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Nucleophilic Substitution at Sulfonyl Sulfur. Kinetic Investigation on the Reactions of Tosyl Chloride with *p*-Substituted Phenol(s) and Triethylamine in Acetone / Acetonitrile

Nagarajan Vembu* and Chandrasekaran Arunmozhithevan¹

*Department of Chemistry, Urumu Dhanalakshmi College, Tamilnadu, Tiruchirapalli, India

¹Department of Chemistry Mookambigai College of Engineering, Tamilnadu, Keeranur, India

ABSTRACT

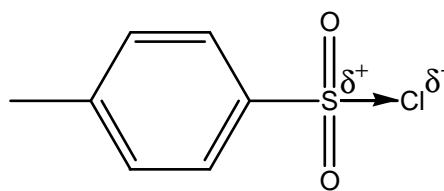
Second order rate constants of the reactions of tosyl chloride with *p*- substituted phenol(s) and triethylamine in acetone / acetonitrile under equimolar conditions are determined. The reaction follow second order overall and first order with respect to each of the reactants viz substrate and nucleophile. The rate constant (k_2) have been determined by conductometric method using Guggenheim principle at four different temperatures. The rate constant increases for electron with-drawing substituents and decreases for electron donating substituents in the nucleophile. Activation parameters are obtained by applying the usual methods. The Hammett and Bronsted plots have been found linear. This may be explained on the basis of electronic effects of substituents at the reaction centre. Kinetic data and product analyses indicate that the reaction proceeds through a synchronous direct bimolecular nucleophilic attack on the sulfur centre.

Keywords: Kinetics, nucleophilic substitutions at sulfur / substituent effects , sulfonyl transfer reactions.

INTRODUCTION

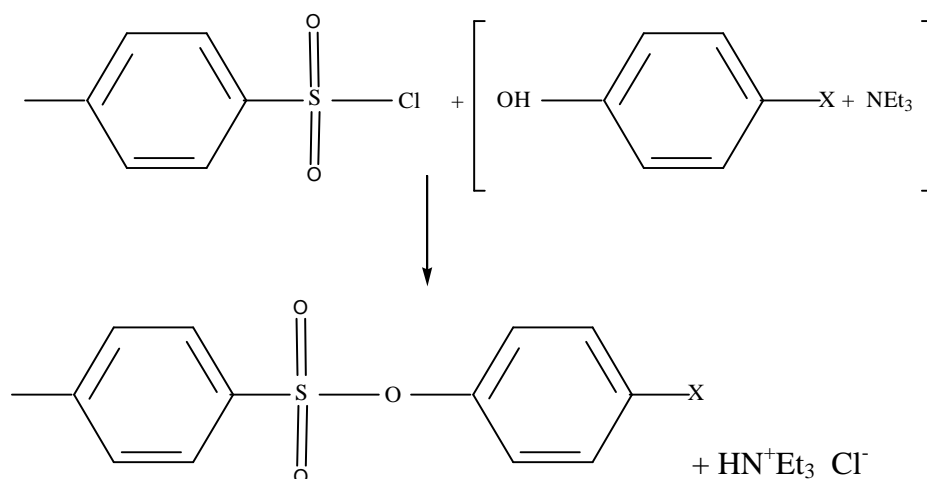
Nucleophilic substitution reactions of sulfonyl chlorides are well known for making sulfonamides, sulfonic acid esters and other sulfonic acid derivatives. Some of these products, notably those sulfonamides known as sulfa drugs, are important in themselves, while others are useful intermediates. Certain sulfonamides are used to make sulfonylureas such as tolbutamide and tolazamide, which are widely used as drugs for non- insulin dependent diabetics[1]. Sulfonyl transfer is an important chemical modification of enzymes[2-3]. Aromatic sulfonyl chlorides find applications in the synthesis of ligands for novel catalytic processes and in radical reactions. Functional aromatic multisulfonyl chlorides have been shown to be valuable intermediates for the preparation of molecular receptors with high and unusual selectivity[4]. Kinetics is concerned with the rate reaction, the influence of various conditions on these rates and mechanism by which a reaction occurs. The subject of chemical kinetics cover not only reaction rate but also covers a wide range of studies, which includes empirical studies of the effects of concentration, temperature, pH, solvent etc., on reaction of various types[5-8].

Arylsulfonyl halides are convenient model compounds for experimental investigations of different nucleophilic processes at sulfonyl sulfur[9-10]. The reactivity of tosyl chloride has been ascribed to a polar effect in which the electron with-drawing Cl induces an electron deficient centre at the tetra co-ordinated sulfur atom holding the halogen atom, thereby, facilitating the approach of a nucleophile towards the sulfur atom.



Much work has not been done on the organic compounds containing the reaction of another activated halide, at a tetra co-ordinate sulfur in the side chain of an aromatic ring, which is found to be a good substrate for nucleophilic substitution reactions [9, 11-13]; However, Banjoko and Okwuiwe have reported the kinetics of nucleophilic substitution reaction of sodium benzoate(s) with benzenesulfonyl chloride in methanol[10]. They concluded that the substitutions at sulfonyl sulfur would take place through the S_N2 mechanism. The kinetics of nucleophilic substitution reaction of tosyl chloride with *p*-substituted benzoic acid(s) and triethylamine in aprotic solvents were reported in the literature [14]. We have also made similar investigation on the reaction of tosyl chloride with *p*-substituted phenol(s) and triethylamine in acetone / ACN with a view to study the substituent effects in the nucleophile and the solvation behaviour of these solvents. We report here our findings on the title reaction.

The reaction of tosyl chloride with *p*-substituted phenol(s) and triethylamine in acetone / ACN were studied under second order conditions, according to the following equation.



X = *p*-NO₂, *p*-CN, *p*-Cl, *p*-Br, *p*-F, *p*-I, *p*-OCH₃
 Rate = $k_2[\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Cl}][\text{p-XC}_6\text{H}_4\text{OH} \cdot \text{NEt}_3]$

MATERIALS AND METHODS

Materials:

Tosyl chloride(TsCl), *p*-substituted phenols (*p*-XC₆H₄OH), triethylamine(NEt₃), acetone and acetonitrile (analytical grade) were purified before use by either recrystallisation (or) distillation until their physical constants (melting point/ boiling point) agreed with the literature values[15-16].

Kinetic Measurements

The equimolar solutions of tosyl chloride (25 mL, 0.025 mol dm⁻³) and *p*-bromophenol - triethylamine mixture (25 mL, 0.025 mol dm⁻³) in acetone were prepared separately. The conductivity cell was rinsed with conductivity water and then washed with acetone. A flat bottomed boiling test tube with B-24 ground joint containing a known volume of solution (10 mL) of TsCl (0.025 mol dm⁻³) and a magnetic stirring bar and a flask containing the mixture of *p*-bromophenol - triethylamine (0.025 mol dm⁻³) in acetone were kept in a thermostat (± 0.1°C) under 303K for about an hour. After attaining the thermal equilibrium, the conductance of the solution of TsCl and 10 mL of the mixture of *p*-bromophenol - triethylamine was added and conductance was measured. The solution (10 mL) of *p*-bromophenol - triethylamine was pipetted out into the boiling tube containing TsCl (10 mL) solution and simultaneously a stop watch was started at the time about half addition from the pipette. The conductivity cell was immediately placed in the reaction mixture and the conductance readings were noted as soon as possible, since the reactants started to react very quickly. Specially devised water-powered magnetic stirrer has been used to stir the reaction mixture continuously during the measurement of conductance[17]. The conductance was measured at

convenient intervals of time (minutes) until the reaction has been completed i.e., a period when a constant value for the conductance was obtained. Second order rate constant (k_2) was deduced from the following special integrated equation[18] which was derived from Guggenheim's principle[19] as explained elsewhere.

$$X_2 - X_1 = k_2 C_0 [t_1 X_1 - t_2 X_2] - k_2 C_\infty X_\infty [t_1 - t_2]$$

Where

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 reactants

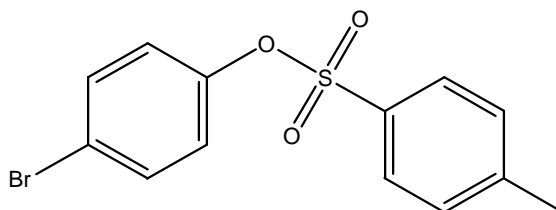
According to this equation, the plot of $(X_2 - X_1)$ against $-(t_1 X_1 - t_2 X_2)$ should be a straight line. From the slope, the second order rate constant k_2 can be calculated by the method of least- squares analysis (LSA). A similar experimental procedure was followed for the same reaction in ACN and for all other *p*-substituted phenols- NEt_3 on TsCl in acetone and ACN. We have repeated the experiments for two times and the value of k_2 was found to be reproducible ($\pm 3\%$).

It was observed from the control experiments that either the conductance of the solution of tosyl chloride with *p*-substituted phenols or triethylamine did not increase with time in acetone / ACN. It indicates that ions responsible for conductance are not liberated from the above solution.

The activation parameters were calculated from a least- squares treatment of a plot of $\ln(k_2/T)$ against T^{-1} [20]. The Hammett and Bronsted slopes, their correlation coefficients were calculated by a least- squares treatment of $\log k_2$ versus σ_p or $\text{p}K_a$ [10].

Product Analyses

Equal volumes of equimolar solutions of tosyl chloride (0.238g, 0.05 mol dm^{-3} , 25mL) and a mixture of *p*-bromophenol and triethylamine (0.108-0.063g, 0.05 mol dm^{-3} , 25mL) in acetone were mixed under kinetic conditions and kept overnight at about 303K. The crystalline solid formed was filtered and evaporated. This solid product was washed well with acetone [yield 52% (0.065g), Mp:252-254°C (lit[21] mp 254-256°C)].Thin layer chromatography tests on this solid, using methanol as an eluent showed a single spot. The solid product was identified as triethylammonium chloride. The filtrate was completely evaporated in vacuum to get residue, which was dissolved in diethyl ether and dried over anhydrous Na_2SO_4 . The solid was thrown out .It was filtered off and tested by TLC using chloroform as eluent and a single spot was obtained. The solid product was recrystallized from toluene [yield 67% (0.175g), Mp:108°C].The product was identified as (4-bromophenyl) 4-methylbenzenesulfonate (Figure. 1) from IR(FT) and ^1H and ^{13}C NMR(DMSO- d_6) spectral data. IR: 3077v C-H (aromatic),1167v S-O (sym),1364v S-O (asy),541v C-Br(aromatic),735,666v C-S,2961v C-H (aliphatic),843v S-O-C cm^{-1} . ^1H NMR (300 MHz,DMSO- d_6): δ 2.39(s,3H), 6.99(d, J =9.0Hz,2H),7.46(d, J= 8.4 Hz,2H),7.57(d, J =8.7 Hz,2H),7.74 (d, J =9.9Hz,2H) ppm. ^{13}C NMR (75 MHz, DMSO- d_6): δ 148.2,145.9,132.9,131.0,130.2,128.2,124.3,120.0,21.1 ppm.



(4-bromophenyl) 4-methylbenzenesulfonate

Figure. 1

Similar procedures were followed for other *p*-substituted phenol(s)- NEt_3 (*p*- NO_2 , *p*- CN , *p*- Cl , *p*- F , *p*- I , *p*- OCH_3) on tosyl chloride and identified the products by TLC and IR(FT), ^1H and ^{13}C NMR(DMSO- d_6) spectral data as (4-nitrophenyl) 4-methylbenzenesulfonate, (4-cyanophenyl) 4-methylbenzenesulfonate, (4-chlorophenyl) 4-methylbenzenesulfonate, (4-fluorophenyl) 4-methyl benzenesulfonate, (4-iodophenyl) 4-methylbenzenesulfonate and (4-methoxyphenyl) 4-methylbenzenesulfonate respectively.

RESULTS AND DISCUSSION

Concentration effect

The rate constant for the reaction of tosyl chloride with *p*-substituted phenol(s) and NEt_3 in acetone / ACN has been determined by the conductometric method under varying equimolar concentrations at 303K, (Table 1). It was observed that the rate constants were almost constant, for different equimolar concentrations of each *p*-substituted phenol(s)- NEt_3 on TsCl. The rate data indicates that the reaction is second order with respect to the whole and first order with respect to each reactants.

Table 1 Second order rate constants for the reaction of TsCl with *p*-substituted phenol(s)- NEt_3 in acetone / ACN at different concentrations at 303K

Substituent X	[TsCl]= [<i>p</i> -XC ₆ H ₄ OH-N Et ₃] mol dm ⁻³	k ₂ dm ³ mol ⁻¹ min ⁻¹	
		Acetone	ACN
<i>p</i> -NO ₂	0.01	40.77	159.10
	0.015	41.23	159.85
	0.02	41.55	160.25
	0.025	42.19	160.75
	0.03	42.76	161.60
<i>p</i> -CN	0.01	50.15	201.75
	0.015	50.96	202.36
	0.02	51.86	202.96
	0.025	52.65	203.25
<i>p</i> -Cl	0.01	20.63	120.75
	0.015	20.86	120.95
	0.02	21.85	121.25
	0.025	22.16	121.65
<i>p</i> -Br	0.01	15.27	90.75
	0.015	15.68	91.16
	0.02	15.94	91.55
	0.025	16.05	91.73
<i>p</i> -F	0.01	30.73	145.65
	0.015	30.90	146.23
	0.02	31.05	146.57
	0.025	31.78	146.69
<i>p</i> -I	0.01	10.59	60.66
	0.015	10.85	62.45
	0.02	11.20	63.77
	0.025	11.97	64.86
<i>p</i> -OCH ₃	0.01	6.25	51.63
	0.015	6.55	52.75
	0.02	7.10	53.87
	0.025	7.89	54.63
	0.03	8.36	55.78

Table. 2 Second order rate constants for the reaction of TsCl with *p*-substituted phenol(s)- NEt_3 in acetone / ACN at different temperatures

Substituent X	k ₂ dm ³ mol ⁻¹ min ⁻¹							
	Acetone				ACN			
	288K	293K	303K	313K	303K	313K	323K	333K
<i>p</i> -NO ₂	12.65	20.89	42.19	94.60	160.75	321.35	650.7	1540.8
<i>p</i> -CN	14.79	23.15	52.65	116.75	203.25	410.5	835.60	1695.7
<i>p</i> -Cl	6.75	10.96	22.16	52.12	121.65	249.3	550.6	1250.6
<i>p</i> -Br	5.30	7.65	16.05	38.35	91.73	185.6	380.96	770.85
<i>p</i> -F	8.59	14.85	31.78	75.26	146.69	305.86	680.74	1405.5
<i>p</i> -I	3.45	5.50	11.97	28.95	64.86	136.58	279.95	605.50
<i>p</i> -OCH ₃	2.25	3.57	7.89	18.65	54.63	115.26	238.96	486.75

[CH₃C₆H₄-SO₂-Cl] = [*p*-XC₆H₄OH-NEt₃] = 0.025M (X = *p*-NO₂, *p*-CN, *p*-Cl, *p*-Br, *p*-F, *p*-I, *p*-OCH₃)

Effect of substituents

The reactions were studied at different temperatures in acetone / ACN (Table 2). The substituent effect on the rate constant shows that the reaction rate depends on the electron density on the oxygen atom of the *p*-substituted phenol(s)-NEt₃: electron with-drawing groups enhances the rate, while electron donating substituents decreases the rate. The reactivity order of the substituents in phenol-NEt₃ is *p*-CN > *p*-NO₂ > *p*-F > *p*-Cl > *p*-Br > *p*-I > *p*-OCH₃. Electron with-drawing and electron donating groups in the nucleophile (*p*-XC₆H₄OH-NEt₃) in ACN medium show a higher order of the reactivity than the acetone medium.

This order of nucleophilic reactivity in ACN may be explained on the basis of the relation between basicity / polarizability of *p*-substituted phenol(s)-NEt₃ solvation and the charge on the sulfur atom of tosylate in the TS[22]. Electron attracting sulfonyl group induces the polarizability on S-Cl bond. This may facilitate the usual backside attack by the (*p*-XC₆H₄OH-NEt₃). The residual positive charge on S atom may lead to the strong interaction with the phenoxide anion. This may cause for the lowering the energy of the TS, which in turn increases the rate. This interaction may depend on the basic strength of phenoxide anion and the magnitude of solvation by ACN. The less basic phenoxide anion will be solvated less. Thus, the order of reactivity of phenoxide anion falls in the order of basic strength. The hydrogen bonding interaction between acetone and unionized phenol(s) as well as the TS may be the factor for the variation in the reactivity.

A comparison of our results with those of the reaction of benzoic acid(s)-NEt₃ on tosyl chloride [14] shows that phenoxide ions react more fastly than benzoate ions. i.e. phenoxide ions are stronger nucleophiles than benzoate ions [23]. This may be due to the less nucleophilicity of the triethylammonium benzoates.

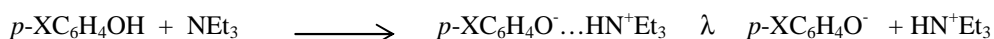
Table 3 A comparison of second order rate constants of reaction of tosyl chloride with various *p*-substituted phenol-triethylamine complexes at 303 K

$$[TsCl] = [p\text{-XC}_6\text{H}_4\text{OH-NEt}_3] = 0.025 \text{ mol dm}^{-3}$$

Phenols	pKa	k ₂ dm ³ mol ⁻¹ min ⁻¹		Relative ratio of rate constants
		Acetone	ACN	
<i>p</i> -Nitrophenol	7.15	42.19	160.75	1:3.8
<i>p</i> -Cyanophenol	7.74	52.65	203.25	1:3.8
<i>p</i> -Chlorophenol	9.38	22.16	121.65	1:5.5
<i>p</i> -Bromophenol	9.35	16.05	91.73	1:5.7
<i>p</i> -Fluorophenol	9.95	31.78	146.69	1:4.6
<i>p</i> -Iodophenol	9.30	11.97	64.86	1:5.4
<i>p</i> -Methoxyphenol	10.21	7.89	54.63	1:6.9

We have attempted to compare the reactivities of tosyl chloride with various *p*-substituted phenol-triethylamine in these solvents viz., in ACN (highly dipolar aprotic solvent), and in acetone (moderately dipolar aprotic solvent). The k₂ values along with pK_a and relative ratio of rate constant values in these solvents are given in Table 3.

The high reactivity in ACN is due to anion desolvation[24-25], which increases the nucleophilicity of the phenoxide anions. In ACN the phenol-amine complex can exist as a tight ion-pair and is in equilibrium with the dissociated ion-pair.



(X = *p*-NO₂, *p*-CN, *p*-Cl, *p*-Br, *p*-F, *p*-I, *p*-OCH₃)

In general, the increase in pK_a values of the *p*-substituted phenol(s)-NEt₃ complex decreases the rate constants both in acetone and ACN medium. Among the halophenols, fluorine is most reactive than other halo analogs. In the case of nitrophenoxide ion because of resonance stabilization, negative charge in 'O' is delocalized to NO₂ group. Hence less reactive than cyano analog. Eventhough nitrophenol is more acidic than cyanophenol.

Activation Parameters

The activation parameters are listed in Table 4. Activation parameters have been evaluated by the usual methods[22,26-27]. Experiments were conducted at different temperatures (288,293,303 and 313K in acetone and 303,313,323 and 333K in ACN) and corresponding rate data obtained and the values of activation parameters (E_a, ΔH[#], ΔS[#] and ΔG[#]) were calculated based on Eyring's equation[28-29]. The linear plots of ln(k₂ / T) against the reciprocal of temperature were made as per the Eyring's equation (Figures 2,3).

$$k = k_B T/h * e^{-\Delta G^\# / RT}$$

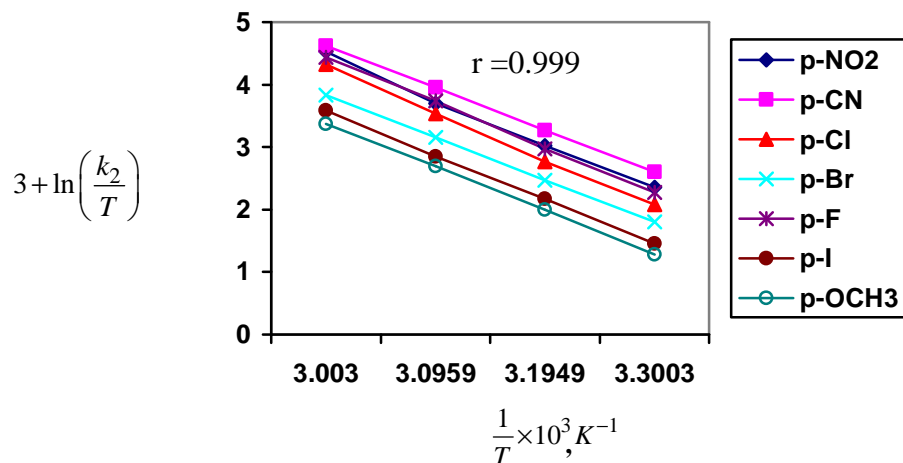


Figure 2. Eyring's plot of $\ln\left(\frac{k_2}{T}\right)$ versus $\frac{1}{T}$ in ACN

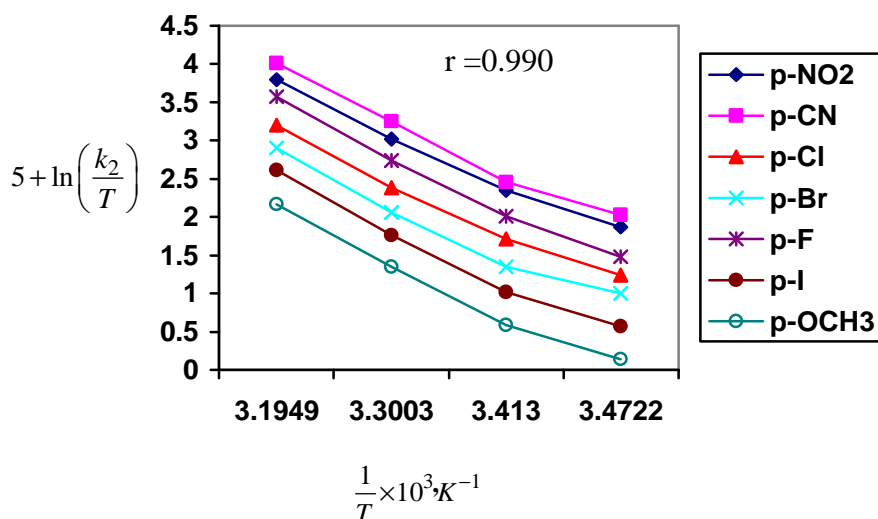


Figure 3. Eyring's plot of $\ln\left(\frac{k_2}{T}\right)$ versus $\frac{1}{T}$ in acetone

Table 4 Activation parameters for the reaction of TsCl with p-substituted phenol(s)-NEt₃ in acetone / ACN

Substituent X	Ea KJ mol ⁻¹	ΔH [#] KJ mol ⁻¹	-ΔS [#] J mol ⁻¹ K ⁻¹	ΔG [#] KJ mol ⁻¹
p-NO ₂	62.79 (59.24)	60.19 (56.64)	14.82 (20.21)	64.82 (65.56)
p-CN	61.81 (59.11)	59.21 (56.51)	10.34 (24.91)	62.44 (64.30)
p-Cl	65.26 (60.10)	62.66 (57.50)	12.51 (32.09)	66.57 (67.54)
p-Br	59.44 (59.29)	56.84 (56.69)	4.78 (7.24)	58.34 (58.95)
p-F	65.29 (63.93)	62.69 (61.32)	22.48 (27.93)	69.72 (70.06)
p-I	62.97 (62.12)	60.37 (59.52)	10.71 (16.74)	63.72 (64.75)
p-OCH ₃	62.86 (60.98)	60.26 (58.37)	5.62 (12.82)	62.01 (62.38)

Values in parentheses are for acetone

The entropies of activation are negative as we expected for nucleophilic bimolecular reactions. The high negative ΔS^\ddagger observed with respect to all the substituents studied support the operation of “electrostriction” in these compounds pointing to more polar TS. The average values were -20.28 in (acetone) and -11.60 in (ACN) $\text{J mol}^{-1}\text{K}^{-1}$ respectively. The difference in the values of entropy can be explained on the basis of solvent participation in the TS of the reaction. Acetone may highly solvate the TS by H bonding than ACN, which results in the decrease of entropy. The values of ΔH^\ddagger in ACN are slightly higher than those in acetone. This can be explained on the basis of solvation. *p*-Substituted phenol(s)- NEt_3 may be desolvated more in ACN than in acetone due to the protogenic character of ACN [30-31]. This may rise the energy of nucleophile (*p*- $\text{XC}_6\text{H}_4\text{OH-NEt}_3$) and diminish the energy gap between the reactants and TS, which increases the rate.

In comparing the activation entropy values between the reactions of TsCl with *p*-substituted phenol(s)- NEt_3 and benzoate ions [14], it is evident that there is a difference between the two series average values -20.28 in (acetone) and -11.60 in (ACN) for the *p*- $\text{XC}_6\text{H}_4\text{OH-NEt}_3$ and average values -61.41 in (acetone) and -40.43 in (ACN) $\text{J mol}^{-1}\text{K}^{-1}$, for the benzoate ions series respectively. The differences may be due to greater solvent participation in the TS of the reaction of tosyl chloride with *p*-substituted phenol(s)- NEt_3 than with triethylammonium benzoate ions. In this case of benzoate ion, there is a already a formal charge on the oxygen atom and the change from reactants to transition state results only in the spreading out of an already existing charge. The solvation contribution to the activation entropy would then be expected to operate in the opposite sense to that in the *p*- $\text{XC}_6\text{H}_4\text{OH-NEt}_3$ series, leading to a smaller decrease of entropy[23].

Thus the rate constants and activation parameters in Table 2 and 4 may reasonably be assumed to refer to a bimolecular substitution reaction at tetra co-ordinated sulfur.

Isokinetic Relationship

A knowledge of the isokinetic relationship may assist in treating experimental quantity to serve as a measure of reactivity and be correlated with theoretical predictions. Leffler[32] deduced the following isokinetic equation in modification of the Hammett equation.

$$E_a = E^\circ + 2.303R \beta \log A$$

$$\Delta H^\ddagger = \Delta H^\circ + \beta \Delta S^\ddagger$$

which holds good for a series of related reactions. The validity of the isokinetic relation can be tested graphically by plotting ΔH^\ddagger versus ΔS^\ddagger (Figures. 4, 5).

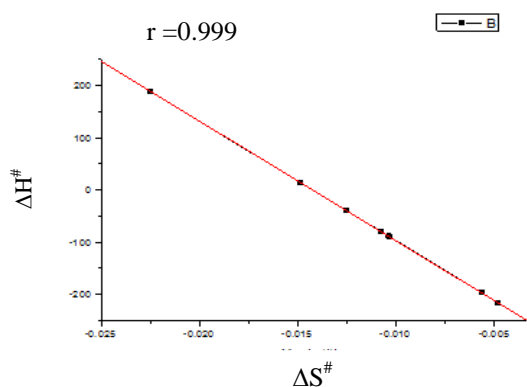


Figure. 4 Leffler plot of ΔH^\ddagger versus ΔS^\ddagger in ACN

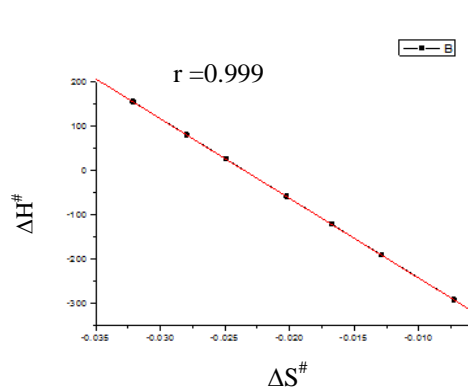


Figure. 5 Leffler plot of ΔH^\ddagger versus ΔS^\ddagger in acetone

This linear relationship between activation enthalpies and activation entropies in a series of related reaction is called isokinetic relationship[27]. The slope of the plot, ΔH^\ddagger versus ΔS^\ddagger is the isokinetic temperature, ‘ β ’ and it has an important physical meaning. It represents a temperature at which all reactions of the series should proceed at the same rate and the reaction constant attains the value of zero at the temperature.

$$\beta = 296\text{K (ACN)} \quad r = 0.999$$

$$\beta = 291\text{K (acetone)} \quad r = 0.999$$

Further the plots of ΔH^\ddagger versus E_a were also made as per the Leffler's modified equation. The values of β were determined from the slope of such plots (Figures. 6, 7).

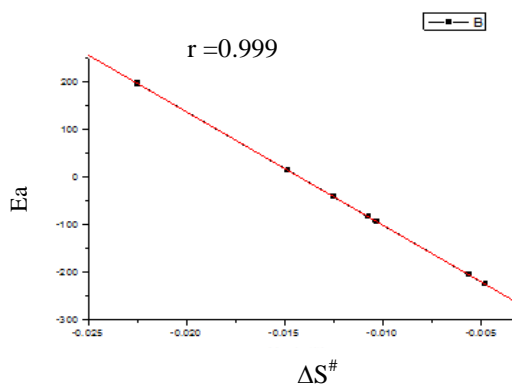


Figure. 6 Modified Leffler plot of E_a versus ΔS^\ddagger in ACN

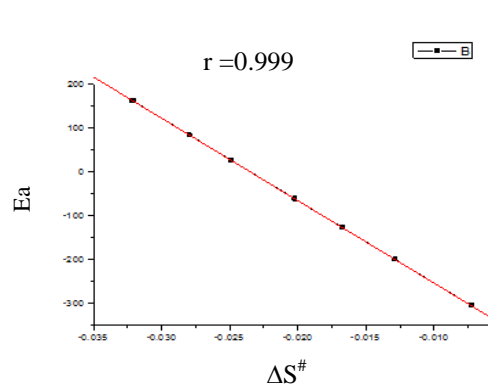


Figure. 7 Modified Leffler plot of E_a versus ΔS^\ddagger in acetone

$$\beta = 297 \text{ K (ACN)} \quad r = 0.999$$

$$\beta = 292 \text{ K (acetone)} \quad r = 0.999$$

It was found that these β values were in agreement with the β values obtained from the isokinetic plots (ΔH^\ddagger versus ΔS^\ddagger) already discussed (Figures. 4, 5). This supports that the reactions of all the *p*-substituted phenol(s)- NEt_3 on TsCl used to proceed through a similar mechanism. This linear relationship shown by the majority of the substituents is indicative of a single mechanism [33].

The validity of isokinetic plot is questionable[34] because the quantities ΔS^\ddagger and ΔH^\ddagger are mutually dependent, both being derived from the experimental rate constants. An alternative graphical method for finding out the isokinetic temperature was suggested by Exner. A plot of the rate constants measured at two different temperatures $\log k_2(T_2)$ versus $\log k_2(T_1)$ is known as Exner plot, from the slope b , of the Exner plot, the isokinetic temperature β can be calculated using the following equation[35].

$$\beta = \frac{T_1 T_2 (b - 1)}{b T_2 - T_1}$$

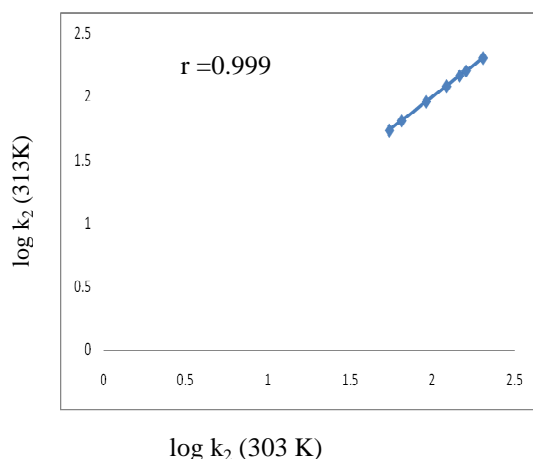


Figure. 8 Exners plot of $\log k_2(313\text{K})$ versus $\log k_2(303\text{K})$ in ACN.

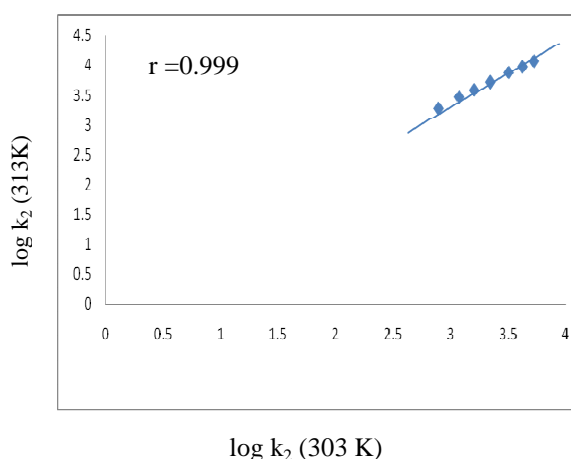


Figure. 9 Exners plot of $\log k_2(313\text{K})$ versus $\log k_2(303\text{K})$ in acetone.

The plot of $\log k_2(303\text{K})$ against $\log k_2(313\text{K})$ (Figures 8,9) gave a linearity with slope $b = 0.932$ ($r = 0.999$), $\beta = 572 \text{ K (ACN)}$ and slope $b = 0.925$ ($r = 0.999$), $\beta = 528\text{K (acetone)}$ respectively. The values of the slope 'b' for this system is less than unity. This indicates that present reaction series is neither isoentropic nor isoenthalpic. The isokinetic temperature in these two solvents is found to be higher than the experimental temperature (ie.313K) indicating enthalpy as a controlling factor. The linear correlation (0.999) and the values of ΔG^\ddagger for different substituents are almost the same, which indicate the operation of similar mechanism in both solvents.

Linear Free Energy Relationships

Hammett Relationship

Figures (10 and 11) in which the Hammett plot is reported, shows that the reaction rate depends on the electron density on the oxygen atom of the *p*-substituted phenol(s)-NEt₃. The value of $\log k_2 / k_2^0$ at 303K is plotted against the value of the Hammett substituent constant in the following Hammett equation.

$$\log k_2 = \log k_2^0 + \rho \sigma$$

The Hammett plot is found to be linear for this reaction series. It is known that the correlation between $\log k_2 / k_2^0$ versus the value of σ_p in these two solvents are fair (Eqs (1) and (2))

$$\log k_2(\text{ACN}) = -3.769 \sigma_p + 3.2026 \quad \text{--- (1)}$$

($r = 0.999$, $n = 7$)

$$\log k_2(\text{acetone}) = -1.839 \sigma_p + 1.9069 \quad \text{--- (2)}$$

($r = 0.999$, $n = 7$)

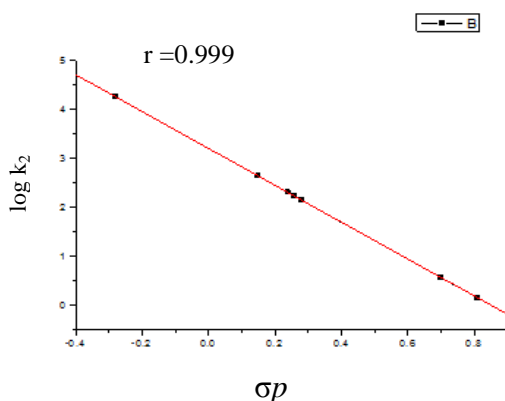


Figure. 10 Hammett plot of $\log k_2$ versus σ_p in ACN at 303K.

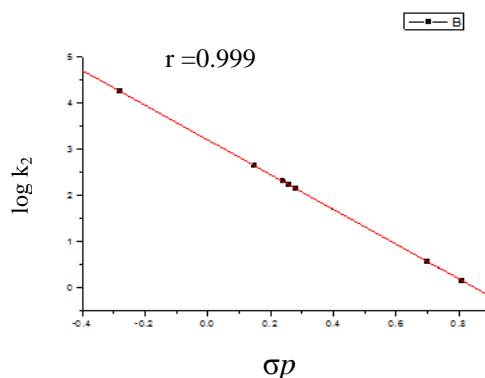


Figure.11 Hammett plot of $\log k_2$ versus σ_p in acetone at 303K.

This is as expected; the reaction constant(ρ), which is a measure of the change in charge at the reaction centre, is related to the extent of bond formation and bond breaking in the TS[36]. The more negative ρ is, the more will bond breaking have proceeded relative to bond making.

The experimental ρ values are -3.769 (ACN) and -1.839 (acetone) is relatively a higher value than that of the reported ρ values were 0.128 (ACN) and 0.164 (acetone) for triethylammonium benzoates with the same substrate[14].

Bronsted Relationship

The extent of S-O bond formation in the TS when the *p*-substituted phenol(s)-NEt₃ approaches the sulfur atom of tosyl chloride is gauged from the Bronsted Coefficient value (β). The values of $\log k_2$ were plotted against the pK_a values of the nucleophiles. The sensitivity of the reaction rates to the basicity of the nucleophile, as measured by the slope ' β ' of the Bronsted plot is -0.579 (ACN) and -0.636 (acetone). It is found that the correlation is fair (Eqs(3) and (4)).

$$\log k_2(\text{ACN}) = -0.579 \text{pK}_a + 5.1948 \quad \text{--- (3)}$$

($r = 0.999$, $n = 7$)

$$\log k_2(\text{acetone}) = -0.636 \text{pK}_a + 5.7166 \quad \text{--- (4)}$$

($r = 0.999$, $n = 7$)

As we have already discussed that the rate constants for the reaction of various *p*-substituted phenol-NEt₃ on tosyl chloride (Table 2) show that electron donating substituents in the nucleophile decrease the rate, while electron attracting substituents increase the rate. The direction of the influence shows that the rate of reaction depends on the electron density on the oxygen atom of the *p*-substituted phenol(s)-NEt₃. Since the basicity also depends on the electron density, one should expect a correlation between rate and basicity of the nucleophiles. That such correlation exists is apparent from the Bronsted plot shown in Figures (12, 13).

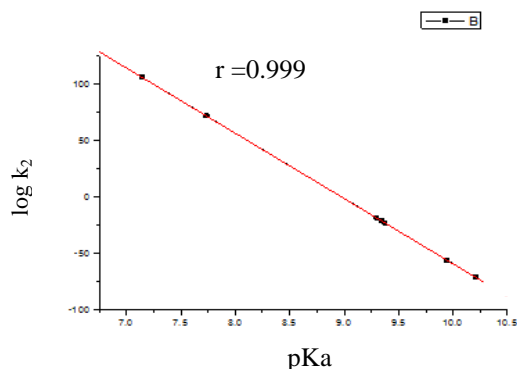


Figure. 12 Bronsted plot of $\log k_2$ versus pK_a in ACN at 303K.

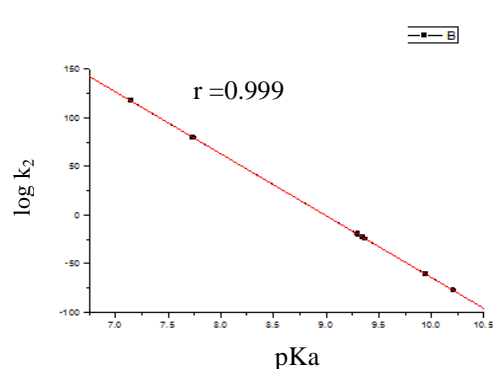


Figure. 13 Bronsted plot of $\log k_2$ versus pK_a in acetone at 303K.

The values of $\log k_2$ (ACN) were plotted against the values of $\log k_2$ (acetone), and the linearity was obtained with ($r = 0.990$, $n = 7$) (Figure. 14). This is one of the probes for the operation of the same mechanism in both the solvents.

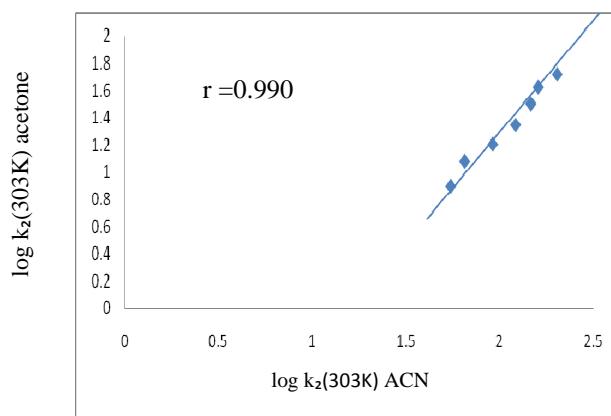
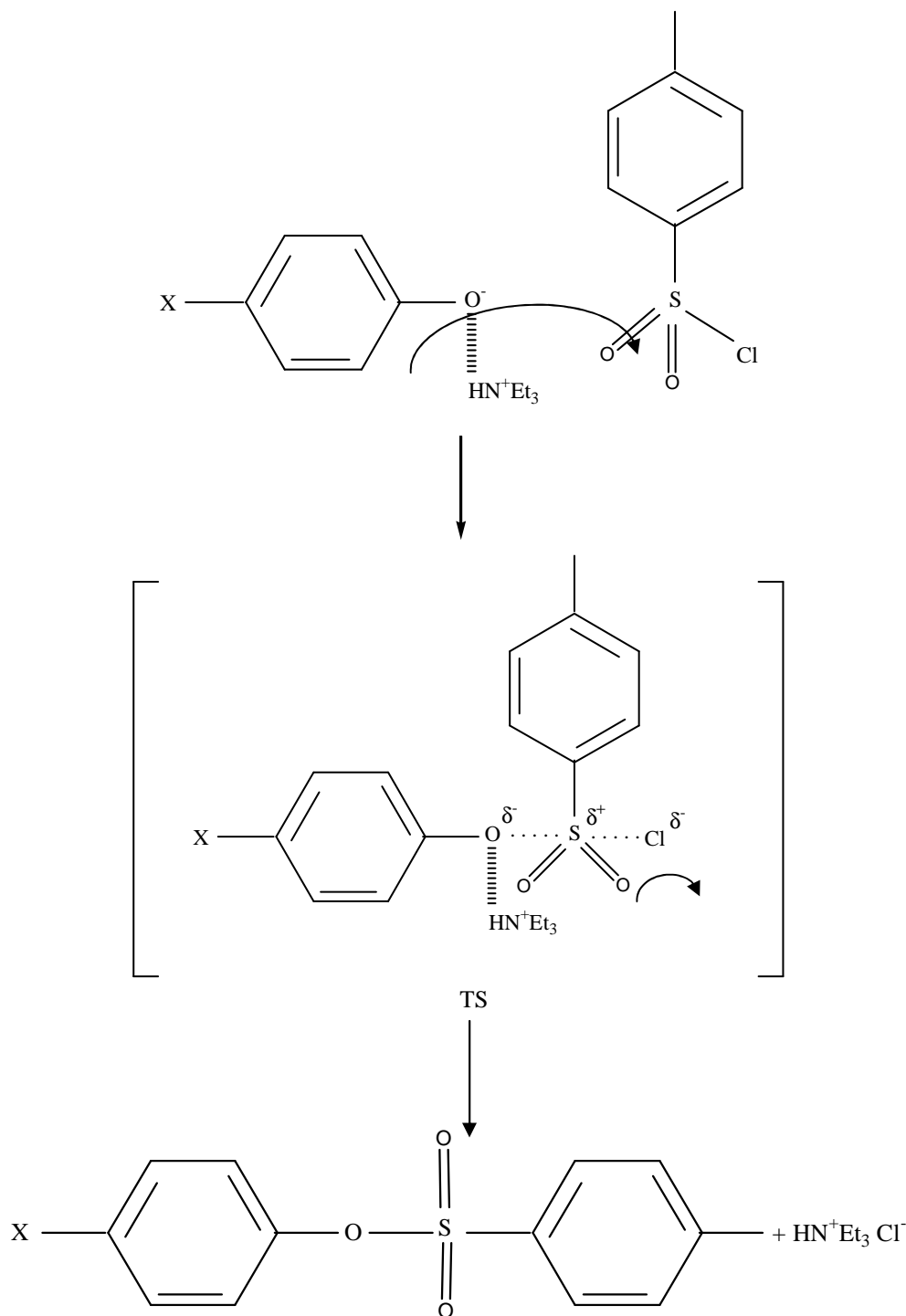


Figure. 14 Plot of $\log k_2(303K)$ acetone versus $\log k_2(303K)$ ACN

Based on the kinetics data, product analyses, stoichiometry and activation parameters, the synchronous direct nucleophilic displacement mechanism of *p*-substituted phenol(s)-NEt₃ at the S atom of tosyl chloride has been proposed for the reaction studied.

Mechanism**CONCLUSION**

Rate constants for the reaction of equimolar concentration of tosyl chloride and *p*-substituted phenol(s)- NEt_3 in acetone/ACN at four different temperatures, have been determined conductometrically by following the increase in conductance due to the formation of triethylammonium chloride, during the course of the reaction. The reaction is found to follow second order kinetics in total and first order with respect to each reactants. The rate constants are enhances for electron with-drawing substituents and decreases for electron donating substituents in the nucleophile. Experiments are conducted at varying temperatures (288, 293, 303 and 313K) in acetone and (303, 313, 323 and 333K) in ACN and corresponding second order rate constants k_2 are obtained, which was derived from the Guggenheim principle and the values of activation parameters (E_a , ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger) are calculated based on Eyring equation. The negative values of ΔS^\ddagger indicates the formation of rigid TS. The values of isokinetic

temperature ' β ' (296K, 297K in ACN and 291K, 292K in acetone) are determined from the slopes of isokinetic plots (ΔH^\ddagger versus ΔS^\ddagger and E_a versus ΔS^\ddagger). It is found that these ' β ' values are almost constant. This supports that the reactions of all the *p*-substituted phenol(s)-NEt₃ on TsCl used to proceed through a similar mechanism. The isokinetic temperature evaluated from the Exner plot is found to be 572K (ACN) and 528K (acetone). These ' β ' value is higher than the experimental temperature (313K) indicating enthalpy as a controlling factor. The almost constant of ΔG^\ddagger values indicates that all these systems undergo substitution via same mechanism. The Hammett [$\rho = -3.769$ (ACN), -1.839 (acetone)] and the Bronsted [$\beta = -0.579$ (ACN), -0.636 (acetone)] plots shows good correlations. A plot of $\log k_2$ (ACN) with $\log k_2$ (acetone) gives a straight line, indicating the operation of similar mechanism in both the solvents. A nucleophilic substitution on sulfur can conceivably take place by a synchronous direct displacement mechanism of *p*-substituted phenol(s)-NEt₃ at the S atom of tosyl chloride. The trigonal bipyramidal structure may be postulated for the S_N2 TS. We proposed the S_N2 mechanism based on the kinetic data and product analysis.

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