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Effect of solvents on activation parameters for the kinetics of reaction between *p*-Toluene sulfonyl Chloride with α -hydroxy acids in the presence of pyridine

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Abstract

The kinetics of the reaction between *p*-Toluene sulfonyl Chloride (Tosyl chloride – TsCl) with α -Hydroxy acids in the presence of Pyridine has been studied at 293, 303 and 313 K in protic and aprotic solvents. Variations in reaction rate as well as activation parameters have been interpreted on the basis of solvation and dielectric properties of the solvents. Thermodynamic parameters such as activation energy (E_a), enthalpy of activation (ΔH^\ddagger), free energy of activation (ΔG^\ddagger) and entropy of activation (ΔS^\ddagger) have been evaluated from the rate data. The isokinetic relationship has been verified. Analysis of activation energy, enthalpy, entropy and free energy reveals that solvation of transition state is larger in polar solvents which restrict the bond formation process. All reactions have appreciable negative entropy of activation which strongly supports the bimolecular nucleophilic displacement mechanism of these reactions.

Keywords: Substitution kinetics, Isokinetic temperature, dielectric constant, activation parameters

1. Introduction

The nucleophilic substitution at a sulfur atom has been a subject of long standing interest of organic chemists. Arylsulfonyl halides are convenient model compounds for experimental investigations of different nucleophilic processes at sulfonyl sulfur centre [1-8]. The effect of solvents plays an important role in substitution kinetics. The effect of pure solvents and mixture of solvents in various compositions on nucleophilic substitution reactions were reported in the literature [9, 10]. In kinetic studies the dependence of rate constants on structure of the reacting molecule or the solvent effects are expressed in terms of activation parameters. The parameters used are activation energy (E_a), enthalpy of activation (ΔH^\ddagger), free energy of activation (ΔG^\ddagger) and entropy of activation (ΔS^\ddagger). These values are used as convenient tools for mechanistic evaluation of these reactions [11].

Extensive investigations on rate of reactions of *p*-Toluenesulfonyl Chloride with Benzoic acid(s) [12], Phenol(s) [13] and α -Hydroxy acids [14] have been reported earlier. However, there is relatively little discussion and limited data on activation parameters of these reactions. Therefore, it was decided to determine the temperature dependence of the rates and activation parameters on the reaction of *p*-Toluene sulfonyl Chloride (TsCl) with α -Hydroxy acids in the presence of Pyridine in various solvents. This paper reports and discusses the activation parameters estimated from kinetic data.

2. Materials and methods

2.1 Materials

p-Toluenesulfonyl chloride (TsCl), Glycolic acid, Lactic acid, Mandelic acid, Pyridine and solvents used (Acetonitrile, Acetone, Dimethylformamide, Benzyl alcohol, propanol and Butanol) (Analytical grade) were purified before use by recrystallization or distillation until their physical constants (melting point/boiling point) agreed with the literature values [15,16].

2.2 Kinetic measurements

The thermostated solutions (± 0.1 °C) of *p*-Toluenesulfonyl chloride (10 ml, 0.05 mol dm⁻³) and the mixture of Glycolic acid - Pyridine (10ml, 0.05 mol dm⁻³) in acetonitrile were mixed. The progress of the reaction was followed by measuring the conductance of the reaction

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mixture at different time intervals. The conductivity is due to pyridinium cation formed by the interaction between glycolic acid and pyridine and chloride anion liberated from TsCl by the attack of pyridinium glycolate. The conductance was measured at convenient time intervals (minutes) till the reaction has completed. Same experimental procedure was adopted for all other α -Hydroxy acids studied. Rate constants were calculated using the following special integrated equation derived from Guggenheim's method [17].

$$x_2 - x_1 = k_2 C_0 [t_1 x_1 - t_2 x_2] - k_2 C_{\infty} x_{\infty} [t_1 - t_2] \text{ ----- (1)}$$

x_1 = Conductance at time t_1
 x_2 = Conductance at time t_2
 x_{∞} = Conductance at time t_{∞}

k_2 = Second order rate constant

C_0 = Initial concentration of the reactant

Plot of $(x_2 - x_1)$ against $-(t_1 x_1 - t_2 x_2)$ should be a straight line. From the slope, the second order rate constant k_2 was calculated by the method of least-Square analysis [18, 25].

3. Results and discussion

The kinetics of the reaction between Tosyl chloride with α -Hydroxy acids in the presence of Pyridine has been studied conductometrically in protic and aprotic solvents. Equimolar concentrations were preferred to determine rate constant (k_2). In our previous investigations we report that the reaction follows second order kinetics [14]. The second order rate constants k_2 at 3 different temperatures are determined in solvents used are presented in Table 1.

Table 1: Second order rate constants (k_2) for the reaction of TsCl with equimolar mixture of X-CHOHCOOH-Pyridine in various solvents at 303 K

Temperature K	Solvents	Rate constant (k_2) $\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$		
		Glycolic acid (X = H)	Lactic acid (X = CH ₃)	Mandelic acid (X = C ₆ H ₅)
293	Acetonitrile	2.346	1.318	3.255
	Acetone	0.494	0.316	0.801
	Dimethylformamide (DMF)	2.017	1.391	3.643
	Benzyl alcohol	0.033	0.024	0.063
	Propanol	0.035	0.025	0.071
	Butanol	0.040	0.023	0.061
303	Acetonitrile	4.791	2.797	7.735
	Acetone	1.130	0.676	1.875
	Dimethylformamide (DMF)	4.204	2.578	7.291
	Benzyl alcohol	0.091	0.055	0.157
	Propanol	0.092	0.054	0.168
	Butanol	0.096	0.057	0.167
313	Acetonitrile	9.813	6.752	15.571
	Acetone	2.443	1.655	3.747
	Dimethylformamide (DMF)	9.709	6.553	15.486
	Benzyl alcohol	0.201	0.133	0.317
	Propanol	0.194	0.119	0.306
	Butanol	0.193	0.125	0.305

[TsCl] = [X-CHOHCOOH + Pyridine] = 0.05 mol dm^{-3}

A temperature range of 293, 303 and 313 K at 10 K intervals was chosen to find out thermodynamic parameters such as activation energy (E_a), enthalpy of activation (ΔH^\ddagger), free energy of activation (ΔG^\ddagger) and entropy of activation (ΔS^\ddagger). The effect of temperature on reaction rate was studied and results show that the values of rate constants were found to be increases with increase in temperature. Increasing the temperature increases the average kinetic energy of molecules and ions, causing them to collide more frequently and with greater energy, which increases the reaction rate. Rate data were used to calculate activation parameters [18-27].

The equations (2) to (5) were used to calculate the activation E_a , ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger .

$$\text{Energy of activation } (E_a) = [T_1 T_2 / (T_2 - T_1)] * R * \ln [k_2 / k_1] \text{ --- (2)}$$

$$\text{Enthalpy of activation } (\Delta H^\ddagger) = E_a - RT \text{ ----- (3)}$$

$$\text{Entropy of activation } (\Delta S^\ddagger) = R \ln (k/T) - R \ln (k_B/h) + [(\Delta H^\ddagger) / T] \text{ ----- (4)}$$

$$\text{Free energy of activation } (\Delta G^\ddagger) = (\Delta H^\ddagger) - T(\Delta S^\ddagger) \text{ ----- (5)}$$

Where h is Planck's constant and k_B is Boltzmann's constant. The values of activation parameters are given in Table 2.

Table 2: Activation parameter for the reaction of TsCl with mixture of α -Hydroxy acid - Pyridine in different solvents

α -Hydroxy acid	Solvents	E_a kJ mol^{-1}	ΔH^\ddagger kJ mol^{-1}	$-\Delta S^\ddagger$ $\text{J K}^{-1} \text{mol}^{-1}$	ΔG^\ddagger kJ mol^{-1}
Glycolic acid (X = H)	Acetonitrile	52.703	50.184	66.392	70.300
	Acetone	61.134	58.615	50.577	73.939
	Dimethylformamide (DMF)	54.208	51.689	62.509	70.629
	Benzyl alcohol	74.023	71.504	29.028	80.299
	Propanol	71.823	69.304	36.189	80.269
	Butanol	64.039	61.519	61.460	80.142
Lactic acid (X = CH ₃)	Acetonitrile	55.538	53.019	61.511	71.656
	Acetone	56.049	53.294	71.633	75.234
	Dimethylformamide (DMF)	45.541	43.022	95.182	71.861

	Benzyl alcohol	62.053	59.534	72.614	81.535
	Propanol	58.818	56.299	83.377	81.563
	Butanol	69.638	67.119	47.226	81.429
Mandelic acid (X = C ₆ H ₅)	Acetonitrile	63.888	61.369	25.495	69.094
	Acetone	62.822	60.303	40.794	72.663
	Dimethylformamide (DMF)	51.212	48.693	67.819	69.242
	Benzyl alcohol	67.024	64.505	47.535	78.908
	Propanol	63.242	60.723	59.420	78.727
	Butanol	74.733	72.214	21.546	78.742

$$[\text{TsCl}] = [\text{X-CHOHCOOH} - \text{Pyridine}] = 0.05 \text{ mol dm}^{-3}$$

The activation energy was found to be higher in polar protic solvents; therefore, the rates of reaction in protic solvents are much lower than the other solvents. The activation enthalpies are almost the same for the reaction in protic and aprotic solvents. On the other hand, larger differences were observed for the activation entropies. The variation in ΔS^\ddagger values are may be due to steric interaction or changes in solvation between the reactants and transition state. The negative values of entropy of activation reflect that the transition states are more rigid than the initial stage, and this confirms that all these reactions follow the bimolecular substitution kinetics. The large negative ΔS^\ddagger values indicates a rigid transition state in these reactions and support the operation of "electrostriction" in these compounds pointing towards more polar transition state. In the transition state, it is shown that the sulfonyl sulphur of TsCl is subjected to S_N2 reaction by the oxygen of the hydrogen bonded glycolate anion (where X=H) and chlorine atom being pulled out as Pyridinium chloride. The nearly constant ΔG^\ddagger indicates that similar mechanisms are operative for the substitution reactions of hydroxy acids with tosyl chloride.

3.1 Isokinetic temperature

A linear relationship between activation entropy and activation enthalpy is known as isokinetic relationship or the compensation effect [28-30]. Leffler deduced the following Isokinetic equation which holds good for a series of related reactions [28].

$$\Delta H^\ddagger = \Delta H^0 + \beta \Delta S^\ddagger \text{-----} (6)$$

Where, β is the isokinetic temperature and ΔH^0 is the activation enthalpy at the standard state. The value of β can be less than or greater than the reaction temperature T. Generally the reaction rate will be accelerated below the isokinetic temperature and suppressed above the isokinetic temperature as long as the isokinetic relationship is sustained, but in some reactions it will occur in vice-versa [32]. If the β value is small then the reaction is entropy controlled and if the β value is large then the reaction is enthalpy controlled. The two factors which may have a predominant influence on the low isokinetic temperature are the steric configuration of the activated complex in the reaction medium and the nature of the solvent applied [30, 32]. According to Leffler isokinetic relationship it is found that the activation enthalpies (ΔH^\ddagger) and entropies (ΔS^\ddagger) for the reaction in different solvents are linearly related. The linear relation implies that the series of the reactions studied follows the same mechanism. The Leffler plot for glycolic acid, lactic acid and mandelic acid in different solvents are shown in (Fig 1). The β values for the reaction series in various solvents are obtained from the slope of leffler linear plots is given in Table 3.

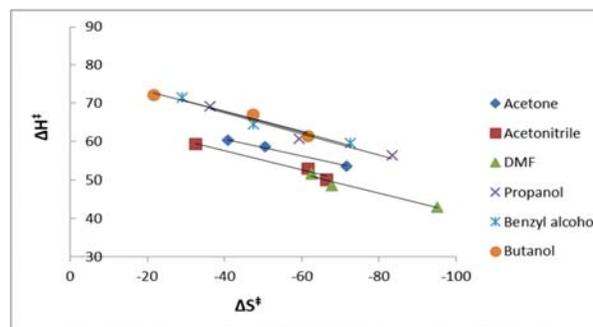


Fig 1: Plot of ΔH^\ddagger versus ΔS^\ddagger for the reaction of TsCl with α -Hydroxy acids-Pyridine in solvents used

Further the plots of ΔH^\ddagger versus Ea (Fig. 2) were also made as per Leffler's modified equation. The value of β was determined from the slope and it was found that this β value was in agreement with the β value obtained from the isokinetic plot (ΔH^\ddagger versus ΔS^\ddagger).

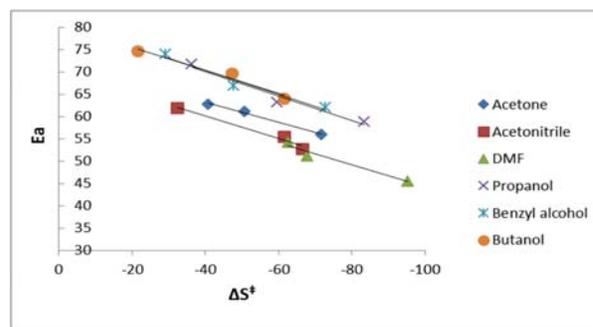


Fig 2: Plot of Ea versus ΔS^\ddagger for the reaction of TsCl with α -Hydroxy acids-Pyridine in solvents used

Exner suggested an alternative graphical method for testing the validity of isokinetic relationship [26-31]. The isokinetic relationship is tested by plotting the logarithms of rate constants at two different temperatures ($T_2 > T_1$) against each other according to following equation.

$$\beta = [T_1 T_2 (b-1)] / b T_2 - T_1 \text{-----} (7)$$

Isokinetic temperature for this series in various solvents has been determined by plotting $\log k_2$ at 313 K vs. $\log k_2$ at 303 K, which gives a linear plots (Fig. 3). From the slope values the isokinetic temperature for this series in various solvents was found out and it lies in between 360 - 375 K. The isokinetic temperature based on Exner equation is given in Table 3. The value of the slope 'b' for this series is less than unity. This indicates that the present reaction series is neither isentropic nor isenthalpic. The isokinetic temperature for all the acids are above the experimental temperature, hence the reaction is enthalpy controlled.

Table 3: Leffler and Exner β values for the reaction of TsCl with mixture of α -Hydroxy acid - Pyridine in solvents used

Solvents	Leffler β		Exner plot Slope	Exner β
	ΔS^\ddagger vs ΔH^\ddagger	ΔS^\ddagger vs Ea		
Acetonitrile	251	251	0.8188	367
Acetone	223	223	0.8007	360
Dimethylformamide (DMF)	246	246	0.8277	372
Benzyl alcohol	270	270	0.8333	374
Propanol	275	275	0.8354	376
Butanol	259	259	0.8345	375

[TsCl] = [X-CHOHCOOH - Pyridine] = 0.05 mol dm⁻³

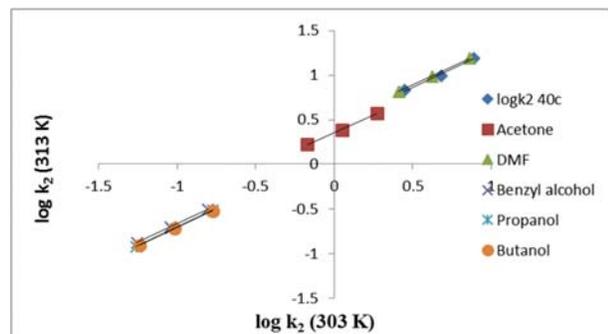


Fig 3: Plot of $\log k_2$ (303 K) vs $\log k_2$ (313 K) for the reaction of TsCl with α -Hydroxy acids-Pyridine in solvents used

In Protic solvents the nucleophile is more stabilized by solvation than the transition state. As a result, the ground state energy of the nucleophile is reduced to higher degree than the transition state. This leads to a higher activation energy and thus lower the rate [31]. In polar aprotic solvents the nucleophile is more reactive, because the nucleophile is less solvated and less stabilized in the ground state than in protic solvents. Hence, in polar aprotic solvents the activation energy is lower and the reaction rate is higher. Negative entropy of activation indicates a greater degree of ordering in the transition state than in the initial state, which may be due to an increase in solvation during the activation process. The influence of solvent on the rate of any reaction can be described in terms of solvation which is a stabilization process. The operation of isokinetic relationship reveals that the nucleophilic substitution at sulfur center takes place through a common mechanism in all the reactions studied.

4. Conclusion

The kinetics of the reaction between Tosyl chloride with α -Hydroxy acids in the presence of Pyridine has been studied at 293, 303 and 313 K in protic and aprotic solvents. Rate of the reaction is found to be higher in aprotic solvents than protic solvents. This variation is due to solvation behaviour of these solvents on transition state. The activation parameters in different solvents were determined empirically and compared with each other to obtain important information about the reaction mechanism. The overall second order reaction rate, the negative activation entropy and almost same free energy of activation supported a bimolecular nucleophilic substitution (S_N2) mechanism for the title reaction in all solvents used. Isokinetic relationship has been verified. Isokinetic temperature for these reaction series in all the solvents lies in between 360 - 375 K.

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