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Der Chemica Sinica, 2013, 4(1):46-55



Kinetics of the reaction of tosyl chloride with *p*-substituted phenol(s) and triethylamine in methanol

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ABSTRACT

The rate constants and activation parameters for the reaction of tosyl chloride with p- substituted phenol(s) - triethylamine in methanol have been determined conductometrically by following the increase in conductance due to the formation of HN^+Et_3 Cl, during the course of the reaction. The reaction is second order overall and first order with respect to both substrate and nucleophile. The rate constants are greater for electron donating substituents and lower for electron withdrawing groups in the nucleophile. The substituent effects are correlated by Hammett ($\rho = -0.777$) and Bronsted ($\beta = -0.667$) equations respectively. The results are compared with the corresponding data for the reaction of tosyl chloride with p- substituted benzoic acid(s)- triethylamine reaction, reported in the literature. The kinetic results are interpreted as a synchronous direct bimolecular nucleophilic substitution reaction. A linear relationship exists between $\Delta H^{\#}$ and $\Delta S^{\#}$ which is indicative of a single mechanism.

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

INTRODUCTION

The study of bimolecular nucleophilic substitution has received considerable attention [1]. Ronge[2] has reported the kinetics of benzenesulfonyl chloride (BSC) with substituted anilines in methanol at different temperatures. Ryan and Humffray[3], have interpreted the kinetics of reactions of picryl chloride with substituted phenoxide ions and anilines, respectively, while Mohanty and Nayak[4], have studied the kinetics of the same compound with substituted benzoate ions, thus providing a comparison of this compound with oxygen and nitrogen nucleophiles. Banjoko and Okwuiwe [5] have reported the reaction of benzenesulfonyl chloride with a large excess of the substituted benzoate ions in methanol which is pseudo first order with respect to benzenesulfonyl chloride. Krishna Pillay and co-workers investigated the kinetics of reactions of phenacyl bromide with carboxylic acids in the presence of tertiary amines and concluded that the H-bonded ion-pair is the active nucleophile [6,7].Thus the interaction of weak acids such as aliphatic and aromatic carboxylic acids or phenol(s) with tertiary amines would result suitable nucleophile for the reaction.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[8-11].

The nature of active species of the nucleophile involved between weak acids and tertiary amines will be any one or many of the following structures.

$$\begin{array}{ccc} R-A-H &+ & NR_3 \\ I & & II \end{array} \qquad \begin{array}{c} R-A-H \dots NR_3 \\ III \end{array}$$

Non proton-transferred

 $R-A^{-}_{IV}$ $HN^{+}R_{3}$ Proton-transferred species

 $R\text{-}A^{-}\parallel HN^{+}R_{3}$

v

Solvent separated

We report here similar study involving the reaction of another activated halide, at a tetra co-ordinate sulfur in the side chain of an aromatic ring, with p- substituted phenol(s)-NEt₃ in methanol with a view to comparing its reaction with benzoic acid(s)- NEt₃ in methanol reported in the literature [12].

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



 $X = p-NO_{2}, p-CN, p-Cl, p-Br, p-F, p-I, p-OCH_{3}$ Rate = k₂[CH₃C₆H₄SO₂Cl][p-XC₆H₄OH -NEt₃]

MATERIALS AND METHODS

Materials

Tosyl chloride(TsCl), *p*-substituted phenols(p-XC₆H₄OH), triethylamine(NEt₃), methanol (analytical grade) were purified before use by either recrystallisation (or) distillation until their physical constants (melting point/ boiling point) agreed with the literature values[13-14].

Kinetic measurements

The solutions of tosyl chloride(25mL,0.025 mol dm⁻³) and the mixture of *p*-nitrophenol and triethylamine (25 mL, 0.025 mol dm⁻³) were prepared in methanol, thermostated and mixed. The conductivity is due to $HN^+Et_3Cl^-$ (liberated from tosyl chloride by the attack of *p*-substituted phenol(s) - NEt₃). In every case, the kinetic run was followed to almost 70% completion and the second order rate constants k₂ were determined at three different temperatures from conductivity data by least-squares analysis (LSA) method using the following equation[15] which was derived from Guggenheim principle[16].

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

where

$$\begin{split} X_1 &= \text{Conductance at time } t_1 \\ X_2 &= \text{Conductance at time } t_2 \\ X_\infty &= \text{Conductance at time } t_\infty \\ k_2 &= \text{Second order rate constant} \\ C_0 &= \text{Initial concentration of the reactants} \end{split}$$

It was observed from control experiments that either the conductance of the solution of tosyl chloride with *p*-substituted phenol(s) or NEt₃ did not increase with time in methanol. It indicates that ions responsible for conductance are not liberated from the above solution. All rates were run in duplicate. The rate constants were reproducible to within $\pm 3\%$.

The activation parameters were calculated from a least- squares treatment of ln(k2/T) against 1/T being linear in all cases[17].

The Bronsted and Hammett slopes, their correlation coefficients were calculated by least- squares treatment of log k_2 versus pK_a or $\sigma_p[5]$.

Product analyses

Equal volumes of equimolar solutions of tosyl chloride (0.238g,0.05 mol dm⁻³,25mL) and a mixture of *p*-nitrophenol and triethylamine(0.087-0.063g,0.05 mol dm⁻³,25mL) in methanol 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 61% (0.076g) Mp:252-254°C (lit[18] mp 254-256°C)].Thin layer chromatography tests on this solid, using chloroform as an eluent showed a single spot. The solid product was dissolved in diethyl ether and dried over anhydrous Na₂SO₄. The light yellow 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 70% (0.185g), Mp:103°C]. The product was identified as (4-nitrophenyl) 4-methylbenzenesulfonate (Figure. 1) from IR(FT) and ¹H and ¹³C NMR(DMSO-d6) spectral data. IR: 2931vC-H(aromatic), 1171v S-O(sym), 1303v S-O(asy), 1405v O-N-O(sym), 966v C-N(aromatic), 657-595v C-S, 728v S-O-C cm⁻¹; ¹H NMR(300MHz, DMSO-d6): δ 2.38(s, 3H), 7.33(d, J=9.0Hz, 2H), 7.47(d, J=8.4Hz, 2H), 7.78(d, J=8.4Hz), 8.25(d, J=9.0Hz, 2H)ppm. ¹³C NMR (75MHz, DMSO-d6): δ 153.2, 146.3, 145.9, 130.8, 130.4, 128.2, 125.7, 123.2, 21.1ppm.



(4-nitrophenyl) 4-methylbenzenesulfonate Figure. 1

Similar procedures were followed for other *p*-substituted phenol(s)- NEt₃ (*p*-CN, *p*-Cl, *p*-Br, *p*-F, *p*-I, *p*-OCH₃) on tosyl chloride and identified the products by TLC and IR(FT), ¹H and ¹³C NMR(DMSO-d6) spectral data as (4-cyanophenyl) 4-methylbenzenesulfonate, (4-chlorophenyl) 4-methylbenzenesulfonate, (4-bromophenyl) 4-methylbenzenesulfonate, (4-fluorophenyl) 4-methyl benzenesulfonate, (4-iodophenyl) 4-methylbenzenesulfonate and (4-methoxyphenyl) 4-methyl benzenesulfonate respectively.

RESULTS AND DISCUSSION

The rate constant for the reaction of equimolar concentrations of tosyl chloride and *p*-substituted phenol(s) – triethylamine in methanol have been determined by conductometric method at three different temperatures. The second order overall rate constants k_2 were obtained, which was derived from the Guggenheim principle[16] as explained elsewhere. It was found that the reaction is overall a second order kinetics and first order being one with respect to substrate(TsCl) and nucleophiles (*p*-XC₆H₄OH -NEt₃).

Effect of substituents

The rate constants for the reaction of tosyl chloride with *p*-substituted phenol(s)- NEt₃ (Table 1) show that electron donating substituents in the *p*- XC₆H₄OH -NEt₃ increase the rate, while electron withdrawing substituents decrease the rate. The direction of the influence shows that the rate of the 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 nucleophilic reagents. The observed rate conform following order of reactivity: *p*-OCH₃>*p*-F>*p*-Cl>*p*-Br>*p*-I>*p*-CN>*p*- NO₂.

No.	Substituent X	$k_2 (dm^3 mol^{-1} min^{-1})$			
		303K	313K	323K	
1.	$p-NO_2$	3.30	7.75	16.50	
2.	<i>p</i> -CN	5.55	11.79	24.75	
3.	p-Cl	11.78	23.69	47.85	
4.	<i>p</i> -Br	10.78	21.69	44.85	
5.	<i>p</i> -F	12.95	25.30	51.15	
6.	p-I	8.79	17.50	35.05	
7.	p-OCH ₃	17.96	36.75	75.90	

Table – 1 Second order rate constants for the reaction of tosyl chloride with *p*-substituted phenol(s) - NEt₃ in methanol at three different temperatures

 $[p-CH_3C_6H_4SO_2Cl] = [p-XC_6H_4OH-NEt_3] = 0.025M (p-NO_2, p-CN, p-Cl, p-Br, p-F, p-I, p-OCH_3)$

A comparison of our results with those of the reaction of benzenesulfonyl chloride with benzoate ions [5] and tosyl chloride with triethylammonium benzoates [12] shows that p-substituted phenol(s)- NEt₃ react faster with the substrate(TsCl) than the other series of compounds. i.e. phenoxide ions are stronger nucleophiles than benzoate ions. This may be due to the less nucleophilicity of the triethylammonium benzoates and metal benzoates.

Activation Parameters

The activation parameters were noted in Table 2 together with the linear correlation coefficients(r). Activation parameters have been evaluated by the usual methods [19-20]. The rate of the reactions were determined at three different temperatures (303,313 and 323K) in methanol and it was observed that the rate increased with an increasing temperature (Table 1). From the slopes of these linear plots of $\ln\left(\frac{k_2}{T}\right)$ against the reciprocal of

temperature (Figure. 2), the enthalpy of activation (<H[#]) was calculated. The activation energy (Ea), the entropy of activation (<S[#]), and the free energy of activation (<G[#]) were calculated using the Eyring's equation respectively [21-22].

$$5 + \ln\left(\frac{k_2}{T}\right)$$

$$2$$

$$3$$

$$2.5$$

$$1$$

$$0$$

$$3.096$$

$$3.1949$$

$$3.3003$$

$$\frac{1}{T} \times 10^3 K^{-1}$$
Figure. 2. Eyring's plot of $\ln\left(\frac{k_2}{T}\right)$ versus $\frac{1}{T}$ in methanol

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

Table - 2 Activation parameters for the reaction of tosyl chloride with p-substituted phenol(s)-NEt₃ in methanol

No.	Substituent	Ea	r	$\Delta H^{\#}$	$-\Delta S^{\#}$	$\Delta G^{\#}$
	Х	KJmol ⁻¹		KJmol ⁻¹	Jmol ⁻¹ K ⁻¹	KJmol ⁻¹
1.	$p-NO_2$	65.52	0.9998	62.92	27.46	71.51
2.	<i>p</i> -CN	60.82	0.9998	58.22	38.75	70.35
3.	p-Cl	57.02	0.9997	54.42	45.06	68.52
4.	<i>p</i> -Br	57.99	0.9996	55.39	42.63	68.73
5.	<i>p</i> -F	55.87	0.9994	53.27	48.11	68.33
6.	p-I	56.27	0.9998	53.67	49.98	69.31
7.	p-OCH ₃	58.63	0.9997	56.03	36.23	67.37

The trends in variation of the activation parameters are the same as with benzoate ions. The values of the activation energies show a regular variation with substituents in p-XC₆H₄OH-NEt₃, electron- donating substituents decrease and electron – withdrawing groups increase E_a . This may be due to the electromeric effect contribute to the nucleophiles. The activation energies are smaller in the phenoxide ion series than in benzoate ion series; this can be accounted for, in part at least, by differences in the energy required for rehybridisation of the oxygen (phenoxide ions) and by differences in stabilisation by solvation[3].

The entropies of activations are negative as expected for the bimolecular reactions. The average value is $-41.17 \text{Jmol}^{-1} \text{K}^{-1}$ whereas -64.25Jmol⁻¹K⁻¹ and -64.47Jmol⁻¹K⁻¹ had been reported for the reaction of benzenesulfonyl chloride with substituted sodium benzoates[5] and tosyl chloride with *p*-substituted benzoic acid-NEt₃ in methanol[12]. This difference could be attributed to a greater solvent participation in the transition state of the reaction of tosyl chloride with *p*- substituted phenol(s)-NEt₃ than with benzoate ion(s) in methanol. In the case of benzoate ion, there is already a formal charge on the oxygen atom and the change from reactants to transition state (TS) 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 phenoxide ion series i.e., there will thus be less loss of freedom of solvent in benzoate ion than in the phenoxide ion series , leading to a smaller decrease of entropy[4].

The values of $\Delta H^{\#}$ are seen to decrease with increasing electron–donating ability of the substituents. At the same time, $\Delta S^{\#}$ becomes more negative, reflecting a more heavily solvated TS. The fact that structural variations give quite precise free-energy relationships although the effects on $\Delta H^{\#}$ and $\Delta S^{\#}$ are irregular, can be explained by assuming that the variations in activation parameters occur from the interplay of two structure –sensitive factors. These factors are thought to be: first, polar effects, ie., the electronic influence of substituents, which are considered to affect only $\Delta H^{\#}$ but not $\Delta S^{\#}$ and secondly ,solute-solvent interactions which influence $\Delta H^{\#}$ and $\Delta S^{\#}$ in a compensating manner so that there is little effect on $\Delta G^{\#}$. Thus a slight variation in $\Delta G^{\#}$ arises mainly from variation in the polar contribution to $\Delta H^{\#}$, which may reasonably be taken as a measure of the potential energy change. It is thus possible that the observed variations in rate with the *p*-XC₆H₄OH-NEt₃ substituents reflect differences in repulsion energy between the reactants. Since potential-energy changes are usually considered to be at the basis of free energy relations, the Hammett and Bronsted plots are accounted for[23].

Isokinetic relationship

methanol

A linear relationship between the entropy of activation($\Delta S^{\#}$) and the enthalpy of activation($\Delta H^{\#}$) has been observed in a series of related reaction is called isokinetic relationship (Figure 3). The data can be fitted in the Leffler's equation $\Delta H^{\#} = \Delta H^{0} + \beta \Delta S^{\#}$ [24]. The value of ΔH^{0} has been found to be 69.36 KJmol⁻¹. The slope of the plot is the isokinetic temperature, ' β ' and it has a 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 this temperature . The value of ' β ' is 318 K for the reaction of TsCl with *p*- XC₆H₄OH -NEt₃ (r =0.999). The further plot of E_a versus $\Delta S^{\#}$ was also made as per the Leffler's modified equation. The value of ' β ' is 316 K (r = 0.999) was determined from the slope of such plot (Figure 4). It was found that this ' β ' value is in agreement with the ' β ' value obtained from Leffler's plot already discussed .This supports that the reactions of all the *p*-substituted phenol(s)- NEt₃ on TsCl used to proceed through a similar mechanism.



 $\Delta \mathbf{S}^{\#}$ in methanol

The validity of isokinetic plot is questionable because the quantities $\Delta S^{\#}$ and $\Delta H^{\#}$ are mutually dependent; both being derived from the experimental rate data [25]. An alternative graphical method for finding out the isokinetic temperature was suggested by Exner's. A plot of rate constants measured at two different temperatures log $k_2(T_2)$ versus log $k_1(T_1)$ is known as Exner plot. From the slope b, of the Exner plot, the isokinetic temperature ' β ' can be evaluated using the equation.

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

The plot of log k_2 (313 K) against log k_2 (303 K) gave a linearity with slope 0.907 (r = 0.998), $\beta = 462$ K for the reaction of each *p*-substituted phenol- NEt₃ nucleophile on TsCl (Figure. 5). The value of the slope 'b' for this system is less than unity. This indicates that the present reaction series is neither isoentropic nor isoenthalpic .The value of β from the Exner plot calculated, was higher than the experimental temperature (313 K) indicating enthalpy as controlling factor. The linear correlation and the almost constant of $\Delta G^{\#}$ values indicate that all these systems undergo substitution via same mechanism. The linear relationship shown by the majority of the substituents indicates that one mechanism prevails in all cases[26].



Figure. 5 Exner plot of log $k_2(313K)$ versus log $k_2(303K)$ in methanol

Linear free energy relationships Hammett relationship

Figure. 6, in which the Hammett plot is reported, shows that the reaction constant ρ for the reaction is -0.777 (r =0.999). The negative value indicates that the reaction rate is sensitive to the substituents and increased with electron donating power of the substituents[27].

Log $k_2/k_0 = -0.777\sigma_p + 1.1938$ (r = 0.999, n = 7)

The value of ρ is an indication of the extent of charge development at the S-atom of the substrate in passing from ground state to transition state[5,26]. The experimental ρ value – 0.777 is relatively a higher value than that of the reported ρ value (-0.35) for sodium benzoates and (- 0.119) for triethylammonium benzoates with ArSO₂Cl in methanol.

The more negative ρ (-0.777) indicates that TsCl makes bond breaking at S-Cl faster than S-O bond making with *p*-substituted phenol(s)- NEt₃ reaction.

Bronsted relationship

The Bronsted plot of the reaction is obtained by plotting the log k_2 versus the pK_a values of the corresponding *p*-substituted phenol(s) with $\beta = -0.667$, r = 0.999 (Figure. 7). The linear line indicates that the reaction rate may depend on the basicity of the nucleophilic reagents. The slope is related to the degree of S-O bond formation in the TS[28-30]. It is found that the correlation is fair.

 $\label{eq:k2} \begin{array}{l} \text{Log } k_2(\text{methanol}) = -0.667 \; pK_a + 6.0038 \\ (\; r = 0.999, \, n = 7 \;) \end{array}$



Figure. 6 Hammett plot of log k_2 versus σp in methanol at 303 K

The kinetics, products, stoichiometry and activation parameters of the reactions of tosyl chloride with *p*-substituted phenol(s)-triethylamine are consistent with the mechanism of a bimolecular direct nucleophilic substitution at sulfonyl sulfur as reported in the reaction of tosyl chloride with *p*-substituted benzoic acid(s)-NEt₃ in methanol[12]. One would , however, expect TsCl to be more susceptible to nucleophilic attack, owing to the good leaving ability of the chloride ion and the high electronegativity of the sulfonyl group [31]. A nucleophilic substituted substituted by a synchronous direct displacement mechanism of *p*-substituted phenol(s)-NEt₃ at the S atom of tosyl chloride has been proposed for the reaction studied.



Figure. 7 Bronsted plot of log k_2 versus pKa in methanol at 303 K

Mechanism



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CONCLUSION

Rate constants for the reaction of equimolar concentration of tosyl chloride and p-substituted phenol(s)- NEt₃ in methanol at three 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 overall and first order with respect to both substrate(TsCl) and nucleophile (p- XC₆H₄OH -NEt₃).The rate constants are greater for electron donating substituents and lower for electron withdrawing substituents in the nucleophile. Experiments are conducted at varying temperatures(303,313 and 323K) and corresponding second order rate constants k₂ are obtained, which was derived from the Guggenheim principle and the values of activation parameters (E_a , $\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$) are calculated based on Eyring equation. The negative values of $\Delta S^{\#}$ indicates the formation of rigid TS. The values of isokinetic temperature ' β ' (318K and 316K) are determined from the slope of isokinetic plots ($\Delta H^{\#}$ versus $\Delta S^{\#}$ and E_a versus $\Delta S^{\#}$). 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 462K. This ' β ' value is higher than the experimental temperature (313K) indicating enthalpy as a controlling factor. The almost constant of $\Delta G^{\#}$ values indicates that all these systems undergo substitution via same mechanism. The Hammett ($\rho = -0.777$) and the Bronsted ($\beta = -0.667$) correlations have been found to be valid yielding linear relationships. Thus the rate constants and activation parameters in Table 1 and 2 may reasonably be assumed to refer to a synchronous direct bimolecular nucleophilic substitution reaction of p-substituted phenol(s)-NEt₃ on TsCl at tetra co-ordinated sulfur. The trigonal bipyramidal structure may be postulated for the $S_N 2$ TS. We proposed the $S_N 2$ mechanism based on the kinetic data and product analysis.

Acknowledgment

We thank Mr. N. Parthasarathi and Mr. P. Sasikumar for experimental assistance.

REFERENCES

- [1] (a) J. Miller, Rev. Pure Appl. Chem., 1951, 1, 171;
- (b) S. Ross, Progr. Phys. Org. Chem., 1963, 1, 31;
- (c) J. Miller; Aromatic Nucleophilic Substitution, Elsevier, New York, 1968.
- [2] O. Rogne, J. Chem. Soc., 1971, (B), 1855.
- [3] J. J. Ryan, A. A. Humffray, J. Chem. Soc., 1967, B, 1300.
- [4] P. L. Nayak, T. R. Mohanty, J. Chem. Soc. Perkin Trans., 1975, 2, 242.
- [5] O. Banjoko, R. Okwuiwe, J. Org. Chem., 1980, 45, 4966-4968.
- [6] M. Krishna Pillay, K. Kannan, P. Ramasubramanian, Tetrahedran, 1983, 39, 3899.
- [7] M. Krishna Pillay and G. Balasubramanian, J. Indian Chem. Soc., 1987, LXII, 24.
- [8] T.G.Devi, G.Thota, P.Srinivas, Der Chemica Sinica, 2011, 2(2), 35.
- [9] S.Hussain, S.R.Gour, M.Farooqui, Der Chemica Sinica, 2011, 2(1), 61.
- [10]S.M.Lonkar, S.S.Mokle, A.Y.Vibhute, Y.B.Vibhute, Der Chemica Sinica, 2010, 1(2), 119.
- [11] S.Parimala Vaijayanthi, N.Mathiyalagan, Der Chemica Sinica, 2011, 2(3), 41.
- [12] S. Ananthalakshmi, PhD thesis, Bharathidasan University (Tiruchirapalli, India, 2007).
- [13]A. I. Vogel; A Text Book of Practical Organic Chemistry, 4th edn., ELBS, London, 1978.
- [14]The Merck Index, 10th edn., Merck Rahway, New Jersey, **1983**.
- [15]M. Krishnapillay, R. Jeyaraman, M. Nallu, P. Venuvanalingam, M. Ramalingam, *Indian J. Chem. Soc.*, **1997**, 36, 414.
- [16]E. A. Guggenheim, J. E. Prue, Physico-Chemical Calculations, Interscience, London, 1955.
- [17]O. Rogne, J. Chem. Soc., 1970, B, 728.
- [18] J. H. Choi, B. C. Lee, H. W. Lee, I. Lee, J. Org. Chem., 2002, 67, 1277.
- [19] K. J. Lailder; Chemical Kinetics, Tata-McGraw Hill, New Delhi, 1965.
- [20] K. Chokalingam, C. Vaithiyalingam, Croat Chem. Acta., 2001, 74(1), 51.
- [21] Sheila Srivastava, Paul Srivastava, Der Chemica Sinica, 2010, 1(1), 13-19.
- [22] K. G. Sekar, S. K. Periyasamy, Der Chemica Sinica, 2012, 3(3), 645.
- [23] O. Rogne, J. Chem. Soc., 1970, B, 730.
- [24] J. E. Leffler, J. Org. Chem., 1955, 20, 1202.
- [25] O. Exner, Coll. Czech Chem. Commun., 1964, 20, 1094.
- [26] (a) P. L. Nayak, M. K. Rout, J. Indian Chem. Soc., 1970, 47, 807.
- (b) K. Bowden, N. B. Chapman, J. Shorter, J. Chem. Soc., 1964, 337.
- [27] Soo Dong Yoh, Doo Jung Kim, J. Korean Chem. Soc., 1981, 6, 25.
- [28] J. E. Leffler, E. Grunwald; Rates and Equilibria of Organic Reactions, Wiley, New York, 1963.
- [29] R. A. Marcus, J. Phys. Chem., 1968, 72, 891.

[30] L. T. Stangeland, L. Senatore, E. Ciuffarin, J. Chem. Soc. Perkin Trans., 1982, 2, 852.

[31] S. L. Johnson, Adv. Phys. Org. Chem, 1967, 5, 237.