

# Regression analyses of $\log k_2$ against various solvent parameters for the reaction of *p*-toluenesulfonyl Chloride with $\alpha$ -hydroxy acid(s) in the presence of pyridine

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## Abstract

Kinetics of the reaction of *p*-toluenesulfonyl Chloride (TsCl) with  $\alpha$ -hydroxy acid(s) in the presence of pyridine under equimolar conditions in various solvents has been studied by conductometric method. The rate constants were obtained by least square method. Kinetic data shows that the reaction follows second order kinetics and first order with respect to each of the reactants. In order to understand the effect of solvent parameters on the reaction rate, the second order rate constants were subjected to simple and multiple regression analyses. Various solvent parameters at macroscopic and microscopic levels were used. The signs of the equation co-efficient show the contribution of each parameter on the reaction rate.

**Keywords:** Substitution kinetics, Sulfonyl ester, Solvent effects, Microscopic and macroscopic properties, Regression analysis

## 1. Introduction

Bimolecular nucleophilic substitution ( $S_N2$ ) is important in chemical synthesis, especially for interchanging functional groups and for carbon – carbon bond formation (Vollhardt K.P.C & Shore N. E, 2007). It is one of the most widely studied reactions in physical organic chemistry (Sason S *et al.*, 1992). Usually, solvent effects are superimposed onto the intrinsic reaction dynamics, which strongly

affects the reactivity. So, solvent effects are mainly used to predict the rate constants in solvents and to understand the various influences that might affect reaction rates.

The kinetics of the reaction of phenacyl bromide with benzoate (Krishnapillay M *et al.*, 1983), phenoxyacetates (Krishnapillay M *et al.*, 1983), and cinnamates (Krishnapillay M & Balasubramanian G, 1987) have been reported in acetone and acetone – water medium containing various amount of water. Nallu *et al.* extensively studied the effect of binary aqueous – organic solvents on the reaction of phenacyl bromide with nitrobenzoic acid(s) in the presence of triethylamine (Nallu M *et al.*, 2004). Kinetic studies on the reactions of TsCl with *p*-substituted Benzoic acids in the presence of triethylamine in aprotic solvents have been extensively studied by Ananthalakshmi and Nallu (Ananthalakshmi S & Nallu M, 2008). Vembu *et al.* have studied solvent effect on the reaction of TsCl with para substituted phenols and triethylamine (Vembu *et al.*, 2013).

Though many discussions of solvent effects on reaction rates of nucleophilic substitution processes have been reported, systematic regression

investigations of reaction series are relatively few. Hence, we planned to study the solvent effects of the nucleophilic substitution reaction of TsCl with  $\alpha$ -hydroxy acid(s) in the presence of pyridine at macroscopic and microscopic level using simple and multiple regression analyses.

## 2. Materials and Methods

### 2.1 Materials

*p*-toluenesulfonyl chloride (TsCl), Glycolic acid, Lactic acid, Mandelic acid, Pyridine and all the solvents (Analytical grade) used were purified before use by recrystallization or distillation until their physical constants (melting point / boiling point) agreed with the literature values (Vogel A. I, 1978, *The Merck Index*, 1983, Perrin D. D & Armarego W. L. F, 1988).

In order to understand the role of the solvents on the rate, correlation and regression technique was employed. Value of  $\log k_2$  was correlated with different solvent parameters by simple and multiple regression analysis. Regression analyses were done by using SPSS statistical software.

### 2.2 Methods

Kinetics of the reaction of *p*-toluenesulfonyl Chloride (TsCl) with  $\alpha$ -hydroxy acid(s) in the presence of pyridine under equimolar conditions in various solvents has been studied by conductometric method. The progress of the reaction was followed by measuring the conductance of the reaction mixture at

different time intervals. Second order rate constant ( $k_2$ ) was obtained from the following special integrated equation which was derived from Guggenheim's method (Guggenheim E. A & Pure J. E, 1955).

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

$x_1$  = Conductance at time  $t_1$

$x_2$  = Conductance at time  $t_2$

$x_{\infty}$  = Conductance at time  $t_{\infty}$

$k_2$  = 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. Different solvent parameters at macroscopic and microscopic levels are given in Table 1.

## 3. Results and Discussion

The second order rate constants for the reaction of tosyl chloride with  $\alpha$  - hydroxy acid(s) (X - CHO<sub>2</sub>COOH) and pyridine in 7 aprotic and 6 protic solvents at 30 °C are determined (Kavitha R & Ananthalakshmi S, 2017) In order to understand the role of the solvents on the rate, correlation technique is employed. Value of  $\log k_2$  of examined acids in aprotic and protic solvents are correlated with different solvent parameters at microscopic and macroscopic levels using simple and multiple regression analyses.

Table 1– Solvent properties at macroscopic and microscopic level

Solvent	At macroscopic level					At microscopic level			
	$\epsilon$	$\mu_D$	$\rho$	$\gamma$	$\eta$	$(\epsilon-1)/(2\epsilon+1)$	$E_T(30)$	$\pi^*$	$\log k_2$ (n-Pr <sub>3</sub> N + MeI)
<b>Aprotic</b>									
Acetonitrile	35.9	3.92	0.787	28.7	0.369	0.479	46.0	0.850	-0.328
Acetone	20.7	2.88	0.780	23.5	0.306	0.469	42.4	0.720	-0.827
Dimethylformamide	37.0	3.86	0.945	36.7	0.802	0.480	43.8	0.880	-0.222
Ethylmethylketone	18.5	2.70	0.805	23.9	0.405	0.461	41.3	0.670	-1.100
Dichloromethane	8.93	1.60	1.325	27.2	0.413	0.420	41.1	0.800	-0.553
Chlorobenzene	5.63	1.70	1.107	32.9	0.753	0.377	37.5	0.710	-1.155
Chloroform	4.64	1.30	1.484	26.7	0.537	0.344	39.1	0.760	-0.886
<b>Protic</b>									
Methanol	32.7	2.87	0.792	22.1	0.544	0.470	55.5	0.600	-1.886
Ethanol	24.5	1.69	0.789	21.9	1.074	0.470	51.9	0.540	-2.022
Propanol	20.3	1.68	0.802	20.9	1.950	0.464	50.7	0.510	-2.131
Isopropylalcohol	19.4	1.66	0.785	23.3	2.038	0.462	48.6	0.460	-
Butanol	17.5	1.71	0.810	24.9	2.544	0.458	50.2	0.430	-2.337
Benzyl alcohol	13.1	1.70	1.045	38.8	5.474	0.444	50.8	0.980	-1.237

$\epsilon$  = Dielectric constant,  $\mu_D$  = Dipole moment  $\rho$  = Density,  $\gamma$  = Surface tension,  $\eta$  = Viscosity,  $(\epsilon-1)/(2\epsilon+1)$  = Kirkwood function,  $E_T(30)$  = Dimroth – Reichardt constant,  $\pi^*$  = Polarity / Polarizability,  $\log k_2$  LJ =  $\log k_2$  ( $n\text{-Pr}_3\text{N} + \text{MeI}$ ) = Lassau and Jungers scale

### 3.1 Simple regression analyses

The  $\log k_2$  of the second order rate constants for the reaction of tosyl chloride with  $\alpha$  – hydroxy acid(s) [X – CH(OH)COOH] and pyridine in 7 aprotic and 6 protic solvents at 30 °C are correlated with different solvent parameters by simple regression analyses using the following equation (Shorter J, 1954., Taft R. W, 1981)

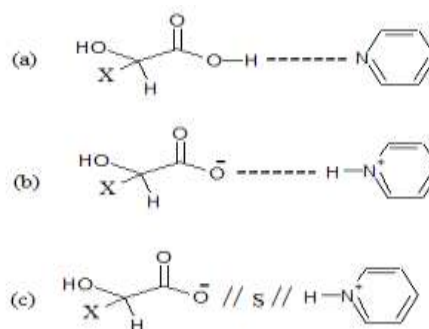
$$\log k_2 = \log k_0 + m X$$

Where, X is independent variable and m is coefficient.

Table – 2 and 3 gives the result of simple regression analyses of  $\log k_2$  in 7 aprotic and 6 protic solvents with  $\epsilon$  (Dielectric constant),  $\mu_D$  (Dipole moment),  $\rho$  (Density),  $\gamma$  (Surface tension),  $\eta$  (Viscosity),  $(\epsilon-1)/(2\epsilon+1)$  (Kirkwood function),  $E_T(30)$  (Dimroth – Reichardt constant),  $\pi^*$  (Polarity / Polarizability), and  $\log k_2$  ( $n\text{-Pr}_3\text{N} + \text{MeI}$ ) (Lassau and Jungers scale) respectively.

The results show that only dielectric constant ( $\epsilon$ ) of aprotic solvents and dipole moment ( $\mu_D$ ) of protic

solvents shows good correlation and the other parameters shows very poor correlation. This reflects in the r values of given set of regression equations (Kirkwood J. G, 1939, Drougard Y & Decroocq D, 1969). The best – fit regression equations are given in Table 4. This proves that none of the single properties influence the rates of the reactions (Kapadi U. R *et al.*, 1997) Rand also reveals that the existence of reactive species and the activated complex in each solvent may not be the same (Grahain Dawber J & Ward Williams J, 1988). The reactive species,  $\alpha$  – hydroxy acid(s) and pyridine can exists as (a) hydrogen bonding with pyridine (b) a tight ion pair with complete proton transfer or (c) solvent separated ion pair.



**Table 2 – Simple regression of  $\log k_2$  vs solvent parameter for the reaction between TsCl and X-CH(OH)COOH-Pyridine (X = H, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>) (Aprotic solvents)**

Solvent parameter	Regression Equation $\log k_2 =$	n	r	s	F	Eqn. no.
$\epsilon$	<b>0.022 <math>\epsilon - 0.226</math></b>	<b>7</b>	<b>0.931</b>	<b>0.1278</b>	<b>32.727</b>	<b>1</b>
	(0.022 $\epsilon - 0.336$ )	(7)	(0.851)	(0.2033)	(13.086)	2
	<b>[0.023 <math>\epsilon - 0.050</math>]</b>	<b>[7]</b>	<b>[0.925]</b>	<b>[0.1424]</b>	<b>[29.569]</b>	<b>3</b>
$\mu_D$	0.267 $\mu_D - 0.497$	7	0.893	0.1577	19.794	4
	(0.278 $\mu_D - 0.634$ )	(7)	(0.846)	(0.2062)	(12.604)	5
	[0.283 $\mu_D - 0.339$ ]	[7]	[0.889]	[0.1717]	[18.785]	6
$\rho$	-0.562 $\rho + 0.768$	7	0.495	0.3052	1.620	7
	(-0.792 $\rho + 0.898$ )	(7)	(0.633)	(0.2995)	(3.343)	8
	[-0.591 $\rho + 0.998$ ]	[7]	[0.488]	[0.3268]	[1.564]	9
$\gamma$	0.033 $\gamma - 0.752$	7	0.493	0.3056	1.603	10
	(0.021 $\gamma - 0.530$ )	(7)	(0.290)	(0.3702)	(0.460)	11
	[0.034 $\gamma - 0.580$ ]	[7]	[0.476]	[0.3293]	[1.464]	12
$\eta$	0.270 $\eta + 0.049$	7	0.164	0.3464	0.138	13
	(0.176 $\eta - 0.010$ )	(7)	(0.097)	(0.3850)	(0.047)	14
	[0.303 $\eta + 0.233$ ]	[7]	[0.172]	[0.3688]	[0.153]	15
$(\epsilon+1)/(2\epsilon+1)$	3.808 $(\epsilon+1)/(2\epsilon+1) - 1.460$	7	0.644	0.2687	3.540	16
	(4.724 $(\epsilon+1)/(2\epsilon+1) - 1.965$ )	(7)	(0.725)	(0.2663)	(5.548)	17
	[3.903 $(\epsilon+1)/(2\epsilon+1) - 1.302$ ]	[7]	[0.383]	[0.2941]	[3.105]	18

$E_T(30)$	0.095 $E_T(30) - 3.768$ (0.090 $E_T(30) - 3.654$ ) [0.099 $E_T(30) - 3.739$ ]	7 (7) [7]	0.841 (0.721) [0.677]	0.1900 (0.2682) [0.2127]	12.085 (5.404) [10.486]	19 20 21
$\pi^*$	3.223 $\pi^* - 2.294$ (1.898 $\pi^* - 1.382$ ) [3.331 $\pi^* - 2.177$ ]	7 (7) [7]	0.774 (0.414) [0.563]	0.2223 (0.3521) [0.2474]	7.482 (1.035) [6.454]	22 23 24
$\log k_2$ (LJ)	0.699 $\log k_2$ (LJ) + 0.694 (0.479 $\log k_2$ (LJ) + 0.427) [0.721 $\log k_2$ (LJ) + 0.910]	7 (7) [7]	0.797 (0.496) [0.595]	0.2119 (0.3357) [0.2384]	8.733 (1.636) [7.335]	25 26 27

 Value in ( ) is for glycolic acid ( $X = CH_3$ )

 Value in [ ] is for mandelic acid ( $X = C_6H_5$ )

**Table 3 – Simple regression of  $\log k_2$  vs solvent parameter for the Reaction between TsCl and X-CH(OH)COOH-Pyridine ( $X = H, CH_3, C_6H_5$ ) (Protic solvents)**

Solvent parameter	Regression Equation $\log k_2 =$	n	r	s	F	Eqn. no.
$\epsilon$	0.058 $\epsilon - 0.2074$	6	0.835	0.2891	9.204	28
	(0.057 $\epsilon - 2.284$ )	(6)	(0.829)	(0.2909)	(8.793)	29
	[0.058 $\epsilon - 1.824$ ]	[6]	[0.836]	[0.2853]	[9.250]	30
$\mu_D$	<b>0.972 <math>\mu_D - 2.667</math></b>	<b>6</b>	<b>0.972</b>	<b>0.1238</b>	<b>67.938</b>	<b>31</b>
	<b>(0.963 <math>\mu_D - 2.882</math>)</b>	<b>(6)</b>	<b>(0.975)</b>	<b>(0.1166)</b>	<b>(75.589)</b>	<b>32</b>
	<b>[8.325 <math>\mu_D - 14.821</math>]</b>	<b>[6]</b>	<b>[0.945]</b>	<b>[0.1701]</b>	<b>[33.268]</b>	<b>33</b>
$\rho$	-1.058 $\rho + 0.050$	6	0.230	0.5111	0.224	34
	(-0.994 $\rho - 0.235$ )	(6)	(0.218)	(0.5076)	(0.200)	35
	[-1.049 $\rho + 0.278$ ]	[6]	[0.231]	[0.5052]	[0.225]	36
$\gamma$	-0.017 $\gamma - 0.408$	6	0.243	0.5095	0.250	37
	(-0.046 $\gamma - 0.019$ )	(6)	(0.139)	(0.5152)	(0.078)	38
	[-0.049 $\gamma + 0.514$ ]	[6]	[0.148]	[0.5135]	[0.089]	39
$\eta$	-0.136 $\eta - 0.528$	6	0.498	0.4554	1.320	40
	(-0.131 $\eta - 0.768$ )	(6)	(0.488)	(0.4541)	(1.249)	41
	[-0.134 $\eta - 0.295$ ]	[6]	[0.497]	[0.4500]	[1.311]	42
$(\epsilon+1) / (2\epsilon+1)$	23.671 $(\epsilon+1) / (2\epsilon+1) - 11.740$	6	0.484	0.4596	1.224	43
	(20.832 $(\epsilon+1) / (2\epsilon+1) - 10.677$ )	(6)	(0.434)	(0.4687)	(0.927)	44
	[17.337 $(\epsilon+1) / (2\epsilon+1) - 8.585$ ]	[6]	[0.417]	[0.4714]	[0.840]	45
$E_T(30)$	0.177 $E_T(30) - 9.914$	6	0.877	0.2519	13.388	46
	(0.176 $E_T(30) - 10.101$ )	(6)	(0.882)	(0.2455)	(13.953)	47
	[0.176 $E_T(30) - 9.632$ ]	[6]	[0.884]	[0.2421]	[14.348]	48
$\pi^*$	0.037 $\pi^* - 0.857$	6	0.016	0.5251	0.001	49
	(0.061 $\pi^* - 1.102$ )	(6)	(0.026)	(0.5200)	(0.003)	50
	[0.041 $\pi^* - 0.623$ ]	[6]	[0.018]	[0.5185]	[0.001]	51
$\log k_2$ (LJ)	0.046 $\log k_2$ (LJ) - 0.712	5	0.037	0.5961	0.004	52
	(0.053 $\log k_2$ (LJ) - 0.928)	(5)	(0.043)	(0.5886)	(0.006)	53
	[0.038 $\log k_2$ (LJ) - 0.487]	[5]	[0.031]	[0.5861]	[0.003]	54

 Value in ( ) is for glycolic acid ( $X = CH_3$ )

 Value in [ ] is for mandelic acid ( $X = C_6H_5$ )

**Table 4 – Best-fit simple regression equation**

Solvent parameter	Regression Equation $\log k_2 =$	n	r	s	F	Eqn. no.
<b>Aprotic solvents</b>						
$\epsilon$	0.022 $\epsilon - 0.226$	7	0.931	0.1278	32.727	1
	[0.023 $\epsilon - 0.050$ ]	[7]	[0.925]	[0.1424]	[29.569]	3
<b>Protic solvents</b>						
$\mu_D$	0.972 $\mu_D - 2.667$	6	0.972	0.1238	67.938	31
	(0.963 $\mu_D - 2.882$ )	(6)	(0.975)	(0.1166)	(75.589)	32
	[8.325 $\mu_D - 14.821$ ]	[6]	[0.945]	[0.1701]	[33.268]	33

### 3.2 Multiple regression – Dual and Triple solvent parameter regression analyses

From the simple regression analyses it is noted that the effect of solvents on reaction rate are more complex and more than one solvent parameter may influence the reactive species. So, in order to obtain a better correlation we have done dual regression analyses and triple regression analyses of  $\log k_2$  with solvent parameters.

Dual regression of  $\log k_2$  with solvent parameters are obtained by using the following equation

$$\log k_2 = \log k_0 + a_1 X_1 + a_2 X_2$$

Where,  $X_1$  and  $X_2$  are variables.

The results of dual regression analyses are given in Table 5 and 6.

Dual regression gives better correlation than simple regression. The best fit dual regression equations are given in Table 7 and 8 for aprotic and protic solvents respectively. From the dual regression analyses for aprotic solvents  $\mu_D$  along with  $(\epsilon-1)/(2\epsilon+1)$ ,  $\pi^*$  and  $\log k_2$  (LJ),  $\epsilon$  along with  $(\epsilon-1)/(2\epsilon+1)$ ,  $E_T(30)$ ,  $\pi^*$  and  $\log k_2$  (LJ),  $\rho$  along with  $\pi^*$ ,  $\gamma$  along with  $E_T(30)$  and  $\eta$  along with  $E_T(30)$  gives satisfactory correlation. For protic solvents  $\mu_D$  along with  $(\epsilon-1)/(2\epsilon+1)$ ,  $E_T(30)$ ,  $\pi^*$  and  $\log k_2$  (LJ) and  $\epsilon$  along with  $(\epsilon-1)/(2\epsilon+1)$  and  $E_T(30)$  gives good correlation.

**Table 5 – Dual regression of  $\log k_2$  vs solvent parameter for the Reaction between TsCl and X – CH(OH)COOH–Pyridine (X = H, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>) (Aprotic solvents)**

Correlation $\log k_2$ vs Solvent parameters	n	r	s	F	Regression equation ( $\log k_2 =$ )	Eqn. no
$\mu_D + (\epsilon-1)/(2\epsilon+1)$	7	<b>0.958</b>	<b>0.1125</b>	<b>22.352</b>	<b>0.471 <math>\mu_D - 4.520 (\epsilon-1)/(2\epsilon+1) + 0.936</math></b>	<b>55</b>
	(7)	(0.849)	(0.2287)	(5.158)	(0.324 $\mu_D - 0.996 (\epsilon-1)/(2\epsilon+1) - 0.319$ )	56
	[7]	[ <b>0.971</b> ]	[ <b>0.1009</b> ]	[ <b>32.447</b> ]	[ <b>0.530 <math>\mu_D - 5.480 (\epsilon-1)/(2\epsilon+1) + 1.399</math></b> ]	<b>57</b>
$\mu_D + E_T(30)$	7	0.900	0.1708	8.568	0.208 $\mu_D + 0.025 E_T(30) - 1.401$	58
	(7)	(0.849)	(0.2288)	(5.153)	(0.321 $\mu_D - 0.018 E_T(30) + 0.011$ )	59
	[7]	[0.892]	[0.1895]	[7.763]	[0.238 $\mu_D + 0.019 E_T(30) - 1.023$ ]	60
$\mu_D + \pi^*$	7	<b>0.965</b>	<b>0.1028</b>	<b>27.183</b>	<b>0.202 <math>\mu_D + 1.764 \pi^* - 1.687</math></b>	<b>61</b>
	(7)	(0.847)	(0.2303)	(5.060)	(0.284 $\mu_D - 0.154 \pi^* - 0.531$ )	62
	[7]	[ <b>0.951</b> ]	[ <b>0.1293</b> ]	[ <b>18.970</b> ]	[ <b>0.218 <math>\mu_D + 1.759 \pi^* - 1.525</math></b> ]	<b>63</b>
$\mu_D + \log k_2$ (LJ)	7	<b>0.940</b>	<b>0.1338</b>	<b>15.222</b>	<b>0.194 <math>\mu_D + 0.332 \log k_2</math> (LJ) - 0.070</b>	<b>64</b>
	(7)	(0.848)	(0.2290)	(5.140)	(0.296 $\mu_D - 0.080 \log k_2$ (LJ) - 0.737)	65
	[7]	[ <b>0.926</b> ]	[ <b>0.1582</b> ]	[ <b>12.012</b> ]	[ <b>0.213 <math>\mu_D + 0.318 \log k_2</math> (LJ) + 0.070</b> ]	<b>66</b>
$\epsilon + (\epsilon-1)/(2\epsilon+1)$	7	<b>0.973</b>	<b>0.0898</b>	<b>36.233</b>	<b>0.038 <math>\epsilon - 4.061 (\epsilon-1)/(2\epsilon+1) + 1.257</math></b>	<b>67</b>
	(7)	(0.731)	(0.2531)	(2.293)	(0.013 $\epsilon + 0.981 (\epsilon-1)/(2\epsilon+1) - 0.636$ )	68
	[7]	[ <b>0.985</b> ]	[ <b>0.0712</b> ]	[ <b>67.193</b> ]	[ <b>0.042 <math>\epsilon - 4.917 (\epsilon-1)/(2\epsilon+1) + 1.743</math></b> ]	<b>69</b>
$\epsilon + E_T(30)$	7	<b>0.933</b>	<b>0.1417</b>	<b>13.349</b>	<b>0.024 <math>\epsilon - 0.010 E_T(30) + 0.145</math></b>	<b>70</b>
	(7)	(0.728)	(0.2544)	(2.250)	(0.013 $\epsilon + 0.014 E_T(30) - 0.817$ )	71
	[7]	[ <b>0.927</b> ]	[ <b>0.1567</b> ]	[ <b>12.308</b> ]	[ <b>0.027 <math>\epsilon - 0.020 E_T(30) + 0.714</math></b> ]	<b>72</b>
$\epsilon + \pi^*$	7	<b>0.962</b>	<b>0.1066</b>	<b>25.115</b>	<b>0.017 <math>\epsilon + 1.287 \pi^* - 1.130</math></b>	<b>73</b>
	(7)	(0.798)	(0.2236)	(3.498)	(0.022 $\epsilon - 1.676 \pi^* + 0.902$ )	74
	[7]	[ <b>0.950</b> ]	[ <b>0.1310</b> ]	[ <b>18.453</b> ]	[ <b>0.019 <math>\epsilon + 1.232 \pi^* - 0.917</math></b> ]	<b>75</b>
$\epsilon + \log k_2$ (LJ)	7	<b>0.945</b>	<b>0.1287</b>	<b>16.606</b>	<b>0.018 <math>\epsilon + 0.203 \log k_2</math> (LJ) - 0.001</b>	<b>76</b>
	(7)	(0.806)	(0.2197)	(3.698)	(0.025 $\epsilon - 0.434 \log k_2$ (LJ) - 0.754)	77
	[7]	[ <b>0.933</b> ]	[ <b>0.1506</b> ]	[ <b>13.483</b> ]	[ <b>0.020 <math>\epsilon + 0.172 \log k_2</math> (LJ) + 0.138</b> ]	<b>78</b>
$\rho + (\epsilon-1)/(2\epsilon+1)$	7	0.655	0.2965	1.506	0.257 $\rho + 4.969 (\epsilon-1)/(2\epsilon+1) - 2.228$	79
	(7)	(0.725)	(0.2978)	(2.221)	(- 0.043 $\rho + 4.534 (\epsilon-1)/(2\epsilon+1) - 1.838$ )	80
	[7]	[0.625]	[0.3269]	[1.282]	[0.207 $\rho + 4.832 (\epsilon-1)/(2\epsilon+1) - 1.918$ ]	81
$\rho + E_T(30)$	7	0.843	0.2115	4.893	0.050 $\rho + 0.098 E_T(30) - 3.952$	82
	(7)	(0.758)	(0.2821)	(2.706)	(- 0.377 $\rho + 0.066 E_T(30) - 2.294$ )	83
	[7]	[0.823]	[0.2376]	[4.213]	[0.046 $\rho + 0.102 E_T(30) - 3.908$ ]	84
$\rho + \pi^*$	7	<b>0.939</b>	<b>0.1351</b>	<b>14.880</b>	<b>- 0.604 <math>\rho + 3.320 \pi^* - 1.744</math></b>	<b>85</b>

	(7) [7]	(0.773) <b>[0.915]</b>	(0.2747) <b>[0.1693]</b>	(2.963) <b>[10.237]</b>	(- 0.817 $\rho$ + 2.035 $\pi^*$ - 0.643) <b>[- 0.633 <math>\rho</math> + 3.437 <math>\pi^*</math> - 1.604]</b>	86 <b>87</b>
$\rho + \log k_2$ (LJ)	7 (7) [7]	0.888 (0.756) [0.862]	0.1805 (0.2832) [0.2119]	7.465 (2.670) [5.804]	- 0.448 $\rho$ + 0.652 $\log k_2$ (LJ) + 1.123 (- 0.720 $\rho$ + 0.404 $\log k_2$ (LJ) + 1.117) [- 0.472 $\rho$ + 0.671 $\log k_2$ (LJ) + 1.362]	88 89 90
$\gamma + (\epsilon-1)/(2\epsilon+1)$	7 (7) [7]	0.807 (0.778) [0.777]	0.2318 (0.2717) [0.2638]	3.738 (3.074) [3.041]	0.032 $\gamma$ + 3.785 ( $\epsilon-1$ )/(2 $\epsilon+1$ ) - 2.375 (0.021 $\gamma$ + 4.707 ( $\epsilon-1$ )/(2 $\epsilon+1$ ) - 2.552) [0.033 $\gamma$ + 3.873 ( $\epsilon-1$ )/(2 $\epsilon+1$ ) - 2.243]	91 92 93
$\gamma + E_T(30)$	<b>7</b> (7) <b>[7]</b>	<b>0.958</b> (0.766) <b>[0.934]</b>	<b>0.1128</b> (0.2781) <b>[0.1496]</b>	<b>22.233</b> (2.843) <b>[13.662]</b>	<b>0.031 <math>\gamma</math> + 0.093 <math>E_T(30)</math> - 4.553</b> (0.019 $\gamma$ + 0.088 $E_T(30)$ - 4.146) <b>[0.032 <math>\gamma</math> + 0.097 <math>E_T(30)</math> - 4.547]</b>	<b>94</b> 95 <b>96</b>
$\gamma + \pi^*$	7 (7) [7]	0.774 (0.417) [0.751]	0.2485 (0.3933) [0.2765]	2.994 (0.421) [2.588]	0.002 $\gamma$ + 3.130 $\pi^*$ - 2.290 (0.005 $\gamma$ + 1.728 $\pi^*$ - 1.380) [0.002 $\gamma$ + 3.245 $\pi^*$ - 2.177]	97 98 99
$\gamma + \log k_2$ (LJ)	7 (7) [7]	0.812 (0.493) [0.786]	0.2294 (0.3764) [0.2588]	3.858 (0.643) [3.235]	0.012 $\gamma$ + 0.627 $\log k_2$ (LJ) + 0.305 (0.007 $\gamma$ + 0.425 $\log k_2$ (LJ) + 0.180) [0.012 $\gamma$ + 0.651 $\log k_2$ (LJ) + 0.513]	100 101 102
$\eta + (\epsilon-1)/(2\epsilon+1)$	7 (7) [7]	0.738 (0.790) [0.716]	0.2648 (0.2652) [0.2921]	2.395 (3.325) [2.109]	0.616 $\eta$ + 4.437 ( $\epsilon-1$ )/(2 $\epsilon+1$ ) - 2.048 (0.281 $\eta$ + 0.749 ( $\epsilon-1$ )/(2 $\epsilon+1$ ) + 0.468) [0.661 $\eta$ + 4.571( $\epsilon-1$ )/(2 $\epsilon+1$ ) - 1.930]	103 104 105
$\eta + E_T(30)$	<b>7</b> (7) <b>[7]</b>	<b>0.968</b> (0.807) <b>[0.953]</b>	<b>0.0988</b> (0.2554) <b>[0.1269]</b>	<b>29.577</b> (3.742) <b>[19.788]</b>	<b>0.837 <math>\eta</math> + 0.115 <math>E_T(30)</math> - 5.011</b> (0.703 $\eta$ + 0.106 $E_T(30)$ - 4.697) <b>[0.899 <math>\eta</math> + 0.120 <math>E_T(30)</math> - 5.072]</b>	<b>106</b> 107 <b>108</b>
$\eta + \pi^*$	7 (7) [7]	0.775 (0.414) [0.751]	0.2481 (0.3938) [0.2765]	3.007 (0.415) [2.589]	- 0.074 $\eta$ + 3.270 $\pi^*$ - 2.291 (- 0.024 $\eta$ + 1.916 $\pi^*$ - 1.383) [- 0.050 $\eta$ + 3.365 $\pi^*$ - 2.178 ]	109 110 111
$\eta + \log k_2$ (LJ)	7 (7) [7]	0.806 (0.490) [0.781]	0.2325 (0.3771) [0.2613]	3.703 (0.633) [3.135]	0.190 $\eta$ + 0.693 $\log k_2$ (LJ) + 0.593 (0.490 $\eta$ + 0.463 $\log k_2$ (LJ) + 0.348) [0.222 $\eta$ + 0.714 $\log k_2$ (LJ) + 0.791]	112 113 114

 Value in ( ) is for X = CH<sub>3</sub>

 Value in [ ] is for X = C<sub>6</sub>H<sub>5</sub>
**Table 6 – Dual regression of log k<sub>2</sub> vs solvent parameter for the Reaction between TsCl and X-CH(OH)COOH-Pyridine (X = H, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>) (Protic solvents)**

Correlation log k <sub>2</sub> vs Solvent parameters	n	r	s	F	Regression equation log k <sub>2</sub> =	Eqn. no
$\mu_D + (\epsilon-1)/(2\epsilon+1)$	<b>6</b>	<b>0.976</b>	<b>0.1322</b>	<b>30.081</b>	<b>5.775 <math>\mu_D</math> + 4.186 (<math>\epsilon-1</math>)/(2<math>\epsilon+1</math>) - 12.650</b>	<b>115</b>
	(6)	(0.978)	(0.1263)	(32.443)	(5.747 $\mu_D$ + 3.586 ( $\epsilon-1$ )/(2 $\epsilon+1$ ) - 12.591)	116
	[6]	[0.977]	[0.1274]	[31.786]	[5.716 $\mu_D$ + 3.924 ( $\epsilon-1$ )/(2 $\epsilon+1$ ) - 12.225]	117
$\mu_D + E_T(30)$	<b>6</b>	<b>0.973</b>	<b>0.1399</b>	<b>26.647</b>	<b>6.696 <math>\mu_D</math> - 0.017 <math>E_T(30)</math> - 0.025</b>	<b>118</b>
	(6)	(0.976)	(0.1319)	(29.588)	(6.599 $\mu_D$ - 0.023 $E_T(30)$ - 11.213)	119
	[6]	[0.974]	[0.1356]	[27.846]	[6.446 $\mu_D$ - 0.018 $E_T(30)$ - 10.738]	120
$\mu_D + \pi^*$	<b>6</b>	<b>0.975</b>	<b>0.1339</b>	<b>29.259</b>	<b>6.037 <math>\mu_D</math> - 0.194 <math>\pi^*</math> - 11.096</b>	<b>121</b>
	(6)	(0.977)	(0.1273)	(31.884)	(5.990 $\mu_D$ - 0.169 $\pi^*$ - 11.259)	122
	[6]	[0.977]	[0.1285]	[31.164]	[5.981 $\mu_D$ - 0.186 $\pi^*$ - 10.767]	123
$\mu_D + \log k_2$ (LJ)	<b>5</b>	<b>0.992</b>	<b>0.0936</b>	<b>59.941</b>	<b>6.486 <math>\mu_D</math> - 0.021 <math>\log k_2</math> (LJ) - 12.061</b>	<b>124</b>
	(5)	(0.975)	(0.0892)	(52.523)	(6.984 $\mu_D$ - 0.017 $\log k_2$ (LJ) - 12.732)	125
	[5]	[0.989]	[0.1068]	[44.395]	[6.371 $\mu_D$ - 0.026 $\log k_2$ (LJ) - 11.632]	126
$\epsilon + (\epsilon-1)/(2\epsilon+1)$	<b>6</b>	<b>0.951</b>	<b>0.1868</b>	<b>14.345</b>	<b>0.108 <math>\epsilon</math> - 36.152 (<math>\epsilon-1</math>)/(2<math>\epsilon+1</math>) + 13.502</b>	<b>127</b>
	(6)	(0.951)	(0.1869)	(14.305)	(0.108 $\epsilon$ - 36.116 ( $\epsilon-1$ )/(2 $\epsilon+1$ ) + 13.488)	128
	[6]	[0.953]	[0.1825]	[14.696]	[0.107 $\epsilon$ - 35.836 ( $\epsilon-1$ )/(2 $\epsilon+1$ ) + 13.618]	129
$\epsilon + E_T(30)$	<b>6</b>	<b>0.902</b>	<b>0.2623</b>	<b>6.532</b>	<b>0.025 <math>\epsilon</math> + 0.118 <math>E_T(30)</math> - 7.435</b>	<b>130</b>
	(6)	(0.902)	(0.2624)	(6.519)	(0.025 $\epsilon$ + 0.118 $E_T(30)$ - 7.425)	131
	[6]	[0.906]	[0.2535]	[6.887]	[0.024 $\epsilon$ + 0.121 $E_T(30)$ - 7.283]	132
$\epsilon + \pi^*$	6	0.894	0.2720	5.969	0.066 $\epsilon$ + 0.790 $\pi^*$ - 2.710	133

	(6)	(0.894)	(0.2721)	(5.955)	(0.066 $\epsilon$ + 0.788 $\pi^*$ - 2.708)	134
	[6]	[0.894]	[0.2686]	[5.974]	[0.066 $\epsilon$ + 0.778 $\pi^*$ - 2.450]	135
$\epsilon + \log k_2$ (LJ)	5	0.884	0.3421	3.569	0.064 $\epsilon$ + 0.388 $\log k_2$ (LJ) - 1.443	136
	(5)	(0.884)	(0.3422)	(3.563)	(0.064 $\epsilon$ + 0.387 $\log k_2$ (LJ) - 1.444)	137
	[5]	[0.882]	[0.3391]	[3.498]	[0.063 $\epsilon$ + 0.371 $\log k_2$ (LJ) - 0.371]	138
$\rho + (\epsilon-1)/(2\epsilon+1)$	6	0.626	0.4735	0.964	4.744 $\rho$ + 60.671 $(\epsilon-1)/(2\epsilon+1)$ - 32.722	139
	(6)	(0.630)	(0.4664)	(0.988)	(4.873 $\rho$ + 60.255 $(\epsilon-1)/(2\epsilon+1)$ - 32.864)	140
	[6]	[0.632]	[0.4643]	[0.996]	[4.805 $\rho$ + 59.919 $(\epsilon-1)/(2\epsilon+1)$ - 32.184]	141
$\rho + E_T(30)$	6	0.887	0.2799	5.550	- 0.598 $\rho$ + 0.174 $E_T(30)$ - 9.248	142
	(6)	(0.887)	(0.2801)	(5.539)	(- 0.599 $\rho$ + 0.174 $E_T(30)$ - 9.240)	143
	[6]	[0.894]	[0.2685]	[5.968]	[- 0.599 $\rho$ + 0.173 $E_T(30)$ - 8.986]	144
$\rho + \pi^*$	6	0.735	0.4115	1.764	- 9.551 $\rho$ + 4.652 $\pi^*$ + 4.442	145
	(6)	(0.735)	(0.4114)	(1.761)	(- 9.545 $\rho$ + 4.648 $\pi^*$ + 4.439)	146
	[6]	[0.718]	[0.4170]	[1.594]	[- 9.558 $\rho$ + 4.595 $\pi^*$ + 4.707]	147
$\rho + \log k_2$ (LJ)	5	0.706	0.5181	0.992	- 6.996 $\rho$ + 1.731 $\log k_2$ (LJ) + 8.461	148
	(5)	(0.706)	(0.5180)	(0.991)	(- 6.992 $\rho$ + 1.729 $\log k_2$ (LJ) + 8.454)	149
	[5]	[0.695]	[0.5166]	[0.934]	[- 6.947 $\rho$ + 1.675 $\log k_2$ (LJ) + 8.550]	150
$\gamma + (\epsilon-1)/(2\epsilon+1)$	6	0.615	0.4788	0.910	- 0.069 $\gamma$ + 58.216 $(\epsilon-1)/(2\epsilon+1)$ - 29.363	151
	(6)	(0.463)	(0.5325)	(0.409)	(- 0.043 $\gamma$ + 18.770 $(\epsilon-1)/(2\epsilon+1)$ - 8.742)	152
	[6]	[0.473]	[0.5279]	[0.431]	[- 0.046 $\gamma$ + 19.004 $(\epsilon-1)/(2\epsilon+1)$ - 8.310]	153
$\gamma + E_T(30)$	6	0.882	0.2858	5.265	0.006 $\gamma$ + 0.174 $E_T(30)$ - 9.593	154
	(6)	(0.900)	(0.2615)	(6.417)	(0.065 $\gamma$ + 0.190 $E_T(30)$ - 12.279)	155
	[6]	[0.901]	[0.2598]	[6.475]	[0.062 $\gamma$ + 0.189 $E_T(30)$ - 11.691]	156
$\gamma + \pi^*$	6	0.571	0.4981	0.727	- 0.089 $\gamma$ + 2.681 $\pi^*$ - 0.167	157
	(6)	(0.141)	(0.5948)	(0.030)	(- 0.049 $\gamma$ - 0.059 $\pi^*$ + 0.082)	158
	[6]	[0.153]	[0.5919]	[0.036]	[- 0.054 $\gamma$ - 0.088 $\pi^*$ + 0.673]	159
$\gamma + \log k_2$ (LJ)	5	0.575	0.5984	0.493	- 0.075 $\gamma$ + 1.176 $\log k_2$ (LJ) + 3.382	160
	(5)	(0.091)	(0.7186)	(0.008)	(- 0.030 $\gamma$ + 0.009 $\log k_2$ (LJ) + 0.009)	161
	[5]	[0.100]	[0.7148]	[0.010]	[- 0.035 $\gamma$ - 0.010 $\log k_2$ (LJ) + 0.201]	162
$\eta + (\epsilon-1)/(2\epsilon+1)$	6	0.545	0.5087	0.633	- 0.497 $\eta$ - 57.707 $(\epsilon-1)/(2\epsilon+1)$ + 26.838	163
	(6)	(0.539)	(0.5058)	(0.615)	(- 0.505 $\eta$ - 59.639 $(\epsilon-1)/(2\epsilon+1)$ + 27.513)	164
	[6]	[0.549]	[0.5006]	[0.648]	[- 0.515 $\eta$ - 60.999 $(\epsilon-1)/(2\epsilon+1)$ + 28.630]	165
$\eta + E_T(30)$	6	0.885	0.2826	5.414	- 0.035 $\eta$ + 0.165 $E_T(30)$ - 9.230	166
	(6)	(0.887)	(0.2769)	(5.559)	(- 0.031 $\eta$ + 0.166 $E_T(30)$ - 9.504)	167
	[6]	[0.891]	[0.2719]	[5.781]	[- 0.033 $\eta$ + 0.165 $E_T(30)$ - 8.994]	168
$\eta + \pi^*$	6	0.769	0.3878	2.172	- 0.316 $\eta$ + 2.057 $\pi^*$ - 1.326	169
	(6)	(0.766)	(0.3860)	(2.134)	(- 0.311 $\eta$ + 2.052 $\pi^*$ - 1.565)	170
	[6]	[0.770]	[0.3825]	[2.179]	[- 0.312 $\eta$ + 2.037 $\pi^*$ - 1.087]	171
$\eta + \log k_2$ (LJ)	5	0.746	0.4867	1.256	- 0.275 $\eta$ + 0.912 $\log k_2$ (LJ) + 1.590	172
	(5)	(0.741)	(0.4845)	(1.219)	(- 0.269 $\eta$ + 0.901 $\log k_2$ (LJ) + 1.327)	173
	[5]	[0.746]	[0.4785]	[1.254]	[- 0.269 $\eta$ + 0.890 $\log k_2$ (LJ) + 1.774]	174

 Value in ( ) is for X = CH<sub>3</sub>

 Value in [ ] is for X = C<sub>6</sub>H<sub>5</sub>
**Table 7 – Best- fit dual regression equation for the Reaction between TsCl and X – CH(OH)COOH–Pyridine (X = H, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>) (Aprotic solvents)**

Correlation log k <sub>2</sub> vs Solvent parameters	n	r	s	F	Regression equation (log k <sub>2</sub> =)	Eqn. no
$\mu_D + (\epsilon-1)/(2\epsilon+1)$	7	0.958	0.1125	22.352	0.471 $\mu_D$ - 4.520 $(\epsilon-1)/(2\epsilon+1)$ + 0.936	55
	[7]	[0.971]	[0.1009]	[32.447]	[0.530 $\mu_D$ - 5.480 $(\epsilon-1)/(2\epsilon+1)$ + 1.399]	57
$\mu_D + \pi^*$	7	0.965	0.1028	27.183	0.202 $\mu_D$ + 1.764 $\pi^*$ - 1.687	61
	[7]	[0.951]	[0.1293]	[18.970]	[0.218 $\mu_D$ + 1.759 $\pi^*$ - 1.525]	63
$\mu_D + \log k_2$ (LJ)	7	0.940	0.1338	15.222	0.194 $\mu_D$ + 0.332 $\log k_2$ (LJ) - 0.070	64
	[7]	[0.926]	[0.1582]	[12.012]	[0.213 $\mu_D$ + 0.318 $\log k_2$ (LJ) + 0.070]	66

$\varepsilon + (\varepsilon-1)/(2\varepsilon+1)$	7 [7]	0.973 [0.985]	0.0898 [0.0712]	36.233 [67.193]	$0.038 \varepsilon - 4.061 (\varepsilon-1)/(2\varepsilon+1) + 1.257$ [ $0.042 \varepsilon - 4.917 (\varepsilon-1)/(2\varepsilon+1) + 1.743$ ]	67 69
$\varepsilon + E_T(30)$	7 [7]	0.933 [0.927]	0.1417 [0.1567]	13.349 [12.308]	$0.024 \varepsilon - 0.010 E_T(30) + 0.145$ [ $0.027 \varepsilon - 0.020 E_T(30) + 0.714$ ]	70 72
$\varepsilon + \pi^*$	7 [7]	0.962 [0.950]	0.1066 [0.1310]	25.115 [18.453]	$0.017 \varepsilon + 1.287 \pi^* - 1.130$ [ $0.019 \varepsilon + 1.232 \pi^* - 0.917$ ]	73 75
$\varepsilon + \log k_2$ (LJ)	7 [7]	0.945 [0.933]	0.1287 [0.1506]	16.606 [13.483]	$0.018 \varepsilon + 0.203 \log k_2$ (LJ) $- 0.001$ [ $0.020 \varepsilon + 0.172 \log k_2$ (LJ) $+ 0.138$ ]	76 78
$\rho + \pi^*$	7 [7]	0.939 [0.915]	0.1351 [0.1693]	14.880 [10.237]	$- 0.604 \rho + 3.320 \pi^* - 1.744$ [ $- 0.633 \rho + 3.437 \pi^* - 1.604$ ]	85 87
$\gamma + E_T(30)$	7 [7]	0.958 [0.934]	0.1128 [0.1496]	22.233 [13.662]	$0.031 \gamma + 0.093 E_T(30) - 4.553$ [ $0.032 \gamma + 0.097 E_T(30) - 4.547$ ]	94 96
$\eta + E_T(30)$	7 [7]	0.968 [0.953]	0.0988 [0.1269]	29.577 [19.788]	$0.837 \eta + 0.115 E_T(30) - 5.011$ [ $0.899 \eta + 0.120 E_T(30) - 5.072$ ]	106 108

Value in ( ) is for X = CH<sub>3</sub>

Value in [ ] is for X = C<sub>6</sub>H<sub>5</sub>

**Table 8 – Best- fit dual regression equation for the Reaction between TsCl and X – CH(OH)COOH – Pyridine (X = H, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>) (Protic solvents)**

Correlation log k <sub>2</sub> vs Solvent parameters	n	r	s	F	Regression equation log k <sub>2</sub> =	Eqn. no
$\mu_D + (\varepsilon-1)/(2\varepsilon+1)$	6	0.976	0.1322	30.081	$5.775 \mu_D + 4.186 (\varepsilon-1)/(2\varepsilon+1) - 12.650$	115
	(6)	(0.978)	(0.1263)	(32.443)	$(5.747 \mu_D + 3.586 (\varepsilon-1)/(2\varepsilon+1)) - 12.591$	116
	[6]	[0.977]	[0.1274]	[31.786]	$[5.716 \mu_D + 3.924 (\varepsilon-1)/(2\varepsilon+1) - 12.225]$	117
$\mu_D + E_T(30)$	6	0.973	0.1399	26.647	$6.696 \mu_D - 0.017 E_T(30) - 0.025$	118
	(6)	(0.976)	(0.1319)	(29.588)	$(6.599 \mu_D - 0.023 E_T(30) - 11.213)$	119
	[6]	[0.974]	[0.1356]	[27.846]	$[6.446 \mu_D - 0.018 E_T(30) - 10.738]$	120
$\mu_D + \pi^*$	6	0.975	0.1339	29.259	$6.037 \mu_D - 0.194 \pi^* - 11.096$	121
	(6)	(0.977)	(0.1273)	(31.884)	$(5.990 \mu_D - 0.169 \pi^* - 11.259)$	122
	[6]	[0.977]	[0.1285]	[31.164]	$[5.981 \mu_D - 0.186 \pi^* - 10.767]$	123
$\mu_D + \log k_2$ (LJ)	5	0.992	0.0936	59.941	$6.486 \mu_D - 0.021 \log k_2$ (LJ) $- 12.061$	124
	(5)	(0.975)	(0.0892)	(52.523)	$(6.984 \mu_D - 0.017 \log k_2$ (LJ) $- 12.732)$	125
	[5]	[0.989]	[0.1068]	[44.395]	$[6.371 \mu_D - 0.026 \log k_2$ (LJ) $- 11.632]$	126
$\varepsilon + (\varepsilon-1)/(2\varepsilon+1)$	6	0.951	0.1868	14.345	$0.108 \varepsilon - 36.152 (\varepsilon-1)/(2\varepsilon+1) + 13.502$	127
	(6)	(0.951)	(0.1869)	(14.305)	$(0.108 \varepsilon - 36.116 (\varepsilon-1)/(2\varepsilon+1) + 13.488)$	128
	[6]	[0.953]	[0.1825]	[14.696]	$[0.107 \varepsilon - 35.836 (\varepsilon-1)/(2\varepsilon+1) + 13.618]$	129
$\varepsilon + E_T(30)$	6	0.902	0.2623	6.532	$0.025 \varepsilon + 0.118 E_T(30) - 7.435$	130
	(6)	(0.902)	(0.2624)	(6.519)	$(0.025 \varepsilon + 0.118 E_T(30) - 7.425)$	131
	[6]	[0.906]	[0.2535]	[6.887]	$[0.024 \varepsilon + 0.121 E_T(30) - 7.283]$	132

Value in ( ) is for X = CH<sub>3</sub>

Value in [ ] is for X = C<sub>6</sub>H<sub>5</sub>

### 3.3 Triple solvent parameter regression analyses

Triple solvent parameter regression analyses were performed against log k<sub>2</sub> for aprotic and protic solvents were obtained by using the equation,

$$\log k_2 = \log k_0 + a_1 X_1 + a_2 X_2 + a_3 X_3$$

Where, X<sub>1</sub>, X<sub>2</sub> and X<sub>3</sub> are independent variables.

The results of triple regression analyses are given in Table 9 and 10.

The best fit triple regression equations are given in Table 11 for aprotic and protic solvents respectively.



**Table 9 – Triple regression of log k<sub>2</sub> vs solvent parameter for the Reaction between TsCl and X-CH(OH)COOH-Pyridine (X = H, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>) (Aprotic solvents)**

Correlation log k <sub>2</sub> vs Solvent parameters	n	r	s	F	Regression equation log k <sub>2</sub> =	Eqn. no
$(\epsilon-1)/(2\epsilon+1) + \mu_D + \log k_2$ (LJ)	7	0.725	0.2511	1.107	$-2.684 (\epsilon-1)/(2\epsilon+1) + 0.273 \mu_D + 0.045 \log k_2$ (LJ) + 0.601	175
	(7)	(0.852)	(0.2605)	(2.657)	$(-1.307 (\epsilon-1)/(2\epsilon+1) + 0.356 \mu_D - 0.086 \log k_2$ (LJ) - 0.330)	176
	[7]	[0.969]	[0.1198]	[15.259]	$[-2.182 (\epsilon-1)/(2\epsilon+1) + 0.313 \mu_D + 0.315 \log k_2$ (LJ) + 0.722]	177
$(\epsilon-1)/(2\epsilon+1) + \mu_D + E_T(30)$	7	0.853	0.1904	2.665	$-4.127 (\epsilon-1)/(2\epsilon+1) + 0.130 \mu_D + 0.093 E_T(30) - 2.307$	178
	(7)	(0.851)	(0.2618)	(2.622)	$(-1.030 (\epsilon-1)/(2\epsilon+1) + 0.354 \mu_D - 0.012 E_T(30) + 0.136)$	179
	[7]	[0.990]	[0.0694]	[47.541]	$[-6.070 (\epsilon-1)/(2\epsilon+1) + 0.451 \mu_D + 0.047 E_T(30) - 0.095]$	180
$(\epsilon-1)/(2\epsilon+1) + \mu_D + \pi^*$	7	0.723	0.2516	1.098	$-2.669 (\epsilon-1)/(2\epsilon+1) + 0.280 \mu_D + 0.073 \pi^* + 0.489$	181
	(7)	(0.852)	(0.2609)	(2.646)	$(-1.538 (\epsilon-1)/(2\epsilon+1) + 0.361 \mu_D - 0.355 \pi^* + 0.093)$	182
	[7]	[0.970]	[0.1181]	[15.748]	$[-1.583 (\epsilon-1)/(2\epsilon+1) + 0.299 \mu_D + 1.449 \pi^* - 0.834]$	183
$\log k_2$ (LJ) + $\mu_D + E_T(30)$	7	0.794	0.2216	1.705	$-0.249 \log k_2$ (LJ) - 0.032 $\mu_D + 0.106 E_T(30) - 4.407$	184
	(7)	(0.848)	(0.2639)	(2.564)	$(-0.035 \log k_2$ (LJ) + 0.314 $\mu_D - 0.012 E_T(30) - 0.239)$	185
	[7]	[0.934]	[0.1733]	[6.778]	$[0.436 \log k_2$ (LJ) + 0.284 $\mu_D - 0.041 E_T(30) - 1.697]$	186
$\log k_2$ (LJ) + $\mu_D + \pi^*$	7	0.693	0.2627	0.924	$-0.342 \log k_2$ (LJ) + 0.169 $\mu_D + 1.828 \pi^* - 1.982$	187
	(7)	(0.853)	(0.2599)	(2.674)	$(-0.473 \log k_2$ (LJ) + 0.130 $\mu_D + 1.791 \pi^* - 2.449)$	188
	[7]	[0.978]	[0.1015]	[21.663]	$[-0.934 \log k_2$ (LJ) + 0.282 $\mu_D + 5.568 \pi^* - 5.301]$	189

 Value in ( ) is for X = CH<sub>3</sub>

 Value in [ ] is for X = C<sub>6</sub>H<sub>5</sub>
**Table 10 – Triple regression of log k<sub>2</sub> vs solvent parameter for the Reaction between TsCl and X-CH(OH)COOH-Pyridine (X = H, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>) (Protic solvents)**

Correlation log k <sub>2</sub> vs Solvent parameters	n	r	s	F	Regression equation log k <sub>2</sub> =	Eqn. no
$(\epsilon-1)/(2\epsilon+1) + \mu_D + \log k_2$ (LJ)	5	0.995	0.1006	34.880	$5.899 (\epsilon-1)/(2\epsilon+1) + 8.310 \mu_D + 0.033 \log k_2$ (LJ) - 17.721	190
	(5)	(0.994)	(0.1144)	(26.212)	$(4.897 (\epsilon-1)/(2\epsilon+1) + 6.062 \mu_D + 0.090 \log k_2$ (LJ) - 13.596)	191
	[5]	[0.992]	[0.1293]	[20.309]	$[5.128 (\epsilon-1)/(2\epsilon+1) + 6.013 \mu_D + 0.079 \log k_2$ (LJ) - 13.172]	192
$(\epsilon-1)/(2\epsilon+1) + \mu_D + E_T(30)$	6	0.979	0.1513	15.403	$5.241 (\epsilon-1)/(2\epsilon+1) + 6.890 \mu_D - 0.042 E_T(30) - 12.918$	193
	(6)	(0.980)	(0.1455)	(16.391)	$(4.530 (\epsilon-1)/(2\epsilon+1) + 6.756 \mu_D - 0.038 E_T(30) - 12.832)$	194
	[6]	[0.980]	[0.1461]	[16.161]	$[4.955 (\epsilon-1)/(2\epsilon+1) + 6.631 \mu_D - 0.035 E_T(30) - 12.497]$	195
$(\epsilon-1)/(2\epsilon+1) + \mu_D + \pi^*$	6	0.976	0.1617	13.407	$3.274 (\epsilon-1)/(2\epsilon+1) + 5.822 \mu_D - 0.053 \pi^* - 12.315$	196
	(6)	(0.978)	(0.1540)	(14.560)	$(2.643 (\epsilon-1)/(2\epsilon+1) + 5.816 \mu_D - 0.056 \pi^* - 12.244)$	197
	[6]	[0.978]	[0.1531]	[14.656]	$[2.903 (\epsilon-1)/(2\epsilon+1) + 5.788 \mu_D - 0.070 \pi^* - 11.839]$	198
$\log k_2$ (LJ) + $\mu_D + E_T(30)$	5	0.996	0.0868	46.993	$-0.034 \log k_2$ (LJ) + 4.913 $\mu_D + 0.063 E_T(30) - 12.611$	199
	(5)	(0.996)	(0.0963)	(37.082)	$(-0.027 \log k_2$ (LJ) + 4.962 $\mu_D + 0.057 E_T(30) - 12.632)$	200
	[5]	[0.994]	[0.1101]	[28.107]	$[-0.044 \log k_2$ (LJ) + 4.827 $\mu_D + 0.061 E_T(30) - 12.174]$	201
$\log k_2$ (LJ) + $\mu_D + \pi^*$	5	0.997	0.0859	47.901	$1.170 \log k_2$ (LJ) + 6.068 $\mu_D - 2.319 \pi^* - 7.629$	202
	(5)	(0.996)	(0.0956)	(37.671)	$(1.076 \log k_2$ (LJ) + 6.018 $\mu_D - 2.123 \pi^* - 8.070)$	203
	[5]	[0.994]	[0.1093]	[28.526]	$[1.138 \log k_2$ (LJ) + 5.927 $\mu_D - 2.275 \pi^* - 7.287]$	204

 Value in ( ) is for X = CH<sub>3</sub>

 Value in [ ] is for X = C<sub>6</sub>H<sub>5</sub>

**Table 11 – Best-fit triple regression equation for the Reaction between TsCl and X-CH(OH)COOH – Pyridine (X = H, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>)**

Correlation log k <sub>2</sub> vs Solvent parameters	n	r	s	F	Regression equation log k <sub>2</sub> =	Eqn. no
<b>(Aprotic solvents)</b>						
$(\epsilon-1)/(2\epsilon+1) + \mu_D + \log k_2$ (LJ)	[7]	[0.969]	[0.1198]	[15.259]	$[- 2.182 (\epsilon-1)/(2\epsilon+1) + 0.313 \mu_D + 0.315 \log k_2$ (LJ) + 0.722]	177
$(\epsilon-1)/(2\epsilon+1) + \mu_D + E_T(30)$	[7]	[0.990]	[0.0694]	[47.541]	$[- 6.070 (\epsilon-1)/(2\epsilon+1) + 0.451 \mu_D + 0.047 E_T(30) - 0.095]$	180
$(\epsilon-1)/(2\epsilon+1) + \mu_D + \pi^*$	[7]	[0.970]	[0.1181]	[15.748]	$[- 1.583 (\epsilon-1)/(2\epsilon+1) + 0.299 \mu_D + 1.449 \pi^* - 0.834]$	183
$\log k_2$ (LJ) + $\mu_D + \pi^*$	[7]	[0.978]	[0.1015]	[21.663]	$[- 0.934 \log k_2$ (LJ) + 0.282 $\mu_D$ + 5.568 $\pi^*$ - 5.301]	189
$\log k_2$ (LJ) + $\mu_D + E_T(30)$	[7]	[0.934]	[0.1733]	[6.778]	$[0.436 \log k_2$ (LJ) + 0.284 $\mu_D$ - 0.041 $E_T(30)$ - 1.697]	186
<b>(Protic solvents)</b>						
$(\epsilon-1)/(2\epsilon+1) + \mu_D + \log k_2$ (LJ)	5	0.995	0.1006	34.880	$5.899 (\epsilon-1)/(2\epsilon+1) + 8.310 \mu_D + 0.033 \log k_2$ (LJ) - 17.721	190
	(5)	(0.994)	(0.1144)	(26.212)	$(4.897 (\epsilon-1)/(2\epsilon+1) + 6.062 \mu_D + 0.090 \log k_2$ (LJ) - 13.596)	191
	[5]	[0.992]	[0.1293]	[20.309]	$[5.128 (\epsilon-1)/(2\epsilon+1) + 6.013 \mu_D + 0.079 \log k_2$ (LJ) - 13.172]	192
$(\epsilon-1)/(2\epsilon+1) + \mu_D + E_T(30)$	6	0.979	0.1513	15.403	$5.241 (\epsilon-1)/(2\epsilon+1) + 6.890 \mu_D - 0.042 E_T(30) - 12.918$	193
	(6)	(0.980)	(0.1455)	(16.391)	$(4.530 (\epsilon-1)/(2\epsilon+1) + 6.756 \mu_D - 0.038 E_T(30) - 12.832)$	194
	[6]	[0.980]	[0.1461]	[16.161]	$[4.955 (\epsilon-1)/(2\epsilon+1) + 6.631 \mu_D - 0.035 E_T(30) - 12.497]$	195
$(\epsilon-1)/(2\epsilon+1) + \mu_D + \pi^*$	6	0.976	0.1617	13.407	$3.274 (\epsilon-1)/(2\epsilon+1) + 5.822 \mu_D - 0.053 \pi^* - 12.315$	196
	(6)	(0.978)	(0.1540)	(14.560)	$(2.643 (\epsilon-1)/(2\epsilon+1) + 5.816 \mu_D - 0.056 \pi^* - 12.244)$	197
	[6]	[0.978]	[0.1531]	[14.656]	$[2.903 (\epsilon-1)/(2\epsilon+1) + 5.788 \mu_D - 0.070 \pi^* - 11.839]$	198
$\log k_2$ (LJ) + $\mu_D + E_T(30)$	5	0.996	0.0868	46.993	$- 0.034 \log k_2$ (LJ) + 4.913 $\mu_D$ + 0.063 $E_T(30)$ - 12.611	199
	(5)	(0.996)	(0.0963)	(37.082)	$(- 0.027 \log k_2$ (LJ) + 4.962 $\mu_D$ + 0.057 $E_T(30)$ - 12.632)	200
	[5]	[0.994]	[0.1101]	[28.107]	$[- 0.044 \log k_2$ (LJ) + 4.827 $\mu_D$ + 0.061 $E_T(30)$ - 12.174]	201
$\log k_2$ (LJ) + $\mu_D + \pi^*$	5	0.997	0.0859	47.901	$1.170 \log k_2$ (LJ) + 6.068 $\mu_D$ - 2.319 $\pi^*$ - 7.629	202
	(5)	(0.996)	(0.0956)	(37.671)	$(1.076 \log k_2$ (LJ) + 6.018 $\mu_D$ - 2.123 $\pi^*$ - 8.070)	203
	[5]	[0.994]	[0.1093]	[28.526]	$[1.138 \log k_2$ (LJ) + 5.927 $\mu_D$ - 2.275 $\pi^*$ - 7.287]	204

 Value in ( ) is for X = CH<sub>3</sub>

 Value in [ ] is for X = C<sub>6</sub>H<sub>5</sub>

From the dual regression analyses for aprotic solvents  $\mu_D$  along with  $(\epsilon-1)/(2\epsilon+1)$ ,  $\pi^*$  and  $\log k_2$  (LJ),  $\epsilon$  along with  $(\epsilon-1)/(2\epsilon+1)$ ,  $E_T(30)$ ,  $\pi^*$  and  $\log k_2$  (LJ),  $\rho$  along with  $\pi^*$ ,  $\gamma$  along with  $E_T(30)$  and  $\eta$  along with  $E_T(30)$  gives satisfactory correlation.

Triple regression analyses show a good correlation for protic solvents and for aprotic solvents good correlation is obtained only for mandelic acid. Sign of the co-efficients in regression equation shows the contribution of the parameters in the studied reaction.

#### 4. Conclusion

The kinetic studies on the reaction of *p*-toluenesulfonyl Chloride (TsCl) with  $\alpha$ -hydroxy acid(s) in the presence of pyridine under equimolar conditions in various solvents have been investigated by conductometric method. The rate constants are obtained by the least square method. In order to understand the role of solvents in our studied reactions the  $\log k_2$  values against various solvent

parameters at microscopic and macroscopic levels are subjected to simple and multiple regression analyses. Simple regression analyses gives only poor correlation and multiple regression analysis shows good correlation. From the results we conclude that more than one solvent parameter may influence the rate of the reaction.

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