



ISSN Print: 2394-7500
 ISSN Online: 2394-5869
 Impact Factor: 5.2
 IJAR 2017; 3(1): 354-357
 www.allresearchjournal.com
 Received: 20-11-2016
 Accepted: 21-12-2016

R Kavitha
 PG & Research Department of
 Chemistry, Urumu
 Dhanalakshmi College,
 Tiruchirappalli, Tamil Nadu,
 India

S Ananthalakshmi
 PG & Research Department of
 Chemistry, Urumu
 Dhanalakshmi College,
 Tiruchirappalli, Tamil Nadu,
 India

Effects of solvents on kinetics of the reaction between *p*-Toluenesulfonyl Chloride and α -Hydroxy acids in the presence of pyridine

R Kavitha and S Ananthalakshmi

Abstract

The rate constants for the reaction of *p*-Toluenesulfonyl Chloride with α -Hydroxy acids in the presence of Pyridine in various polar aprotic, protic and nonpolar solvents have been investigated. The rate constants of the reaction are 3 – 50 times higher in polar aprotic solvents than in protic solvents. The solvent effects can be explained on the basis of solvation of anions in polar aprotic and protic solvents. The contributions of hydrogen bonding in solvation are discussed. Solvation of S_N2 transition state anions depends on the nature of entering and leaving group. The transition state for these reactions is greatly solvated by methanol than Acetonitrile or DMF. Transition states for S_N2 reactions of similar reactions respond in much similar way to the solvents.

Keywords: Substitution kinetics, solvent effects, solvation, transition state, dielectric constant

1. Introduction

A bimolecular nucleophilic substitution reaction plays an important role in Organic chemistry. Most organic reactions are carried out in solution, where solvents facilitate mixing, help to fix the reaction temperature, stabilize reactive intermediates and mediate proton transfers. Therefore, a special attention is given towards study of solvent effects on different reactions. A solvent would provide not only a background for the reaction to occur but would stabilize the reactants and the transition state by solvating them. The specific choice of solvent can make the difference between success and failure in a particular reaction. Effect of solvent is closely related to the nature and extent of solute-solvent interaction. They can extensively solvate the activated complex and can tremendously alter the properties of the nucleophile^[1, 2].

Solvents influence the chemical or physical processes by solvating the substrate through vander Waals force, hydrogen bonding or by providing solvent pockets or cages for encapsulating the substrate. The functional groups present in the solvent molecule and their orientation play an important role in solvent properties^[3]. The influence of solvents on chemical reaction in solution and the reactivity of bimolecular nucleophilic substitution reactions have been extensively studied over a number of years and some of the effects have been reported^[3]. Comparison of rates of S_N2 reactions in protic and in dipolar aprotic solvents produce some new conclusions about reaction mechanisms, nucleophilic tendencies, leaving group tendencies, steric effects, salt effects and solvent effects^[4].

The rate of the reaction can be changed by merely changing the medium in which the reaction occurs. Therefore, a proper understanding of solvent effects is essential to any model of chemical reactivity. Effect of solvents has been explained on the basis of electrostatics, solvation of solutes by solvents, internal cohesions of the solvents, nature of protic or dipolar aprotic solvents, viscosity etc.. The effect of solvents on the rate is determined by the difference in the free energies, enthalpies and entropies of solvation of reactants and the transition states^[5-7]. The extent of solvation of the reactants and the activated complex can influence the reaction rates. Dielectric constant of the solvents has been most frequently used to study the effect of solvent on bimolecular nucleophilic substitution reactions. The dielectric constant determines the magnitude of forces between well separated ions in solution. Solvating power is not determined by dielectric constant alone. Solvation is the specific interaction between solvent molecules and ions, and it

Correspondence
R Kavitha
 PG & Research Department of
 Chemistry, Urumu
 Dhanalakshmi College,
 Tiruchirappalli, Tamil Nadu,
 India

depends on the factors (1) solvation increases with increase in dipole moment of the solvent. (2) solvation decreases with increase in shielding of dipole moment of the solvent and (3) nature of the solvent atom carrying the dipole charge [8].

Literature review reveals that most of the work had done on solvent effects on aromatic nucleophilic substitutions and influence of structure on S_N2 reactions [9-21]. However, only very few attempts have been made to study the influence of solvents on aliphatic nucleophilic substitution reactions in a more systematic manner. So we planned to study the influence of solvent on aliphatic bimolecular nucleophilic substitution kinetics. The kinetics of the reaction of Tosyl chloride with α -Hydroxy acids in the presence of Pyridine in Acetonitrile has been already reported [22]. In the present work, we report the kinetics of the same reaction in various solvents in a view to understand the effect of solvent on the nature of the active nucleophile.

2. Materials and methods

2.1 Materials

p-Toluenesulfonyl chloride (TsCl), Glycolic acid, Lactic acid, Mandelic acid, Pyridine (Analytical grade) and all solvents were purified before use by standard methods [23,24].

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 mixture at different time intervals (minutes) till the reaction has completed. Same experimental procedure was adopted for

all other α -Hydroxy acids in different solvents. Second order rate constant (k_2) was obtained from the following special integrated equation which was derived from Guggenheim's method [25].

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

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

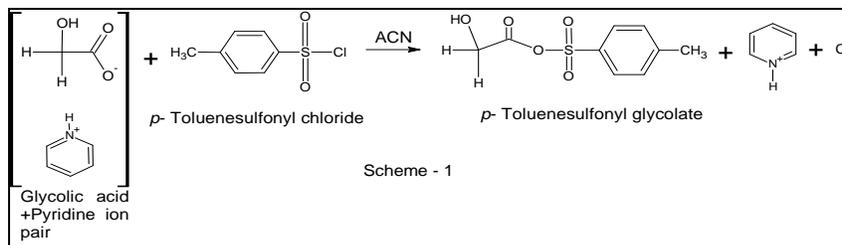
Plot of $(x_2 - x_1)$ against $-(t_1 x_1 - t_2 x_2)$ should be a straight line.

From the slope, the second order rate constant k_2 was calculated by the method of least-square analysis.

3. Results and discussion

The kinetics and mechanism of the nucleophilic substitution reaction of Tosyl chloride with α -Hydroxy acids in the presence of Pyridine were investigated in different polar and nonpolar solvents by conductometric method. Polar protic solvents are hydrogen-bond donors. Dipolar aprotic solvents are not hydrogen-bond donors, but the molecules are highly polar. Polar solvents of dielectric constant values more than 13 are the only ones generally considered when comparing protic and dipolar aprotic solvents.

In a solvent the nucleophile is exists as a proton transferred, hydrogen bonded ion pair complex [For glycolic acid, $\text{OH-CH}_2\text{-COO}^- \dots \text{H}^+ \text{NC}_5\text{H}_5$]. Tosyl chloride is a good substrate for S_N2 nucleophilic substitution reaction. The electron withdrawing Cl atom in Tosyl chloride induces an electron deficient centre at the tetra coordinated sulfur atom and facilitates the approach of a nucleophile towards the sulfur atom. The scheme for the present reaction is represented in scheme 1.



The rate of the reaction will vary depending on the degree of charge separation on α -hydroxy acid-pyridine complex. The charge separation is influenced by the various

properties of solvents. The second order rate constants (k_2) are obtained from the kinetic data by the method of least square for various solvents 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 30 °C

	Solvent	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)
1	Acetonitrile	4.791	2.797	7.735
2	Acetone	1.129	0.676	1.875
3	Dimethylformamide	4.204	2.578	7.291
4	Ethylmethylketone	1.162	0.608	1.807
5	Dichloromethane	0.862	0.606	1.153
6	Chlorobenzene	0.898	0.613	1.328
7	Chloroform	1.018	0.618	1.778
8	Methanol	1.328	0.764	2.229
9	Ethanol	0.093	0.054	0.159
10	Propanol	0.092	0.055	0.168
11	Isopropyl alcohol	0.098	0.056	0.162
12	Butanol	0.096	0.057	0.167
13	Benzyl alcohol	0.091	0.055	0.157

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

The experimental results showed that the reaction reactivity decreases with the decrease in polarity of solvents. This reaction takes place more rapidly in acetonitrile and dimethyl formamide than in methanol. Typical dipolar aprotic solvents Acetonitrile and DMF distinctively promoted the reaction. This fact was successfully explained by the solvation rule for S_N2 reaction. It is evident from the results (Table 1) that the reaction is 3 – 50 times faster in polar aprotic solvents than in protic solvents. This may be due to anion desolvation in aprotic solvents. Desolvation of attacking nucleophile enhances the reaction rate.

In hydroxylic protic solvents, the anion is very rapidly solvated and this leads to much retardation of the reaction. The nucleophile is made less potent by extensive solvation via hydrogen bonding by hydroxylic solvents such as ethanol, and thereby decreases the nucleophilicity. For the glycolic acid reaction, the rate constant in DMF is 3 times higher ($k_2 = 4.204 \text{ dm}^3\text{mol}^{-1}\text{m}^{-1}$) than in methanol ($k_2 = 1.328 \text{ dm}^3\text{mol}^{-1}\text{m}^{-1}$). In alcohols, k_2 appears to remain constant except in methanol, which gives a higher value. In chloroform ($k_2 = 1.018 \text{ dm}^3\text{mol}^{-1}\text{m}^{-1}$), a non-polar solvent, the rate is 11 times greater than in ethanol ($k_2 = 0.093 \text{ dm}^3\text{mol}^{-1}\text{m}^{-1}$). In this case the nucleophile is made less potent in ethanol due to extensive solvation through hydrogen bonding, and in chloroform the acid – pyridine complex may have a pseudosymmetric structure. In case of aliphatic chlorinated solvents, the reaction rate in chloroform is greater than dichloromethane, although the

reverse is the polarity order. This also explained on the basis of stabilization of glycolate anion (in case of glycolic acid) by its pseudosymmetric structure in CHCl_3 by hydrogen bonding. Hydrogen bonded glycolate anion interacts with tosyl chloride to form more polar and stable transition state, which in turn increase the rate.

On comparing the k_2 values of alcoholic solvents and acetone, the k_2 values in alcoholic solvents are much lesser than those in acetone. In acetone the anions undergo desolvation and making them more active nucleophiles^[14]. Among the alcoholic solvents, methanol has the highest k_2 value. The reaction under investigation does not take place in nonpolar solvents benzene and carbon tetrachloride. This indicates that pyridine has not caused ionization of α -hydroxy acid in these solvents. But the reaction occurs in chloroform and dichloromethane, because the solvents have intermediate polarity in nature^[14].

Similar results were obtained for the Lactic acid and mandelic acid reaction, where the rate constant in aprotic solvent is 3- 50 times higher than in protic solvents.

3.1 Correlation of the reaction in Acetonitrile with Acetone or methanol

The reaction rate in Acetonitrile is correlated to the rate of same reaction in Acetone or methanol by means of the values of $\log k_2$. The linear line obtained is one of the probes for the operation of same mechanism in both the solvents (Fig 1 & Fig 2).

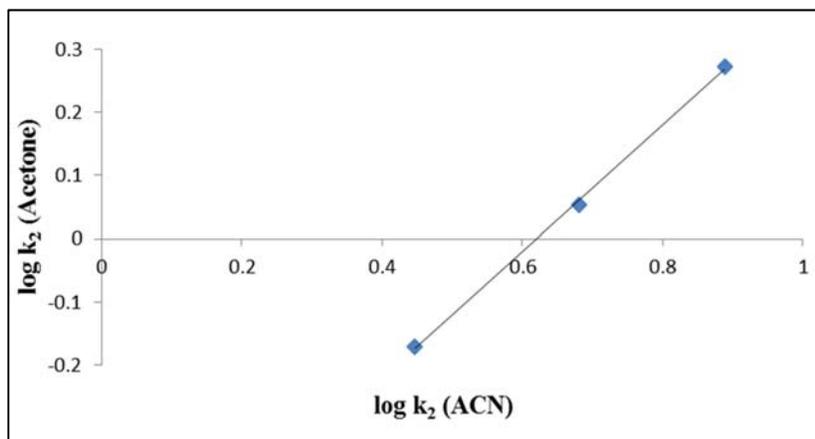


Fig 1: Plot of $\log k_2$ (ACN) with $\log k_2$ (Acetone) for the reaction of TsCl with mixture of α -Hydroxy acid - Pyridine at 30 °C

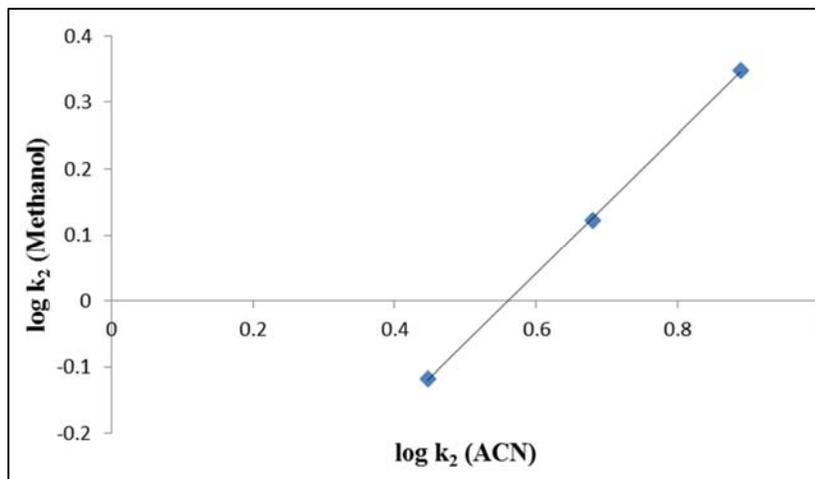


Fig 2: Plot of $\log k_2$ (ACN) with $\log k_2$ (Methanol) for the reaction of TsCl with mixture of α -Hydroxy acid - Pyridine at 30 °C

4. Conclusion

The kinetic studies of *p*-Toluenesulfonyl Chloride with α -Hydroxy acids in the presence of Pyridine was carried out in various polar and non-polar solvents. The results showed that the rate of the reaction was 3 –50 times higher in polar aprotic solvents than protic solvents and the k_2 values in polar aprotic solvents are comparatively higher than in protic solvents, except methanol. The variations in rate constant are explained by the solvation nature of the solvent. $\log k_2(\text{Acetonitrile})$ vs $\log k_2(\text{Acetone})$ and $\log k_2(\text{Acetonitrile})$ vs $\log k_2(\text{Methanol})$ reveals that same mechanism is operated on these solvents.

5. References

- Michael B. Smith. Organic Chemistry. Edn Taylor & Francis Group, 2016; 2(1):125-130.
- Reichardt C. Solvents and solvents effects in Organic Chemistry. 5th edn (VCH, Weinheim), 2003.
- Hartshorn SR. Aliphatic nucleophilic substitution. Cambridge university press, London. 1973, 53-58.
- Lazykov M, Rubloa L, Moises Canle L, Arturo Santaballa J. Solvent network at the transition state in the solvolysis of hindered sulfonyl compounds. Journal of Physical Organic Chemistry. 2016; 30(1).
- Crampton MR, Organic Reaction Mechanisms edited by C A Knipe & W E Watts (John Wiley, New York), 1994, 1996.
- Parker AJ. Rates of Bimolecular substitution reactions in protic and dipolar aprotic solvents. Advances in Physical Organic Chemistry. 1967; 5:173-235.
- Alexander R, Ko ECF, Parker AJ, Broxton TJ. Solvation of ions. XIV. Protic-dipolar aprotic solvent effects on rates of bimolecular reactions. Solvent activity coefficients of reactants and transition states at 25 °. J. Am. Chem. Soc., 1968; 90(19):5049-5069 DOI: 10.1021/ja01021a002
- Kevill DN, Park BC, Park KH, D'Souza MJ, Yaakoubd L, Mlynarski S *et al.* Rate and product studies in the solvolyses of N, N- dimethylsulfamoyl and 2-propanesulfonyl chlorides. Org. Biomol. Chem. 2006; 4:1580-1586.
- Lee I, Sun Koo I. Variation of transition state in reactions of benzenesulfonyl chlorides with anilines in MeOH-MeCN solvents. Tetrahedron. 1983; 39(10):1803-1807.
- Miller J, Parker AJ. Dipolar aprotic solvents in bimolecular aromatic nucleophilic substitution reactions. J Am. Chem. Soc., 1961; 83(1):117-123.
- Pham TV, Westaway KC. solvent effects on nucleophilic substitutin reactions. III. The effect of adding an inert salt on the structure of the transition state. Can. J Chem. 1996; 74:2528-2530.
- Bhuvaneshwari DS, Elango KP. Solvent hydrogen bonding and structural effects on nucleophilic substitution reactions. Part 5. Z. Naturforsch. 2008; 63a:493-504.
- Fathalla MF, Kassem TS, Hamed EA. Kinetics of the reaction between methyl 2,4-dichloro-3,5-dinitrobenzoate and piperidine – solvent effect. Indian Journal of Chemistry. 2008; 47A:1348-1354.
- Krishnapillay M, Kannan K, Rama Subramanian P. Tetrahedron. 1983; 39:3899.
- DeLos F. De Tar, Ronald W. Novak J Am. Chem. Soc. 1970; 92(5):1361-1365.
- Kim JW, Uhm T, Lee I, Koo ISJ. Korean. Chem. Soc. 1985; 29:15.
- Nallu M, Subramanian M, Vembu N, Akbar Hussain A. Int. J Chem. Kinet, 2004; 36:401.
- Raghavan R, Kalavathy S. Proc. Indian Acad, Sci. (Chem. Sci.). 1985; 94:481-485
- Nallu M, Kanagadurgadevi G. Asian J. Chem., 2002; 14(3-4):1320-1324.
- Ranga Reddy S, Maniyamba J. Chem. Sci., May 2006; 118(3):257-260.
- Ranga Reddy S, Maniyamba. Indian J. Chem., May 2004; 43A:1092-1094.
- Kavitha R, Ananthalakshmi S. Kinetic studies on the reaction of p-toluenesulfonyl Chloride with α -Hydroxy acids in the presence of pyridine in acetonitrile. 2016; 2(11):317-321.
- Vogel AI. A Text Book of Practical Organic Chemistry, 4th ed, ELBS, London, 1978.
- The Merck Index. 10th ed, Merck, Rahway, NJ, 1983.
- Guggenheim EA, Pure JE. Physiochemical Calculations. Inter science Publishers, Inc., London, 1955.