to formation of products (remaining steps). Rate constants for all experiments (cases 1, 2, 3 and 4) are calculated and presented in Table 3. Comparison of the reaction spectra between three components (TPA + DEAD + DBM) in the presence and absence of SDS (Fig. 4A, reactions 2 and 1, respectively) reveal that by increasing concentration of SDS, the reaction rate is marginally diminished. So that $step_1$ and $step_2$ (fast steps, parts A and B) become visible in the UV-Vis spectrum over this time scale. Also, the spectra of the two-component reaction between TPA and DEAD in the presence and absence of SDS (Fig. 4B, reactions 4 and 3, respectively) indicate that SDS reacts with the intermediate I_1. The intermediate I_2 generated in part B and part (C) is flat, since there no other compounds in the reaction environment to insert an additional step to it. However, in Fig. 4A, part (C) is not flat due to the presence of the third

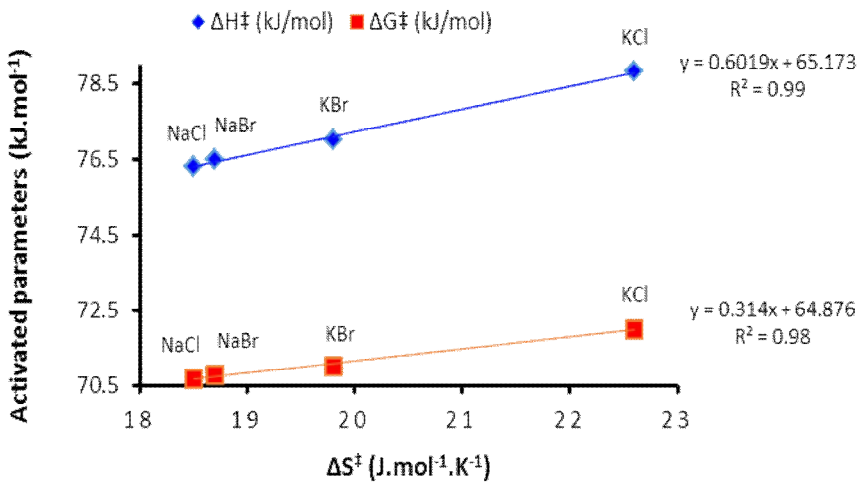


Fig. 2. The plots of $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ *versus* $\Delta S^{\ddagger}$ to demonstrate the reaction mechanism in the presence of different salts (1.00×10^{-2} M) at 300.15 K in methanol.

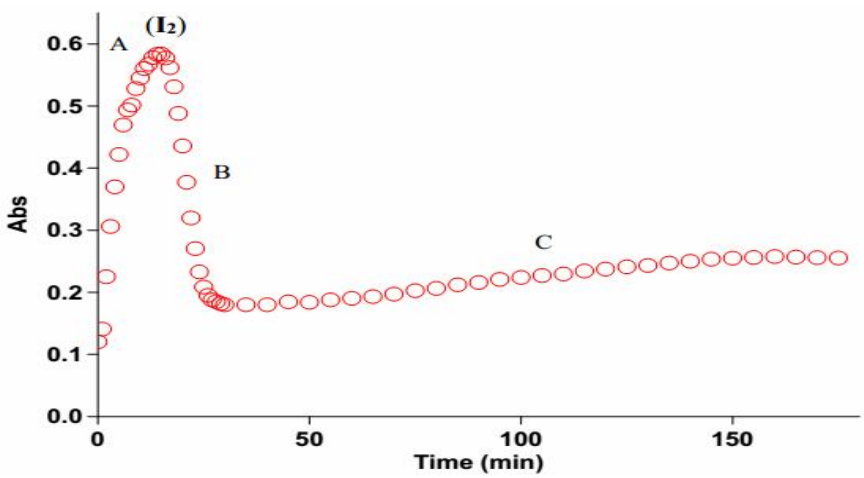


Fig. 3. The reaction between TPA (5.00×10^{-2} M), DEAD (5.00×10^{-2} M) and DBM (1.00×10^{-2} M) in the presence of SDS (7.00×10^{-3} M) at 300.15 K in methanol recorded at 460 nm.

reactant (DBM) which has created the additional steps. In Figs. 4A and B, some points are recognizable. First, in the absence of C-H acid (DBM), SDS reacts with I_1, and in the presence of C-H acid, SDS reacts with I_2. Secondly, the spectra (2) and (4) have the ascending and descending parts appearing in first 30 min. Ascending parts in two spectra are different due to formation of various intermediates (I_1 and I_2). The descending parts relatively overlap with each other indicating similar reactions of I_1 and I_2 with SDS. Finally, spectrum (2) (Fig. 4A) indicates that SDS decreases the reaction rates of $step_1$ and $step_2$ (parts A and B), which could not be determined in spectrum (1) *via* UV-Vis spectrophotometer.

In order to investigate the retarding effect of SDS on the reaction rate, a similar experiment was carried out in the presence of DMAD, under the conditions identical with those in the previous experiments. Figure 5 shows that changing the alkyl group does not change the retarding

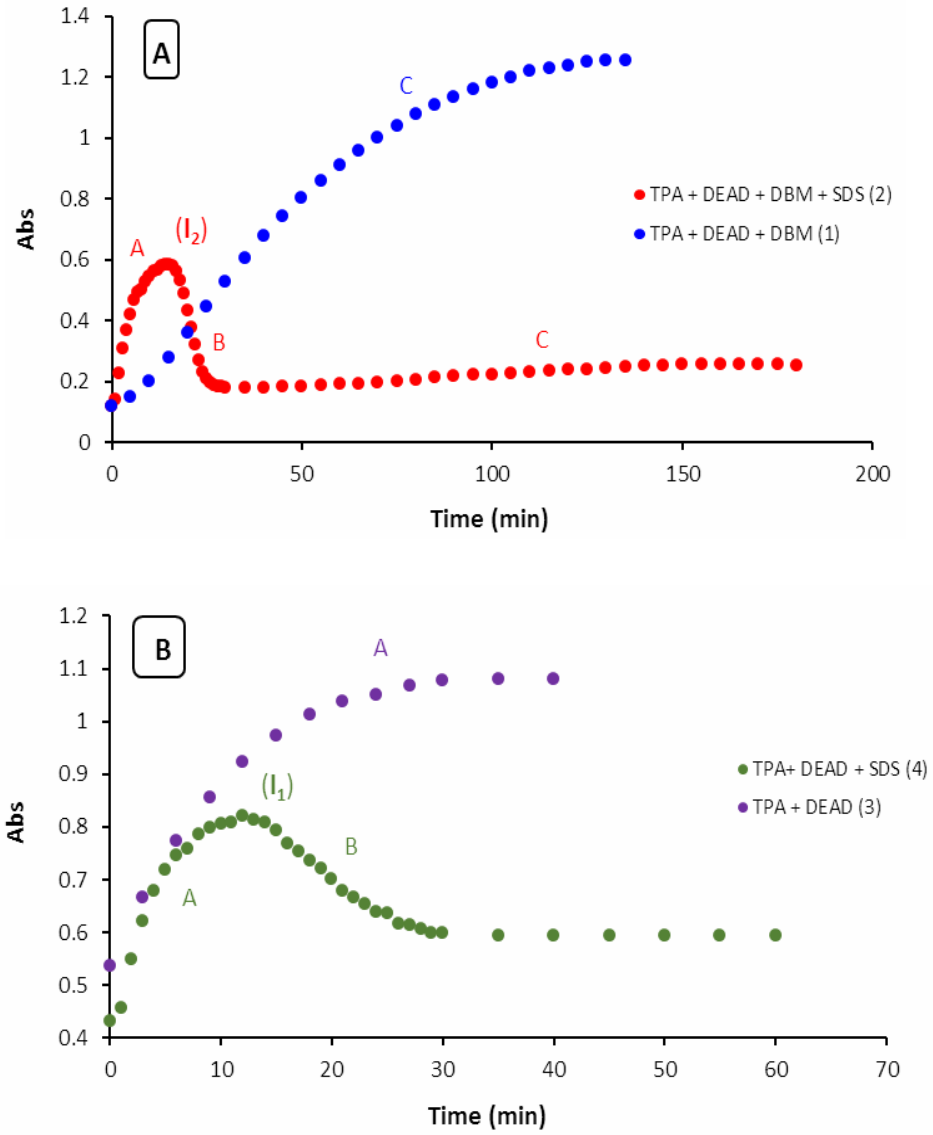


Fig. 4. A: Spectrum of the three-component reaction (TPA, DEAD and DBM) in the presence and absence of SDS taken at 460 nm and 300.15 K. B: Spectrum of the two-component reaction (TPA and DEAD) in the presence and absence of SDS taken at 330 nm and 300.15 K.

effect of SDS.

Effect of Temperature

With an increase in temperature, the rate constant (k_{obs}) increases linearly (Table 4). Using the Arrhenius model (Eq. (5) and Fig. 6) and the Eyring model (Eq. (6) and Fig. 7), activation parameters such as activation energy (E_a), activation enthalpy ($\Delta H^{\ddagger}$), and activation entropy ($\Delta S^{\ddagger}$) were computed and found to be 82.6 kJ mol^{-1}, 80.1 ± 0.6 kJ mol^{-1} and 23.9 ± 2.0 J mol^{-1} K^{-1}, respectively. Also, by utilization the Gibbs-Helmholtz equation (Eq. (7)), the activation Gibbs free energy ($\Delta G^{\ddagger}$) was calculated to be 72.9 ± 1.1 kJ mol^{-1} at 300.15 K. The value of $\Delta S^{\ddagger}$ indicated whether a reaction is associative or dissociative. Entropy values >-10 J mol^{-1} K^{-1} generally refer to associative mechanism [9,12]. Hence, the present reaction has an

Table 3. Values of k_{obs} (M^{-1} min^{-1}) for the Reaction between TPA, DEAD and DBM in the Presence of SDS (7.00×10^{-2} M) in Methanol at 300.15 K

	Reaction	Part A (ascending)	Part B (descending)	Part C (smooth ascending)
1	TPA + DEAD + DBM	-	-	1.295 (0.027)[a]
2	TPA + DEAD + DBM + SDS	28.388 (0.022) (TPA + DEAD → I_1 + DBM → I_2)	26.953 (0.036) (I_2 + SDS → I_3)	0.330 (0.003)
3	TPA + DEAD	17.701 (0.016)	-	-
4	TPA + DEAD + SDS	32.342 (0.019) (TPA + DEAD → I_1)	11.341 (0.005) (I_1 + SDS → I_2)	-

[a]Standard deviation (SD).

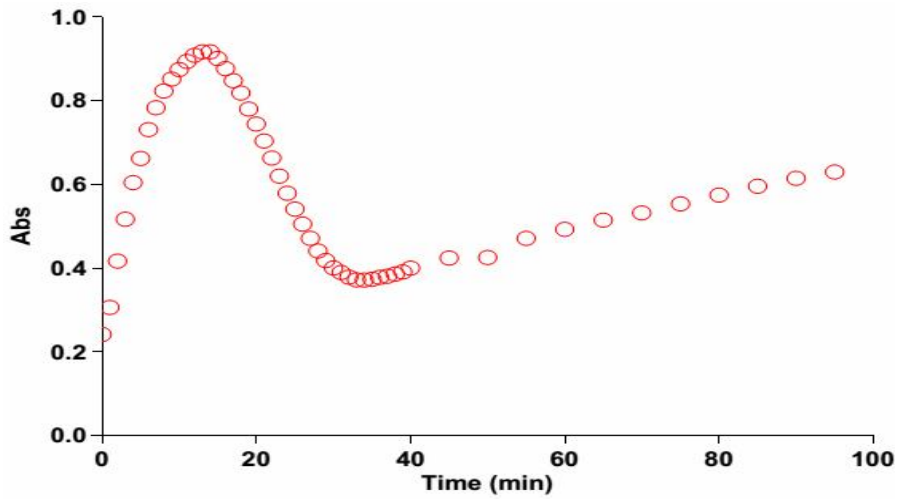


Fig. 5. The reaction between TPA (5.00×10^{-2} M) and DMAD (1.00×10^{-2} M) with DBM (1.00×10^{-2} M) in the presence of SDS (7.00×10^{-3} M) in methanol at 300.15 K taken at 460 nm.

associative mechanism. In addition, the large and positive $\Delta G^{\ddagger}$ value suggests that the reaction requires energy to convert reactants into products, meaning the reaction is endothermic.

$$\ln k = \ln A - \frac{E_a}{RT} \quad (4)$$

$$\ln \frac{k}{T} = -\frac{\Delta H^{\neq}}{RT} + \frac{\Delta S^{\neq}}{R} + \ln \frac{k_B}{h} \quad (5)$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \quad (6)$$

Effect of Solvent Polarity

The effect of polarity of solvent on the reaction rate

Table 4. Values of Observable Rate Constants (k_{obs} M^{-1} min^{-1}) at Different Temperatures and Solvents at 460 nm

Solvent	ε (D)	290.15 K	295.15 K	300.15 K	305.15 K
Methanol	32.7	0.401	0.706	1.295	2.127
		(0.019)[a]	(0.024)	(0.027)	(0.041)
Ethanol	24.5	0.020	0.048	0.116	0.208
		(0.009)	(0.006)	(0.010)	(0.013)

[a]Standard deviation (SD).

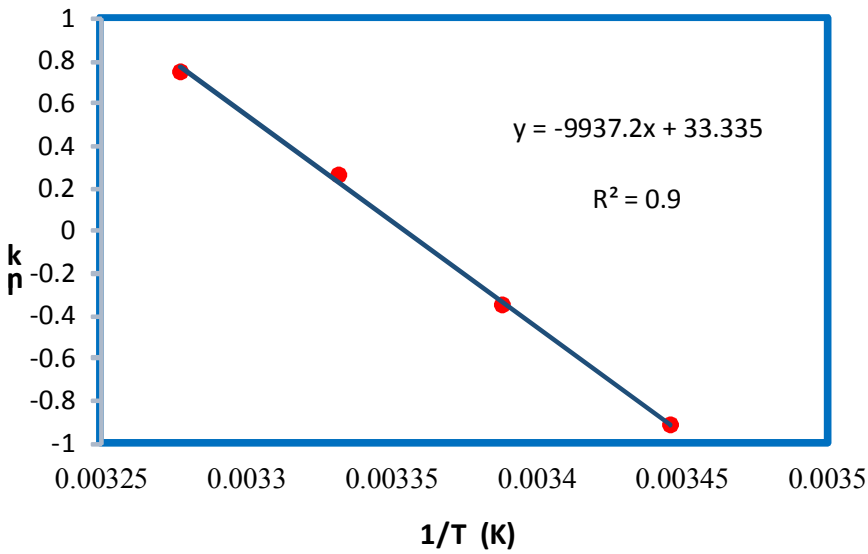


Fig. 6. Arrhenius plot for the reaction between TPA (5.00×10^{-3} M) and DEAD (10^{-2} M) with DBM (1.00×10^{-2} M) in methanol.

gives invaluable information regarding the reaction mechanism, intermediates and the nature of intermediates. The polarity of the medium was changed by the addition of ethanol, keeping other experimental conditions constant. The rate of the reaction was found to be reduced by the addition of ethanol. Thus, a decrease in the dielectric constant of the solvent was found to diminish the reaction rate too. When ionic species are produced as intermediates, the reaction will usually be accelerated in the solvent with higher dielectric constant. The results of this section are presented in Table 4. As can be seen, the reaction rate increased about 10-20 fold when the polarity of the solvent was increased by changing the solvent from ethanol (ε = 24.5) to methanol (ε = 32.7).

Structural Effects

To demonstrate the importance of dialkyl acetylenedicarboxylate structure on the reaction rate, experiments were performed in the presence of DMAD under the same condition for the previous experiments. The reaction rate in DMAD is faster than that in DEAD (Table 5). It seems that both the inductive and the steric factors

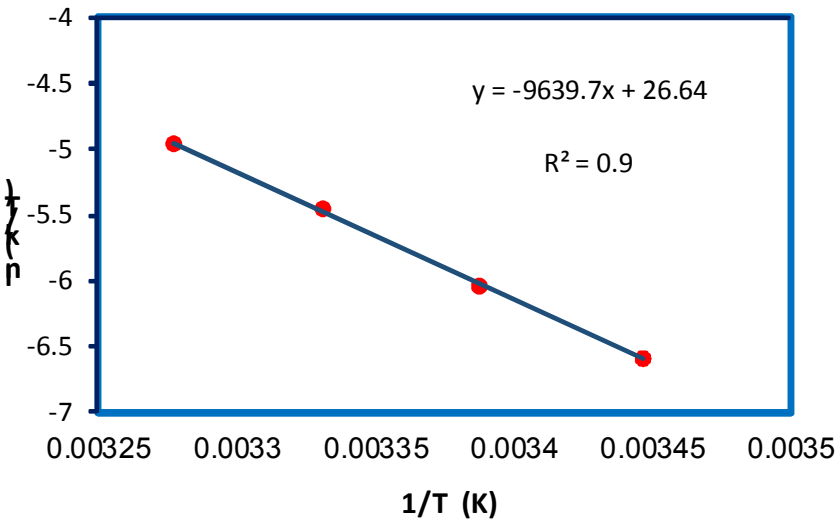
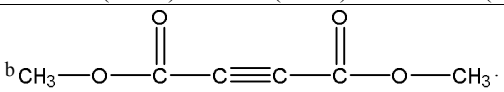
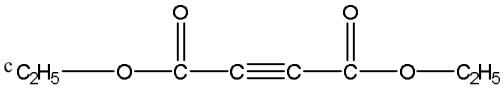


Fig. 7. Eyring plot for the reaction between TPA (5.00×10^{-3} M) and DEAD (1.00×10^{-2} M) with DBM (1.00×10^{-2} M) in methanol for determination of activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$).

Table 5. Values of k_{obs} (M^{-1} min^{-1}) for the Reactions between (TPA and DMAD with DBM) and (TPA and DEAD with DBM) in Methanol at Different Temperatures as Recorded at 460 nm

Reaction	290.15 K	295.15 K	300.15 K	305.15 K
TPA + DMAD[b] + DBM	0.626[a]	1.160	1.952	4.234
	(0.023)	(0.024)	(0.020)	(0.023)
TPA + DEAD[c] + DBM	0.401	0.706	1.295	2.127
	(0.019)	(0.024)	(0.027)	(0.041)

[a]Standard deviation (SD). [b] 

[c] 

tend to reduce the reaction rate.

The Mechanism of the Reaction between TPA and DMAD with DBM in the Presence of SDS

In order to determine the values of k_{obs} for the $step_1$, $step_2$ and slow step, the possible reaction mechanism is given in Fig. 8.

$Step_1$, $step_2$, and $step_3$ were determined as fast steps on the basis of SDS studies (Table 3). $Step_4$ is inherently rapid due to the reaction between the two ionic species. If $step_5$ is the RDS, $step_4$ can be determined as a reversible process, the rate law under this circumstance can be written as:

$$Rate = k_5[I_4] \tag{7}$$

By applying the steady-state approximation, $(Rate)_{mech}$ is determined to be as follows:

$$(Rate)_{mech} = \frac{k_1 k_2 k_5 [TPA][DEAD][DBM]}{(k_{-1} + k_2\,[DBM])\,(k_{-4}\,[SDS] + k_5)} \tag{8}$$

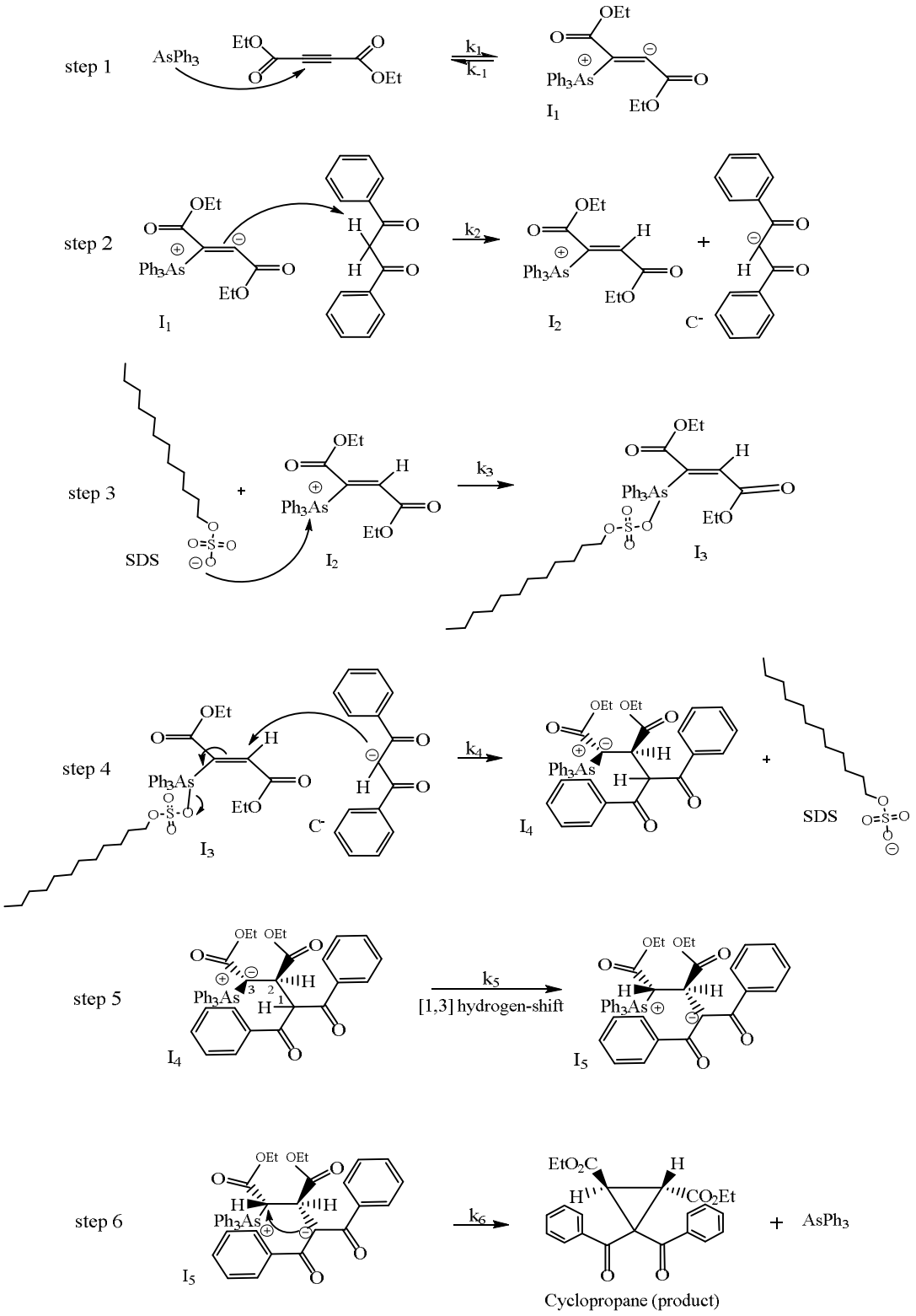


Fig. 8. The possible mechanism for the reaction between TPA and DEAD with DBM in the presence of SDS for the formation of diethyl (1S,2S)-3,3-dibenzoylcyclopropane-1,2-dicarboxylate.

The procedure for obtaining Eq. (8) is presented in Supplementary Materials File.

$Step_1$ is fast ($k_{-1} >> k_2[DBM]$) and with respect to $step_5$ ($k_{-4}[SDS] >> k_5$) is rate determining step, so:

$$(Rate)_{mech} = \frac{k_1 k_2 k_5 [TPA][DEAD][DBM]}{k_{-1} k_{-4} [SDS]} \quad (9)$$

Since the TPA is a catalyst, its concentration is constant and SDS concentration is constant too, thus:

$$(Rate)_{mech} = k_{obs}[DEAD][DBM] \quad (10)$$

$$k_{obs} = \frac{k_1 k_2 k_5 [TPA]}{k_{-1} k_{-4} [SDS]} \quad (11)$$

From the $(Rate)_{mech}$ value in the presence of SDS, it can be understood that SDS reacts with I_2 and no with any other reactant. Also, Eq. (11) shows that k_{obs} is inversely related to SDS concentration and as the experimental results confirmed the retarder effect of SDS in the reaction environment.

CONCLUSIONS

The kinetics and mechanism of formation of diethyl (1S,2S)-3,3-dibenzoylcyclopropane-1,2-dicarboxylate were investigated in the presence of different salts. The reaction was accelerated with changing the medium from non-ionic to ionic. The incremental effect of ionic salts was found to be in this order: NaCl > NaBr > KBr > KCl. Although all four salts have the same ionic strength, the type of ions of each structure is different from one another. Thus, the type of salt affects the reaction rate, which may be due to mobility of ions in the solution and lattice energy or relevant to atomic radius. Isokinetic plots for the reaction in the presence of different ionic salts were obtained and a linear relationship was found which indicated an identical mechanism for all reactions. SDS effect was studied as the effect of ionic surfactant and the reaction rate decreased. With respect to the results obtained in the study regarding the effect of solvent, salt, and SDS, step4 (step 5 in the presence of SDS) of the possible mechanism was recognized as an RDS with higher probability. Under identical experimental conditions, the reaction is about 12-fold faster in methanol than in ethanol. The values of activation parameters were also estimated; the positive value of $\Delta H^{\ddagger}$ confirmed the endothermic process, and the entropy value referred to an associative mechanism.

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