

## Kinetics of aminolysis of 2,4-dinitrophenyl acetate

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The second order rate constants for the reaction of 2,4-dinitrophenyl acetate with aniline and *p*- and *o*-substituted anilines have been reported in 10% acetonitrile-90% water (v/v) mixture at 25°, 30°, 35° and 40°C. In the reaction of *p*-substituted anilines, electron-releasing groups facilitate the reaction while electron-withdrawing groups retard it. The  $\rho$ -value is evaluated to be  $-2.33 \pm 0.16$ . The Brønsted plot is also linear with  $\beta_N = 0.792 \pm 0.027$  at 30°C. The  $\Delta S^\ddagger$  values are all negative as expected for bimolecular nucleophilic substitution reactions. In the case of *o*-substituted anilines, the rate data have been analysed in terms of electronic and steric effects.

A number of kinetic studies have been reported on the reactions of esters<sup>1-9</sup> particularly acetate esters with various nucleophiles such as pyridines<sup>1-7</sup>, oxyanions<sup>1</sup>, imidazole<sup>8</sup>, hydrazine<sup>9</sup> and morpholine<sup>9</sup>. Though a report is available on the reactivity of aniline with acetate esters<sup>1</sup>, no comprehensive studies are reported on the reactivity of aniline and substituted anilines with acetate esters. Title investigation is an attempt to fill this gap.

### Materials and Methods

2,4-Dinitrophenyl acetate was prepared in the laboratory and substituted anilines were either commercial samples or prepared and purified in the laboratory. Purified acetonitrile was used. Triply distilled water was used throughout the study.

All the kinetic runs were carried out in 10% acetonitrile-90% water (v/v) mixture. The kinetics were followed up to 60% or more spectrophotometrically at 360 nm and 400 nm under pseudo-first order conditions ( $[\text{aniline}] = 5 \times 10^{-4}$  to  $2 \times 10^{-2}$  mol dm<sup>-3</sup> depending upon the reactivity of aniline and  $[\text{2,4-dinitrophenyl acetate}] = 5 \times 10^{-5}$  mol dm<sup>-3</sup>) at the required temperature ( $\pm 0.1^\circ\text{C}$ ) and at an ionic strength of 0.2 mol dm<sup>-3</sup> (NaClO<sub>4</sub>). Stock solution of 2,4-dinitrophenyl acetate was prepared in pure acetonitrile.

In all the kinetic runs plots of  $\log(D_\infty - D_t)$  versus  $t$  was linear (corr. coeff. = 0.999) and pseudo-first order rate constants were evaluated from the slopes of the plots. There was no solvolysis of the ester under the experimental condition and therefore no concentration correction was required.

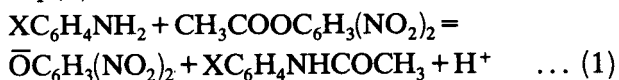
### Product analysis

One of the final products of the reaction of 2,4-dinitrophenyl acetate with aniline was identified as

2,4-dinitrophenolate ion by comparison of the UV spectrum of the reaction sample at infinity time with that of the authentic sample. The reaction mixture was extracted with ether, the organic layer separated and dried. TLC analysis of the product over silica gel using acetone-pet. ether (5:95, %) as solvent system showed two spots, one corresponding to unreacted aniline and other corresponding to authentic acetanilide.

### Results and Discussion

The rates of nucleophilic substitution reaction of 2,4-dinitrophenyl acetate (DNPA) with various anilines were measured at various initial [aniline] (Table 1). Change in  $[\text{DNPA}^-]$  was followed at two different wavelengths, viz. 360 and 400 nm. Rate constants, calculated with the measurements at these two wavelengths, were found to be the same indicating that these UV bands are due to a single reaction product. The plots of  $\log(D_\infty - D_t)$  versus  $t$  were linear showing first order dependence on [DNPA]. The log-log plot of  $k_1$  versus [aniline] was linear, passing through the origin indicating that the reaction followed second order kinetics and the solvolysis of 2,4-dinitrophenyl acetate was negligible. The reaction of aniline with DNPA can be represented by Eq. (1).



where X is the substituent present in the *para*- or *ortho*-position of aniline. The product analysis shows that except acetanilide and 2,4-dinitrophenolate ion, no other product is formed. The observed decrease in the rate of the reaction with decreasing solvent polarity (Table 1) is due to lesser solvation of the polar transition state as compared to that of the

Table 1—Effect of varying [Aniline], [NaClO<sub>4</sub>] and solvent composition on second order rate constants at 30°C

[DNPA] × 10 <sup>5</sup> (mol dm <sup>-3</sup> )	[Aniline] × 10 <sup>3</sup> (mol dm <sup>-3</sup> )	[NaClO <sub>4</sub> ] (mol dm <sup>-3</sup> )	% Acetonitrile in H <sub>2</sub> O	$k_2^a \times 10^2$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	
				360 nm	400 nm
5.0	4.0	0.2	10	10.69 ± 0.09	11.02 ± 0.09
5.0	5.0	0.2	10	11.51 ± 0.62	12.29 ± 0.18
5.0	6.0	0.2	10	11.86 ± 0.14	13.24 ± 0.17
5.0	8.0	0.2	10	11.81 ± 0.08	12.88 ± 0.11
5.0	5.0	0.2	20	6.93 ± 0.14	6.94 ± 0.16
5.0	5.0	0.2	30	4.61 ± 0.03	4.74 ± 0.03
5.0	5.0	0.2	40	2.47 ± 0.04	2.53 ± 0.02
5.0	5.0	0.2	50	1.62 ± 0.09	1.60 ± 0.04
5.0	5.0	0.0	10	16.64 ± 0.34	19.11 ± 0.53
5.0	5.0	0.1	10	13.27 ± 0.16	14.04 ± 0.07
5.0	5.0	0.3	10	10.71 ± 0.05	11.28 ± 0.04
5.0	5.0	0.4	10	9.89 ± 0.03	10.33 ± 0.05

<sup>a</sup> $k_2 = k_1/[\text{aniline}]$ Table 2—Second order rate constants and activation parameters for the reaction of 2,4-dinitrophenyl acetate with *para*- and *ortho*-substituted anilines at 400 nm in 10% acetonitrile-90% water (v/v) mixture[DNPA] = 5 × 10<sup>-5</sup> mol dm<sup>-3</sup>; [Anilines] = 2 × 10<sup>-2</sup> – 5 × 10<sup>-4</sup> mol dm<sup>-3</sup>; [NaClO<sub>4</sub>] = 0.2 mol dm<sup>-3</sup>

Substituent	$k_2 \times 10^2$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> ) at temp. (°C)				$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> ) (at 30°C)	$-\Delta S^\ddagger$ (J K <sup>-1</sup> mol <sup>-1</sup> ) (at 30°C)
	25	30	35	40		
<i>p</i> -OMe	606 ± 4	729 ± 6	853 ± 6	1107 ± 4	23.7 ± 1.4	169.0 ± 4.9
<i>p</i> -Me	286 ± 1	367 ± 1	477 ± 11	547 ± 5	31.5 ± 2.8	149.7 ± 9.7
<i>p</i> -Ph	56.8 ± 0.7	70.9 ± 1.0	80.0 ± 0.6	90.8 ± 2.0	21.1 ± 1.5	197.4 ± 5.2
H	105 ± 1	123 ± 2	162 ± 1	186 ± 1	28.7 ± 0.9	167.9 ± 3.0
<i>p</i> -F	131 ± 1	167 ± 4	216 ± 3	255 ± 7	32.5 ± 1.9	152.9 ± 6.5
<i>p</i> -Cl	33.8 ± 0.2	48.9 ± 0.2	62.8 ± 0.2	84.2 ± 0.4	43.8 ± 3.3	125.6 ± 11.3
<i>p</i> -Br	28.6 ± 0.1	36.9 ± 0.2	48.5 ± 0.3	60.0 ± 0.2	36.2 ± 0.3	153.2 ± 1.2
<i>p</i> -COOH	2.78 ± 0.10	3.14 ± 0.01	3.36 ± 0.01	4.43 ± 0.01	21.9 ± 3.6	220.0 ± 12.2
<i>p</i> -COOMe	1.64 ± 0.05	2.57 ± 0.05	3.29 ± 0.09	3.82 ± 0.10	40.7 ± 2.6	160.5 ± 9.1
<i>o</i> -OMe	43.9 ± 0.8	48.0 ± 1.0	62.4 ± 0.4	79.0 ± 0.8	28.9 ± 1.5	175.0 ± 5.2
<i>o</i> -Me	22.4 ± 0.4	29.4 ± 0.2	35.4 ± 0.2	46.0 ± 1.8	32.4 ± 3.1	167.5 ± 10.8
<i>o</i> -Et	12.5 ± 0.1	16.2 ± 0.1	22.0 ± 0.2	27.1 ± 0.8	37.5 ± 1.5	158.3 ± 5.3
<i>o</i> -Ph	10.2 ± 0.6	13.9 ± 0.6	17.6 ± 1.0	20.8 ± 0.8	39.2 ± 3.6	157.9 ± 12.3
<i>o</i> -F	4.55 ± 0.17	6.30 ± 0.14	7.80 ± 0.25	9.90 ± 0.10	33.5 ± 2.5	170.0 ± 8.2
<i>o</i> -Cl	0.752 ± 0.050	1.08 ± 0.02	1.40 ± 0.01	1.80 ± 0.03	43.4 ± 3.0	158.5 ± 10.2
<i>o</i> -COOH	2.27 ± 0.03	2.90 ± 0.02	4.16 ± 0.08	5.34 ± 0.13	42.0 ± 3.6	154.8 ± 12.5
<i>o</i> -COOMe	2.79 ± 0.03	3.34 ± 0.02	4.06 ± 0.25	4.81 ± 0.28	25.9 ± 3.4	206.9 ± 11.5

reactants. The effect of ionic strength on the rate of the reaction (Table 1) shows that the transition state is polar in nature.

The second order rate constants calculated for the reaction of 2,4-dinitrophenyl acetate with aniline and various substituted anilines at 25°, 30°, 35° and 40°C are given in Table 2. The rate data in

Table 2 show that electron-releasing substituents increase the rate while electron-withdrawing substituents retard it. The order of reactivities of aniline with different *para*-substituents is the same as that observed in the reaction of anilines with phenacyl bromide, ethyl bromoacetate and allyl bromide<sup>10</sup> and also in the reaction of anilines with ethyl 4-bromoc-

rotonate<sup>11</sup>. A comparison of the rate data of different substrates<sup>10,11</sup> with anilines gives the order 2,4-dinitrophenyl acetate > phenacyl bromide > ethyl 4-bromocrotonate > allyl bromide > ethyl bromoacetate.

A good Hammett correlation is found to exist in the reaction series when  $\log k_2$  values are plotted against the  $\sigma/\sigma^-$  constants. The  $\sigma^-$  values are used for electron-withdrawing substituents because of cross conjugation involving electron-withdrawing *para*-substituents and electron-rich reaction site. The results of the correlation are expressed by Eq. (2).

$$\log k_{30^\circ} = -2.33 \sigma/\sigma^- - 0.854 \quad \dots (2)$$

( $\pm 0.16$ )

$$r = 0.985; s = 0.162; n = 9; \psi = 0.196$$

The  $\rho$ -value, which is negative ( $-2.33$ ), as expected for nucleophilic substitution reactions, is comparable with those obtained for the reactions of anilines with ethyl bromoacetate<sup>10</sup> ( $-2.33$ ), phenacyl bromide<sup>10</sup> ( $-2.33$ ), allyl bromide<sup>10</sup> ( $-1.80$ ) and ethyl 4-bromocrotonate<sup>11</sup> ( $-1.95$ ). Relatively larger  $\rho$ -value ( $-2.33$ ) observed in this reaction series suggests that bond making tends to be advanced in the transition state of the reaction<sup>12</sup>.

An excellent Brönsted-type plot has been obtained for the reaction of anilines with 2,4-dinitrophenyl acetate. The result can be expressed by Eq. (3).

$$\log k_{30^\circ} = 0.792 pK_a - 4.485 \quad \dots (3)$$

( $\pm 0.027$ )

$$r = 0.996; s = 0.082; n = 9; \psi = 0.101$$

The linear Brönsted plot is in contrast to that obtained in the reaction of 2,4-dinitrophenyl acetate with substituted pyridines<sup>2</sup>. The positive value of Brönsted coefficient and the negative  $\rho$ -value are indicative of the increase in rate with increase in the basicity of the nucleophile. The present value of Brönsted coefficient (0.792) is comparable with that obtained for the reaction<sup>10</sup> of phenacyl bromide (0.768) and ethyl bromoacetate (0.796) and slightly higher than that observed for the reaction<sup>11</sup> of ethyl 4-bromocrotonate (0.640). This shows that the extent of bond formation in the transition state is the same as that of the reaction of anilines with phenacyl bromide and ethyl bromoacetate.

The values of  $\Delta S^\ddagger$  are all negative (Table 2), as is expected for an  $S_N2$  process. Because of the development of charge in the transition state,  $\Delta S^\ddagger$  values are more negative. Exner plot of  $\log k_2$  (at 313 K) versus  $\log k_2$  (at 298 K) for the reaction of 2,4-dinitrophenyl acetate with anilines is linear ( $r = 0.998$ ) and the isokinetic temperature is found

to be 105 K. Existence of excellent correlation shows that in the reaction series all the anilines follow the same mechanism.

The rate constants and the activation parameters for the reaction of a few *ortho*-substituted anilines with 2,4-dinitrophenyl acetate (Table 2) show that the rate is considerably decreased (except for substituents such as  $-\text{COOH}$  and  $-\text{COOMe}$ ) as compared with that of *para*-substituted anilines. The rate data were analysed on Taft's linear free energy-polar energy and linear free energy-steric energy relationships<sup>13</sup>. The results may be expressed by Eqs (4) and (5). The values of  $\sigma_0^*$  and  $E_s$  used in the correlations are those given by Taft<sup>13</sup>.

$$\log k_{ortho} = -2.221 \sigma_0^* - 1.800 \quad \dots (4)$$

( $\pm 0.529$ )

$$r = 0.864; s = 0.304; n = 8; \psi = 0.581$$

$$\log k_{ortho} = 0.131 E_s - 1.995 \quad \dots (5)$$

( $\pm 0.530$ )

$$r = 0.141; s = 0.740; n = 5; \psi = 1.617$$

The results of the analysis show that the observed rates of *ortho*-substituted anilines with 2,4-dinitrophenyl acetate are not compatible with either the Taft's polar substituent parameters or size of the substituents.

The ratio of the rate constants for similar *ortho*- and *para*-substituted benzene systems has also been taken as a measure of steric effect of the *ortho*-substituents<sup>14</sup>. A poor correlation is obtained when  $\log k_{ortho}/k_{para}$  is plotted against  $E_s$  (Eq. 6).

$$\log \frac{k_{ortho}}{k_{para}} = -0.288 E_s - 1.143 \quad \dots (6)$$

( $\pm 0.230$ )

$$r = 0.586; s = 0.321; n = 5; \psi = 1.046$$

These analyses are indicative of the minor role of primary steric effect. Since the single parameter equations did not yield satisfactory correlations, the rate data were analysed using the Charton's method<sup>15</sup>. The rate constants were correlated using Eqs (7) and (8).

$$\log k_{ortho} = \alpha \sigma_1 + \beta \sigma_R + h \quad \dots (7)$$

$$\log k_{ortho} = \alpha \sigma_1 + \beta \sigma_R + \phi v + h \quad \dots (8)$$

In Eqs (7) and (8),  $\sigma_1$ ,  $\sigma_R$  and  $v$  are inductive, resonance and steric substituent constants respectively, and the values used were those compiled by Aslam *et al.*<sup>16</sup>. The result of regression Eq. (7) may be expressed by the correlations given in Eqs (9) and (10) for planar and orthogonal conformations at 30°C respectively.

**Planar**

$$\log k_{30^\circ} = -2.852 \sigma_I - 1.341 \sigma_R - 1.505 \quad \dots (9)$$

$$\pm 0.761 \quad \pm 0.627$$

$$R = 0.840; SE = 0.408; n = 9; F = 7.20; CL < 95\%$$

**Orthogonal**

$$\log k_{30^\circ} = -3.029 \sigma_I - 1.649 \sigma_R - 1.564 \quad \dots (10)$$

$$\pm 0.776 \quad \pm 0.732$$

$$R = 0.848; SE = 0.399; n = 9; F = 7.69; CL < 95\%$$

In the multiple regression analysis using Eq. (7), correlation coefficient is poor, and the standard error of estimate and the error of regression coefficient are high. The absence of significant correlation with Eq. (7) leads to the conclusion that the electrical effects alone are not sufficient to account for the *ortho*-substituent effect in this reaction.

The result of regression Eq. (8), for both planar and orthogonal conformations at 30°C are given by Eqs (11) and (12), respectively.

**Planar**

$$\log k_{30^\circ} = -2.828 \sigma_I - 1.289 \sigma_R - 0.023 \nu - 1.485$$

$$\pm 0.889 \quad \pm 0.974 \quad \pm 0.308 \quad \dots (11)$$

$$R = 0.840; SE = 0.447; n = 9; F = 4.01; CL = 95\%$$

**Orthogonal**

$$\log k_{30^\circ} = -2.789 \sigma_I - 1.336 \sigma_R - 1.639 \nu - 0.864$$

$$\pm 0.415 \quad \pm 0.395 \quad \pm 0.405 \quad \dots (12)$$

$$R = 0.967; SE = 0.211; n = 9; F = 23.8; CL > 99.5\%$$

The significance of the correlations was tested by means of F-test. In the regression analysis, good correlation is obtained when the parameters calculated for the orthogonal conformation are used rather than those calculated from the coplanar conformation. The confidence levels of  $\sigma_I$ ,  $\sigma_R$  and  $\nu$  terms, based on 'Student t' test, are above 99.5% showing that localised, delocalised and steric effects are significant. The regression coefficients of  $\sigma_I$  and  $\sigma_R$  are negative indicating that electron-releasing substituents accelerate the reaction and electron-withdrawing substituents retard it as in the case of *para*-substituents. The regression coefficient of  $\nu$  is also negative indicating the steric retardation of rate by *ortho*-substituents in this reaction series. The composition of the electrical effect<sup>15</sup>,  $P_R$ , was calculated using Eq. (13).

$$P_R = \frac{|\beta| 100}{|\alpha| + |\beta|} \quad \dots (13)$$

The value of  $P_R = 32.4$  at 30°C, shows that the localised effect is more dominant than the delocalised

one. The magnitude (per cent) of the steric effect<sup>15</sup>,  $P_S$ , was calculated using Eq. (14).

$$P_S = \frac{|\phi| 100}{|\alpha| + |\beta| + |\phi|} \quad \dots (14)$$

The value of  $P_S = 28.4$  at 30°C, shows that the steric effect is considerable.

When the logarithm of the rate constants and the  $pK_a$  values of the corresponding conjugate acid of the *ortho*-substituted anilines are plotted, a fairly linear plot is obtained. The result of correlation is given by Eq. (15).

$$\log k_{30^\circ} = 0.559 pK_a - 3.914$$

$$(\pm 0.104) \quad \dots (15)$$

$$r = 0.897; s = 0.308; n = 9; \psi = 0.501$$

The value of Brönsted coefficient ( $0.559 \pm 0.104$ ) is lower than that observed for the *para*-substituted anilines which may be due to the operation of steric effect. Exner plot of  $\log k_2$  (at 313 K) versus  $\log k_1$  (at 298 K) for *ortho*-substituted anilines is linear ( $r = 0.996$ ), indicating the operation of an identical mechanism in all the *ortho*-substituted anilines.

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**References**

- 1 Bender M L & Turnquest B W, *J Am chem Soc*, 79 (1957) 1656.
- 2 Castro E A & Fredenberg M, *J org Chem*, 45 (1980) 906.
- 3 Jencks W P & Gilchrist M, *J Am chem Soc*, 90 (1968) 2622.
- 4 Bond P M, Castro E A & Moodie R B, *J chem Soc Perkin 2* (1976) 68.
- 5 Butler A R & Robertson I H, *J chem Soc, Perkin 1*, (1975) 661.
- 6 Castro E A, Borquez M T & Parada P M, *J org Chem*, 51 (1986) 5072.
- 7 Castro E A & Steinfort G B, *J chem Soc, Perkin 2*, (1983) 453.
- 8 Bender M L & Turnquest B W, *J Am chem Soc*, 79 (1957) 1652.
- 9 Bruice T L & Schmir G L, *J Am chem Soc*, 79 (1957) 1663.
- 10 Srinivasan C, Shunmugasundaram A & Arumugam N, *Indian J Chem*, 21B (1982) 662.
- 11 Shunmugasundaram A & Radhakrishnan K, *Indian J Chem*, 26A (1987) 827.
- 12 Lee I & Koo I S, *Tetrahedron*, 39 (1983) 1803.
- 13 Taft R W, 'Steric effect in organic Chemistry', edited by M S Newman (John Wiley, New York) 1956, Ch. 13.
- 14 Taft R W, Newman M S & Verhoeck F H, *J Am chem Soc*, 72 (1950) 4511.
- 15 Charton M, *J org Chem*, 40 (1975) 407.
- 16 Aslam M H, Burden A G, Chapman N B, Shorter J & Charton M, *J chem Soc, Perkin 2*, (1981) 500.