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

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Abstract

Kinetics of the reaction of *p*-toluenesulfonyl Chloride (TsCl) with α-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

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investigations of reaction series are relatively few. Hence, we planned to study the solvent effects of the nucleophilic substitution reaction of TsCl with α-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 α-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).

$$x_2-x_1 = k_2\, C_0\, [t_1x_1-t_2x_2] - k_2C_\infty x_\infty\, [t_1-t_2]$$

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 $-(t_1x_1-t_2x_2)$ 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 α – hydroxy acid(s) (X – CHOHCOOH) 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			
Aprotic	**ε**	**μ_D**	**ρ**	**γ**	**η**	**(ε-1)/(2ε+1)**	**$E_T(30)$**	**π***	**log $k_{2\ (n\text{-}Pr3N + MeI)}$**
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
Protic									
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

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ε = Dielectric constant, μ_D = Dipole moment, ρ = Density, γ = Surface tension, η = Viscocity, (ε-1)/(2ε+1) = Kirkwood function, $E_T(30)$ = Dimroth – Reichardt constant, π* = Polarity / Polarizability, log k_2 LJ = log $k_{2\ (n\text{-}Pr3N\ +\ MeI)}$ = 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 α – 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 co-efficient.

Table – 2 and 3 gives the result of simple regression analyses of log k_2 in 7 aprotic and 6 protic solvents with ε (Dielectric constant), μ_D (Dipole moment), ρ (Density), γ (Surface tension), η(Viscosity), (ε-1)/(2ε+1) (Kirkwood function), $E_T(30)$ (Dimroth – Reichardt constant), π* (Polarity / Polarizability), and log $k_{2\ (n\text{-}Pr3N\ +\ MeI)}$ (Lassau and Jungers scale) respectively.

The results show that only dielectric constant (ε) of aprotic solvents and dipole moment (μ_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, α – 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.

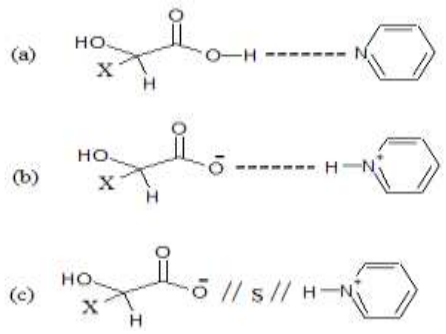

Table 2 – Simple regression of log k_2 vs solvent parameter for the reaction between TsCl and X-CH(OH)COOH-Pyridine (X = H, CH_3, C_6H_5) (Aprotic solvents)

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

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$E_T(30)$	0.095 $E_T(30)$ – 3.768	7	0.841	0.1900	12.085	19
	(0.090 $E_T(30)$ – 3.654)	(7)	(0.721)	(0.2682)	(5.404)	20
	[0.099 $E_T(30)$ – 3.739]	[7]	[0.677]	[0.2127]	[10.486]	21
π*	3.223 π* – 2.294	7	0.774	0.2223	7.482	22
	(1.898 π* – 1.382)	(7)	(0.414)	(0.3521)	(1.035)	23
	[3.331 π* – 2.177]	[7]	[0.563]	[0.2474]	[6.454]	24
log k_2 (LJ)	0.699 log k_2 (LJ) + 0.694	7	0.797	0.2119	8.733	25
	(0.479 log k_2 (LJ) + 0.427)	(7)	(0.496)	(0.3357)	(1.636)	26
	[0.721 log k_2 (LJ) + 0.910]	[7]	[0.595]	[0.2384]	[7.335]	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.
ε	0.058 ε – 0.2074	6	0.835	0.2891	9.204	28
	(0.057 ε – 2.284)	(6)	(0.829)	(0.2909)	(8.793)	29
	[0.058 ε – 1.824]	[6]	[0.836]	[0.2853]	[9.250]	30
μ_D	**0.972 μ_D – 2.667**	**6**	**0.972**	**0.1238**	**67.938**	**31**
	(0.963 μ_D – 2.882)	**(6)**	**(0.975)**	**(0.1166)**	**(75.589)**	**32**
	[8.325 μ_D – 14.821]	**[6]**	**[0.945]**	**[0.1701]**	**[33.268]**	**33**
ρ	– 1.058 ρ + 0.050	6	0.230	0.5111	0.224	34
	(– 0.994 ρ – 0.235)	(6)	(0.218)	(0.5076)	(0.200)	35
	[– 1.049ρ + 0.278]	[6]	[0.231]	[0.5052]	[0.225]	36
γ	– 0.017 γ – 0.408	6	0.243	0.5095	0.250	37
	(– 0.046 γ – 0.019)	(6)	(0.139)	(0.5152)	(0.078)	38
	[– 0.049 γ + 0.514]	[6]	[0.148]	[0.5135]	[0.089]	39
η	– 0.136 η – 0.528	6	0.498	0.4554	1.320	40
	(– 0.131 η – 0.768)	(6)	(0.488)	(0.4541)	(1.249)	41
	[– 0.134 η – 0.295]	[6]	[0.497]	[0.4500]	[1.311]	42
(ε+1) / (2ε+1)	23.671 (ε+1) / (2ε+1) – 11.740	6	0.484	0.4596	1.224	43
	(20.832 (ε+1) / (2ε+1) – 10.677)	(6)	(0.434)	(0.4687)	(0.927)	44
	[17.337 (ε+1) / (2ε+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
π*	0.037 π* – 0.857	6	0.016	0.5251	0.001	49
	(0.061 π* – 1.102)	(6)	(0.026)	(0.5200)	(0.003)	50
	[0.041 π* – 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.
Aprotic solvents						
ε	0.022 ε – 0.226	7	0.931	0.1278	32.727	1
	[0.023 ε – 0.050]	[7]	[0.925]	[0.1424]	[29.569]	3
Protic solvents						
μ_D	0.972 μ_D – 2.667	6	0.972	0.1238	67.938	31
	(0.963 μ_D – 2.882)	(6)	(0.975)	(0.1166)	(75.589)	32
	[8.325 μ_D – 14.821]	[6]	[0.945]	[0.1701]	[33.268]	33

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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 μ_D along with (ε-1)/(2ε+1), π* and log k_2 (LJ), ε along with (ε-1) / (2ε+1), $E_T(30)$, π* and log k_2 (LJ), ρ along with π*, γ along with $E_T(30)$ and η along with $E_T(30)$ gives satisfactory correlation. For protic solvents μ_D along with (ε-1)/(2ε+1), $E_T(30)$, π* and log k_2 (LJ) and ε along with (ε-1)/(2ε+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_3, C_6H_5) (Aprotic solvents)

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

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

Value in ( ) is for X = CH_3

Value in [ ] is for X = C_6H_5

Table 6 – Dual 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)

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

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

Value in ( ) is for X = CH_3

Value in [ ] is for X = C_6H_5

Table 7 – Best- fit dual regression equation for the Reaction between TsCl and X – CH(OH)COOH–Pyridine (X = H, CH_3, C_6H_5) (Aprotic solvents)

Correlation log k_2 vs Solvent parameters	n	r	s	F	Regression equation (log k_2 =)	Eqn. no
μ_D + (ε-1)/(2ε+1)	7 [7]	0.958 [0.971]	0.1125 [0.1009]	22.352 [32.447]	0.471 μ_D – 4.520 (ε-1)/(2ε+1) + 0.936 [0.530 μ_D – 5.480 (ε-1)/(2ε+1) +1.399]	55 57
μ_D + π*	7 [7]	0.965 [0.951]	0.1028 [0.1293]	27.183 [18.970]	0.202 μ_D + 1.764 π* – 1.687 [0.218 μ_D + 1.759 π* – 1.525]	61 63
μ_D + log k_2 (LJ)	7 [7]	0.940 [0.926]	0.1338 [0.1582]	15.222 [12.012]	0.194 μ_D + 0.332 log k_2 (LJ) – 0.070 [0.213 μ_D + 0.318 log k_2 (LJ) + 0.070]	64 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_3

Value in [ ] is for X = C_6H_5

Table 8 – Best- fit dual regression equation for the Reaction between TsCl and X – CH(OH)COOH – Pyridine (X = H, CH_3, C_6H_5) (Protic solvents)

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

Value in ( ) is for X = CH_3

Value in [ ] is for X = C_6H_5

3.3 Triple solvent parameter regression analyses

Triple solvent parameter regression analyses were performed against log k_2 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_1, X_2 and X_3 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.

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Table 9 – Triple 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) (Aprotic solvents)

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

Value in ( ) is for X = CH_3

Value in [ ] is for X = C_6H_5

Table 10 – Triple 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)

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

Value in ( ) is for X = CH_3

Value in [ ] is for X = C_6H_5

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Table 11 – Best- fit triple regression equation for the Reaction between TsCl and X–CH(OH)COOH – Pyridine (X = H, CH_3, C_6H_5)

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

Value in ( ) is for X = CH_3

Value in [ ] is for X = C_6H_5

From the dual regression analyses for aprotic solvents μ_D along with $(\varepsilon-1)/(2\varepsilon+1)$, π^* and log k_2 (LJ), ε along with $(\varepsilon-1)/(2\varepsilon+1)$, $E_T(30)$, π^* and log k_2 (LJ), ρ along with π^*, γ along with $E_T(30)$ and η 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 α-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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