

Kinetics of the reactions of 1-chloro-2,4,6-trinitrobenzene and phenyl-2,4,6-trinitrophenyl ether with aromatic amines in mixed solvents: Effect of amine basicity on hydrogen-bond interactions in toluene-methanol mixtures

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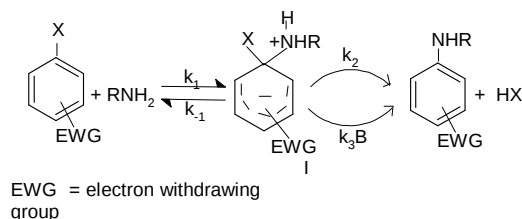
ABSTRACT

The kinetics of the reactions of 1-chloro-2,4,6-trinitrobenzene, **1**, with aniline and *N*-ethylaniline respectively and that of phenyl-2,4,6-trinitrophenyl ether, **2**, with aniline in toluene and toluene-methanol mixtures were studied at different temperatures. The reaction of **1** with the amines are not base-catalysed in toluene and the addition of small amounts of methanol to toluene medium for the reaction of aniline produced a slight diminution in rate up to 0.1% methanol, while methanol contents above 0.1% produced slight rate increase. Continuous moderate rate increase was displayed by *N*-ethylaniline reaction under the same reaction condition. The rates of both reactions were enhanced by increase in temperature. The reaction of phenyl-2,4,6-trinitrophenyl ether, **2**, with aniline was base-catalysed and added methanol produced remarkable rate increase as previously observed for the reaction in benzene-methanol mixtures at 30°C. The reaction displayed negative temperature effect, a reverse of the effect of temperature on the former reactions. The conflicting effects of added methanol and temperature in these reactions were reasonably accommodated by previously proposed cyclic transition state mechanism.

Keywords: Zwitterionic intermediate, Aggregate formation, Base-catalysis, aprotic solvent.

INTRODUCTION

Aromatic nucleophilic substitution plays a dominant role in the synthesis of aromatic derivatives of pharmaceutical and general purpose importance, hence the continued interest of chemists in these reactions.[1] The general mechanism for nucleophilic substitution involving activated aromatic compounds and amines is depicted in Scheme 1.



Scheme 1

Application of steady state hypothesis to Scheme 1 gives Eq. 1, where k_A is the second-order rate constant and B is either a second molecule of nucleophile or an added base acting as catalyst.

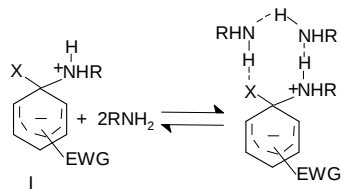
$$k_A = \frac{k_1(k_2 + k_3[B])}{k_{-1} + k_2 + k_3[B]} \quad (1)$$

Equation (1) allows three kinetic forms. If $k_{-1} \ll k_2 + k_3[B]$, then $k_A = k_1$, and reaction is not base catalysed. If $k_{-1} \gg k_2 + k_3[B]$, then the equation has the form in equation (2) and a linear plot of k_A against amine concentration is observed.

$$k_A = \frac{k_1 k_2}{k_{-1}} + \frac{k_1 k_3 [B]}{k_{-1}} \quad (2)$$

If no simplification of the equation is possible, plot of k_A against base concentration are curvilinear downwards.

The significant role of solvents in these reactions has long been recognized in chemical systems.[2] It is well established that the mode of nucleophilic aromatic substitution in low-polar aprotic solvent follows different kinetic pattern compared with that in dipolar aprotic or protic solvents due to the inability of aprotic solvents to stabilize ionic species such as intermediate, **I** in Scheme 1.[3-6] It is common, in low polar aprotic solvent to observe third-order dependence of k_A on amine concentration and this is reflected by the display of upward curvature in the plot of k_A against amine concentration.[7-11] We attributed this anomalous kinetics to the decomposition of the zwitterionic intermediate, **I**, via a cyclic transition state involving two amine molecules as catalysts (Scheme 2).[8,11]

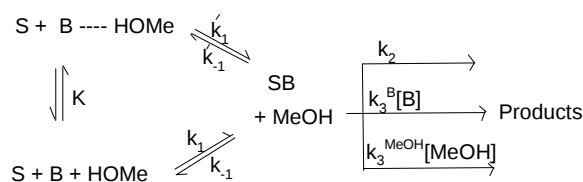


Scheme 2

Nudelman and Palleros on the other hand, proposed that the dimer of the amine which is considered a better nucleophile, attacks the substrate in the first step of the reaction to give an intermediate complex, the decomposition of which may be spontaneous or catalyzed by an amine molecule.[9,10] These workers adduced support for dimer mechanism from the fact that addition of small amounts of methanol to toluene medium produced rate diminution in the reaction of 2,6-dinitroanisole with cyclohexylamine. This observation was attributed to competition between the self association of amine and the methanol-amine aggregation which decrease the amine dimer concentration and lowers the nucleophilicity of the same.[12]

It is worthy of note that some S_NAr reactions in aprotic solvents are not base catalysed,^[13-15] indicating first order kinetics in amine. It is also instructive to note that some S_NAr reactions, though, very few occur with continuous rate increase on addition of small amounts of methanol to aprotic solvent.[16,17] The rate of the reaction of phenyl-2,4,6-trinitrophenyl ether, **2**, with aniline in benzene was accelerated in the presence of small amounts of methanol.[16]

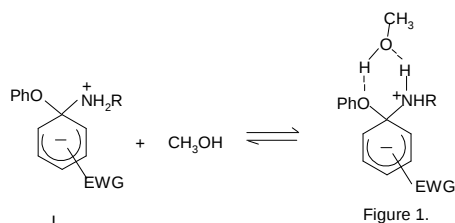
We rationalized, using Scheme 2 the contrasting increase and diminution in rates of some S_NAr reactions in the presence of small amounts of methanol in low- polar aprotic solvents.^[18]



Scheme 2

In Scheme 2, S stands for the substrate, B for the nucleophilic base, B---HOMe for the amine – methanol aggregate, SB for the zwitterionic intermediate, k_3^B and k_3^{MeOH} for the catalytic rate coefficients for conversion of intermediate

into products by the base and methanol respectively. Catalysis by methanol to produce rate increase was assumed reasonably possible in reactions with high catalytic effectiveness and susceptibility to strong hydrogen bonding. Methanol molecule can catalyse via cyclic transition state in the second step as depicted in Figure 1.



In order to have a more general view of the effect of methanol on S_NAr reactions in low-polar aprotic solvents, we decided to investigate the reaction of aniline with a substrate that is not prone base catalysis, since, aniline as nucleophile is involved in one of the few reactions where added methanol to low polar aprotic solvent produced rate increase for base catalysed reaction.[16] In this context, we investigated the reaction of 1-chloro-2,4,6-trinitrobenzene, **1**, with aniline and *N*-methylaniline respectively in toluene and toluene-methanol mixtures at different temperatures. We thought that it would also be of interest to investigate the effect of temperature on the reaction of phenyl-2,4,6-trinitrophenyl ether, **2**, with aniline in toluene and toluene-methanol mixtures, a reaction we earlier studied in benzene and benzene-methanol mixtures at 30 °C.

MATERIALS AND METHODS

The preparation of compounds **1** and **2** and their amine substitution products as well as purification of toluene and aniline were previously described.[21,22] Methanol was the purest available commercial grade. The reactions were monitored in the thermostated cell of Cecil spectrophotometer at temperatures in the range of 25 – 55 °C. For reactions in mixed solvents, the methanol contents (v/v), refers to its final volume in the reaction mixture. Optical densities were recorded at the absorption maximum wavelength of each product. The reactions were carried out under conditions of excess of nucleophile over substrate and in all cases excellent first-order plots were obtained. The second-order rate constants, k_A , were obtained by dividing the first-order rate constant by the amine concentration. All rate determinations were carried out at least in duplicate and the rate constants are accurate to with $\pm 2\%$.

RESULTS AND DISCUSSION

The reactions of **1**, and **2**, with either aniline or *N*-ethylaniline studied in toluene and toluene-methanol mixtures gave the expected substitution products in >95% yield. The second-order rate constants, k_A , for the reactions are presented in Tables 1 and 2. It can be seen from the Tables that the second-order rate constants are insensitive to amine concentration in both toluene and toluene-methanol mixtures. This corresponds to the condition of $k_2 + k_3[B] \gg k_1$ in equation 1 and the equation reduced to $k_A = k_1$. Previous studies have shown that lack of base catalysis in S_NAr reactions may be due to leaving group capability,[19] nature of nucleophile and solvent.[20] The reaction of *N*-ethylaniline, a secondary amine is of several orders of magnitude slower than that of aniline with **1**. In water the pK_A of aniline and *N*-ethylaniline are 4.60 and 5.09 respectively. The large differential in the reactivity of aniline and *N*-ethylaniline can be attributed to the dominance of steric crowding due to the *N*-ethyl group over amine basicity in the reactions.

The reaction of **1** with aniline and *N*-ethylaniline in toluene-methanol mixtures can be interpreted by Scheme 2. The expression for second order rate constant, k_A using the Scheme was exhaustively derived as equation (3) in our previous study.[18]

$$k_A = \frac{\left(\frac{k_1 K [MeOH]}{1 + K [MeOH]} + \frac{k_1}{1 + K [MeOH]} \right) \left(k_2 + \frac{k_3^B [B]}{1 + K [MeOH]} + \frac{k_3^{MeOH} [MeOH]}{1 + K [MeOH]} \right)}{k_1 + k_1 [MeOH] + k_2 + \frac{k_3^B [B]}{1 + K [MeOH]} + \frac{k_3^{MeOH} [MeOH]}{1 + K [MeOH]}} \quad (3)$$

For an uncatalysed reaction in which the first step of reaction is rate limiting, the condition,

$$k_2 + \frac{k_3^B[B]}{1 + K[MeOH]} + K_3^{MeOH}[MeOH] \gg k_1 + k_{-1}[MeOH]$$

holds and on the assumption that hydrogen bonding with methanol reduces the nucleophilicity of the amine, $k_1 \gg k'_{-1}$, Eq. 3 then reduces to Eq. 4

Table 1: Second-order rate constants, k_A for the reaction of 1-Chloro-2,4,6-Trinitrobenzene with aniline in both toluene and toluene-methanol mixtures at different temperatures

[AN] M	%Me (v/v)	25 °C	k_A 30 °C	$dm^3 mol^{-1}s^{-1}$			E_a , kJ/mol	r^a
			35 °C	45 °C	55 °C			
0.01	0		0.127					
0.02	0	0.103	0.127	0.149	0.21	0.274	26.48	0.996
0.005	0		0.113					
0.008	0		0.117					
0.008	0	0.1		0.159	0.215	0.304	29.32	0.978
0.02	0.05	0.088						
0.005	0.05	0.085						
0.008	0.05	0.086		0.149	0.205	0.293	33.19	0.989
0.008	0.1	0.083		0.134	0.163	0.263	29.39	0.979
0.008	0.2	0.092		0.14	0.19	0.27	29.62	0.998
0.008	0.3	0.109		0.189	0.293	0.364	32.69	0.974
0.008	0.5	0.138		0.214	0.321	0.399	29.032	0.985

[substrate] = $5 \times 10^{-5} mol dm^{-3}$, ^a Linear correlation coefficient.
[AN] = [Aniline], M = $mol dm^{-3}$, Me = Methanol

Table 2: Second-order rate constants, k_A for the reaction of 1-Chloro-2,4,6-Trinitrobenzene with N-ethyl aniline (NEA) in both toluene and toluene-methanol mixtures at different temperatures

[NEA] M	%MeOH (v/v)	$10^3 k_A dm^3 mol^{-1}s^{-1}$			E_a , kJ/mol	r^a
		25°C	35°C	45°C		
0.1	0	0.91	1.47	2.48	38.02	0.997
	0.1	0.92	1.62	2.50	37.82	0.998
	0.5	0.98	1.69	3.83	51.32	0.979
	1.0	1.00	1.82	3.90	54.10	0.987
	2.0	1.02	1.96	4.08	54.00	0.993
0.2	0	0.93	1.52	2.72	40.22	0.994
	0.1	0.98	1.53	2.75	38.28	0.989
	0.5	1.01	1.59	2.87	39.42	0.990
	1.0	1.03	1.74	3.16	44.79	0.922
	2.0	1.04	1.85	3.80	50.93	0.992
0.3	0	0.92	1.31	2.86	41.32	0.942
	0.1	0.94	1.36	3.17	46.21	0.938
	0.5	0.99	1.38	-	-	-
	1.0	0.97	1.44	3.26	47.99	0.945
	2.0	1.02	1.55	3.47	47.36	0.946
0.4	0	0.98	1.46	2.76	38.92	0.975
	0.1	0.98	1.49	2.89	40.43	0.976
	0.5	0.99	1.61	2.98	40.93	0.992
	1.0	1.01	1.75	2.26	31.43	0.969
	2.0	-	-	3.51	-	-

[substrate] = $5 \times 10^{-5} mol dm^{-3}$, ^a Linear correlation coefficient.
[AN] = [Aniline], M = $mol dm^{-3}$, Me = Methanol

$$k_A = \frac{k_1}{1 + K[MeOH]} \quad (4)$$

The results in Table 1 show that small additions of methanol to toluene solvent produced slight rate diminution for the reaction of **1** with aniline giving credence to Eq. 4. This is reflected in the lower value of k_A in toluene-methanol mixture compared with that obtained in pure toluene. We had earlier proposed in our investigation of the base catalysed reaction of **2** ether with piperidine[18] that added methanol to non-polar aprotic solvent can produce two effects: rate diminution in the first step of reaction due amine-methanol aggregate formation and rate increase in the second step involving the catalysis of the decomposition of the zwitterionic intermediate by methanol molecule through cyclic transition state as depicted in Figure1. In a reaction that is not base-catalysed only rate diminution comes into play in the first step and this has been attributed to the reduced nucleophilicity of amine due to amine-

methanol aggregate formation. It is worthy of note that in the uncatalysed reaction of aniline with **1** which is first order with respect to amine, the phenomenon of dimer formation is most unlikely. The extent of rate diminution in the said reaction due to added methanol is remarkably smaller than that observed in the uncatalysed reaction of **2** with cyclohexylamine in the same solvent system.^[18] While the rate of the latter decreased remarkably in the presence of small amounts of methanol and less rapidly at higher methanol contents to attain a minimum at 100% methanol, that of the former decreased only slightly till about 0.1% methanol followed by small increase. The small depression in rate due to added methanol for the reaction of **1** with aniline can be reasonably attributed to poor hydrogen bond interaction of methanol with aniline molecule, being weakly basic. The wide difference in the pKa value of aniline (4.60) compared with that of cyclohexylamine (10.49) attests to this assumption. The increase in reaction rate at methanol contents of 0.2 % and above for the reaction can be attributed to increase in medium polarity as methanol concentration increases.

The results in Table 2 show that addition of methanol to toluene medium for the reaction of **1** with *N*-ethylaniline produced gradual rate increase. To a first approximation, we would expect a slight decrease in rate due to *N*-ethylaniline-methanol aggregate formation considering the fact that the ΔpK_a of *N*-ethylaniline and that of aniline is only 0.5. The slight increase rather than diminution in rate can be attributed to increase in polarity of reaction medium as steric requirement at the nitrogen atom of *N*-ethylaniline would prevent amine-methanol aggregate formation that could have lowered the amine nucleophilicity.

Comparisons of the effect of methanol

Added methanol to the reaction of **1** with *N*-ethylaniline in toluene medium produced slight rate increase with no diminution as expected for a reaction that is not base-catalysed. It is, therefore, necessary to compare the extent of rate increase caused by methanol in this reaction to that in a base-catalysed reaction where methanol can produce rate increase by catalysis through cyclic state transition.

Table 3: Second-order rate constants, k_A for the reaction of phenyl-2,4,6-trinitrophenyl ether with aniline in both toluene and toluene-methanol mixtures at different temperatures

[AN] M	% Me (v/v)	$10^{-4}k_A \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$				E_a kJ/mol	r^a
		25°C	35°C	45°C	55°C		
0.2	0	9.00	7.89	7.28	6.79	-7.16	0.979
0.2	0.05	9.88	9.34	8.08	7.83	-6.69	0.943
0.2	0.1	11.48	9.74	9.20	8.27	-8.51	0.972
0.2	0.2	12.93	12.00	10.64	10.30	-6.56	0.968
0.2	0.3	14.35	13.00	12.04	11.25	-6.47	0.995
0.2	0.5	17.98	16.79	15.65	14.55	-5.89	0.995
0.15	0	5.54	4.56	4.04	3.41	-12.84	0.994
0.15	0.05	6.21	5.45	4.16	3.56	-15.455	0.977
0.15	0.1	7.73	6.60	5.86	5.40	-9.63	0.984
0.15	0.2	10.45	9.85	8.86	8.22	-6.60	0.987
0.15	0.3	13.05	12.44	11.87	11.38	-4.56	0.998

[substrate] = $5 \times 10^{-3} \text{ mol dm}^{-3}$, ^a Linear correlation coefficient.

[AN] = [Aniline], M = mol dm^{-3} , Me = Methanol

In the previous study of the base-catalysed reaction of **2** with aniline in benzene,[16] the presence of 0.5% methanol content produced 250% rate increase while the same methanol content for the uncatalysed reaction of **1** with *N*-ethylaniline in toluene (Table 2) produced just about 10% rate increase. The wide difference in the degree of rate increase is clearly indicative of a difference in the effect of methanol on the rates of the two reactions. The rate increase in the former is attributable to catalysis by methanol molecules while that in the latter is due to increase in the polarity of the medium. It was earlier pointed out that only poor amine-methanol hydrogen bond interaction is possible for a weak amine like aniline leading to very slight rate diminution while such interaction in similarly weak *N*-ethylaniline is made almost impossible by steric hinderance at the nitrogen atom. In the absence of amine-methanol aggregates of reduced nucleophilicity, added methanol to low-polar aprotic solvent would only increase the polarity of the medium, hence a moderately enhanced reaction rate.

For the base-catalysed reaction in toluene-methanol mixtures Eq. 3 which can also be re-written as Eq. 5 holds. At constant amine concentration in the presence increasing methanol concentration Eq. 5 reduces to equation 6.

$$k_A = \frac{k_1 k_2}{k_{-1}(1 + K[\text{MeOH}])} + \frac{k_1 k_3^B [\text{B}]^2}{k_{-1}(1 + K[\text{MeOH}]^2)} + \frac{k_1 k_3^{\text{MeOH}} [\text{MeOH}]}{k_{-1}(1 + K[\text{MeOH}])} \quad (5)$$

$$k_A = k' + k''[\text{MeOH}] \quad (6)$$

$$k' = \frac{k_1 k_2}{k_{-1}(1 + K[\text{MeOH}])} + \frac{k_1 k_3^B [\text{B}]^2}{k_{-1}(1 + K[\text{MeOH}]^2)} \quad (7)$$

$$k'' = \frac{k_1 k_3^{\text{MeOH}}}{k_{-1}(1 + K[\text{MeOH}])} \quad (8)$$

The plot of k_A against $[\text{MeOH}]$ for the reaction of **2** with 0.2 M aniline concentration gave a straight line at constant temperature (Figure 2), giving credence to Eq. 6.

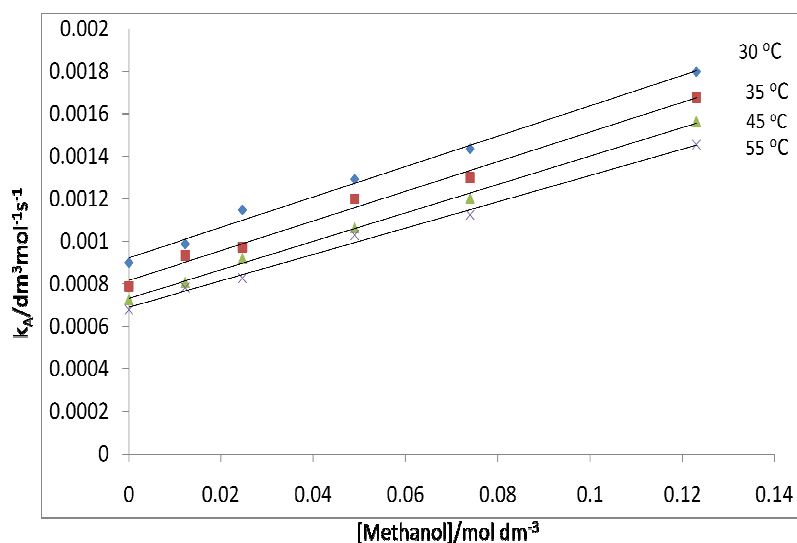


Figure 2. Plot of k_A against $[\text{Methanol}]$ for the reaction of **2** with aniline in the absence and presence of added methanol at 25, 35, 45 and 55 °C.

Effect of Temperature

The second-order rate constants for the reaction of **1** with aniline and *N*-ethylaniline respectively in pure toluene as well as toluene-methanol mixtures increase with increase in temperature, thus resulting in positive activation energies (Tables 1 and 2). Similar results were obtained for the uncatalysed reaction of phenyl-2,4,6-trinitrophenyl ether with cyclohexylamine in benzene-methanol mixtures.[18] In a contrary manner, the rate of base catalysed reaction of **2** with aniline in toluene-methanol mixtures decreased with increase in temperature as shown in Table 3 and it has been previously shown that temperature has similar effect on the reaction in pure benzene.[11]

It is instructive to note that added methanol to toluene medium produced rate increase (though to different extents) for the based-catalysed reaction of **2** with aniline and the uncatalysed reaction of **1** with *N*-ethylaniline while temperature increase produced inverse effects for the two reactions as displayed in Figure 3. In the reaction of **1** with *N*-ethylaniline, the first step is rate determining and an increase in temperature should produce rate increase in the presence of methanol whether there is strong aggregate formation between methanol and amine or not. On the other hand, negative temperature effect is feasible in the former reaction if methanol molecules catalyse the reaction and that, through hydrogen bonding as made possible in the cyclic transition state mechanism, Figure 1.

The effect of temperature on the individual rate constants in Eq. 6 is quite instructive. The slopes and intercepts for the plots of k_A against $[\text{MeOH}]$ for the reaction of **2** with aniline at constant temperatures (Figure 2) are presented in Table 4.

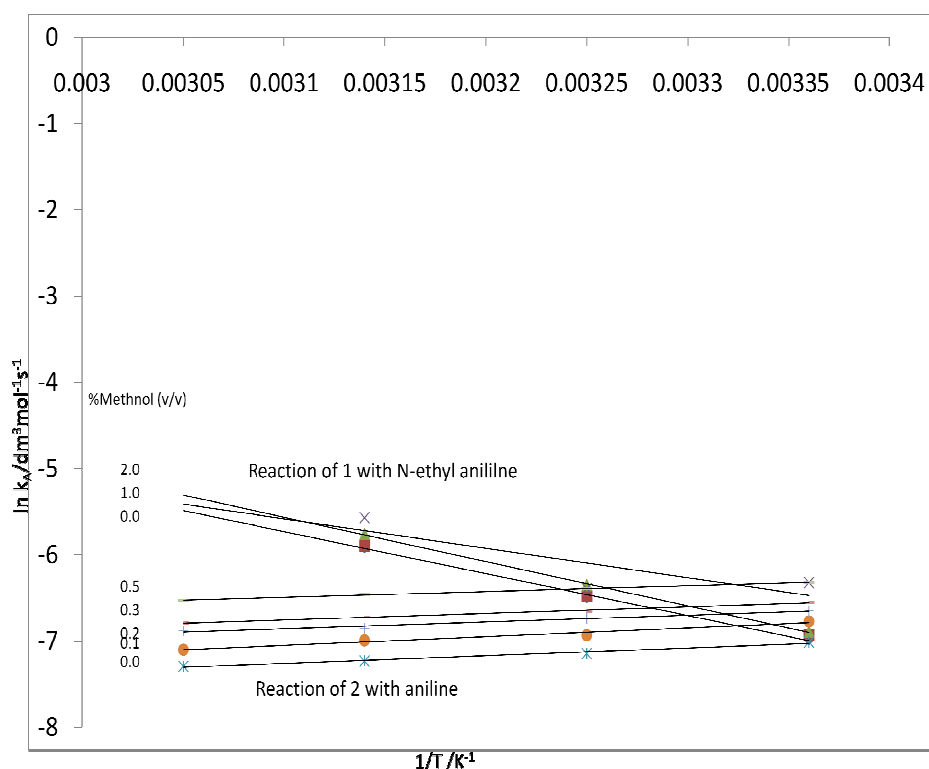


Figure 3. Plot of $\ln k_A$ against $1/T$ for the reaction of 1 with N-ethyl aniline and the reaction of 2 with aniline in the absence and presence of added methanol at 25, 35, 45 and 55 °C.

Table 4: Values of intercepts and slopes of the plot of Second-order rate constants, k_A versus [Methanol] at constant aniline concentration for the reaction of 2 with aniline in toluene and toluene-methanol mixtures at different temperatures

[Aniline] mol dm ⁻³	Temp. °C	10^4 $k' / \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	10^3 $k'' / \text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$	r^a
0.2	25	9.0	7.2	0.992
	35	8.0	7.0	0.991
	45	7.0	6.7	0.998
	55	7.0	6.2	0.994

The intercepts and slopes decrease slightly with increase in temperature. It should be noted that the intercept represented in Eq. 7 is influenced by rate constants k_1 , k_2 , k_3^B (hydrogen bond aided in cyclic transition, Scheme 2) as well as the equilibrium constant K . Temperature increase should ordinarily enhance the value of k_1 (attack of amine on substrate) but depress the association constant, K for amine-methanol aggregate. The spontaneous decomposition of the zwitterionic intermediate, **I** has been agreed to take place unimolecularly in low-polar aprotic solvent via the hydrogen bonded complex represented in Figure 4.[16, 11] Temperature increase would, therefore, decrease the rate of formation of the hydrogen bonded complex which may reflect as reduced k_2 .

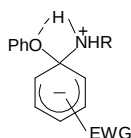


Figure 4.

In the same vein, k_3^B for the base-catalysed rate constant k_3^B (hydrogen bond aided in cyclic transition, Scheme 2) is retarded by temperature increase. The decrease in the values of k_2 and k_3^B may more than compensate for the possible increase in rate due to elevated temperature for k_1 , hence the resultant decrease in intercept. Moreover, the absence of activation energy has been suggested to be indicative of a reaction occurring stepwise,[16,23] the rate-

determining step being preceded by at least one fast equilibrium whereby the expected increase in rate for slow step with increasing temperature would be neutralized by a shift process of the preceding equilibrium. It also indicates that the rate-determining step is not just the final transfer of a proton from the zwitterionic intermediate to the catalyzing amine, but that this is preceded by a process controlled by some geometric factors, presumably the formation of a hydrogen-bonded or a somewhat properly oriented complex.

The slope of the graph in Eq. 8 is influenced by k_1 and k_3^{MeOH} . The catalytic rate constant, k_3^{MeOH} for methanol would decrease with increase in temperature if catalysis by methanol is through hydrogen bonding as depicted in Figure 1. The effect will be decrease in slope as temperature increases.

CONCLUSION

The formation of amine-methanol aggregates in S_NAr reactions on addition of methanol to low-polar aprotic medium depends strongly on the basicity and steric demand of the amine. Strongly basic amine would produce amine-methanol aggregates with reduced nucleophilicity leading to rate diminution in the first step of the reaction. On the other hand, weak amines would have poor hydrogen-bond interaction with methanol, hence little or no effect on amine nucleophilicity and the presence of small amount of methanol may lead to rate increase in the first step especially if the weak amine is also sterically hindered at the amino nitrogen.

For reactions that are not base-catalysed in non-polar aprotic solvent, increase in temperature would produce rate increase in the presence of small amounts of methanol irrespective of whether added methanol produce rate increase or rate diminution. In contrast, a based catalysed reaction in which methanol molecule catalyse the decomposition of zwitterionic intermediate through cyclic transition state would exhibit negative temperature effect as the strength of hydrogen bonding decrease with increasing temperature.

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