Effect of Preferential Solvation on the Kinetics and Thermodynamics of Oxidation of Anilines by Nicotinium Dichromate

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The nicotinium dichromate (NDC) oxidation of anilines, in varying mole fractions of benzene/2-methylpropan-2-ol mixtures, in the presence of *p*-toluenesulfonic acid (TsOH) is first order in NDC and TsOH and zero order with respect to anilines in the concentration range investigated. The NDC oxidation of 15 *meta*- and *para*-substituted anilines complies with the isokinetic relationship but not to any of the linear free energy relationships. The activation free energy data failed to correlate with macroscopic solvent parameters such as ε_r and E_N^T. Correlation of $\Delta G^{\#}$ with Kamlet-Taft solvatochromic parameters (α, β, π^*) suggests that the specific solute-solvent-solvent interactions play a major role in governing the reactivity.

Key words: Solvent Effect, Aniline Oxidation, Kinetics, Chromium(VI)

Introduction

The study of solute-solvent interactions in binary mixtures is more complex than in pure solvents. In a pure solvent the composition of the microsphere of solvation of a solute, the so called cybotatic region, is the same as in the bulk solvent, but in binary mixtures the composition in this microsphere can be different. The solute can interact to a different degree with the components of the mixture, and this difference in the interactions is reflected in the composition of the microsphere of solvation. The effect of varying the composition of the mixture from the bulk solvent to the solvation sphere is called preferential solvation [1].

The kinetics of oxidation of organic compounds in non-aqueous and aquo-organic solvent mixtures has revealed the important role of non-specific and specific solvent effects on reactivity [2–6]. It has been shown that the reactivity is influenced by the preferential solvation of the reactants and/or transition state through non-specific and specific solvent-solvent-solute interactions. Further, it has been established that the technique of correlation analysis may well be used to separate and quantify such solvent-solvent-solute interactions on reactivity.

Furthermore, one of the important tools in deciding the mechanism of reactions is the study of substituent effects and thermodynamic parameters. The Hammett equation and its modified forms [7], all known as Linear Free Energy Relationships (LFER) have been found useful for correlating reaction rates and equilibrium constants for side chain reactions for *meta*- and *para*-substituted derivatives of benzene. The isokinetic relationship is also an important tool for deciding the nature of a mechanism. Keeping this in view, a systematic study of various LFERs and the isokinetic relationship has been made to establish the role of solvent and substituents on reactivity and to decide the nature of the mechanism followed in the oxidation of several *meta*- and *para*-substituted anilines by nicotinium dichromate (NDC) in benzene/2-methylpropan-2-ol mixtures of varying compositions. To the best of our knowledge this is the first systematic kinetic study in the above solvent mixture. This mixture is so chosen that by varying the mole fraction of the constituent solvents, the hydrogen bonding properties of the medium can be varied in a smooth and continuous manner since 2-methylpropan-2-ol is classified as a typical hydrogen bond donor (HBD) and benzene as a typical non-hydrogen bond donor (non-HBD) solvent [8].

Results and Discussion

The kinetics of oxidation of aniline and *para*-(Me, OMe, COMe, NHCOMe, NO$_2$, Br, Cl, F) and *meta*-(Me, COOH, NO$_2$, Et, OMe, COMe) substituted anilines were carried out under pseudo-first-order conditions with [substrate] $\gg$ [NDC] in varying mole

fractions of benzene (0.1305, 0.1465, 0.1766, 0.3170, 0.4192, 0.5199, 0.6679, and 0.8599) in 2-methyl-propan-2-ol. The selection of the mole fractions was based on the fact that the solvatochromic parameters employed in the present study for correlation analysis are available in the literature [1]. The overall reaction is represented as follows.

$$\text{Aniline} + \text{NDC} \underset{K}{\overset{K}{\rightleftharpoons}} [\text{Aniline-NDC}]$$

$$k_{\text{obs}} \searrow \quad k \downarrow \text{TsOH}$$

$$\text{Azobenzene}$$

The first order dependence of the reaction on NDC is obvious from the linearity ($r \geq 0.96$) of plots of log [NDC] *versus* time. Further, the pseudo-first-order rate constants, k_{obs}, do not depend on the initial concentration of NDC (Table 1). The oxidation is zero order in the substrate; the k_{obs} remain constant at different [substrate] (Table 1). The oxidation process is remarkably slow, but is catalyzed in the presence of TsOH, and the reaction preceeds at a comfortable rate. The oxidation is first order in TsOH. The oxidation rate increases with increasing [TsOH] and the plot of k_{obs} *versus* [TsOH] is a straight line passing through the origin ($r = 0.989$, $sd = 7.63 \cdot 10^{-6}$, slope = 0.003). The reaction did not promote polymerization of acrylonitrile indicating absence of free radicals.

Thermodynamic parameters and the isokinetic relationship

The reactions were studied at different temperatures to evaluate various thermodynamic parameters. The Arrhenius equation was found to be followed for each of the anilines studied. The various thermodynamic parameters as evaluated on the basis of these Arrhenius plots are recorded in Table 2. A perusal of the data in Table 2 indicates that the oxidation is neither isoenthalpic nor isoentropic but complies with the compensation law also known as the isokinetic relationship:

$$\Delta H^{\#} = \Delta H^{\circ} + \beta \Delta S^{\#}$$

The isokinetic temperature β is the temperature at which all the compounds of the series react equally fast. Also, at the isokinetic temperature the variation of substituent has no influence on the free energy of activation. In an isoentropic oxidation the isokinetic temperature lies at infinite and only enthalpy of activation determines the reactivity. The isokinetic tempera-

Table 1. Pseudo-first-order rate constants for the oxidation of aniline by NDC at 299 K in benzene/2-methylpropan-2-ol mixture.

Mole fraction of benzene	Sub-stituent	10^2 [Sub] (M)	10^3 [NDC] (M)	10^2 [TsOH] (M)	$10^6 k_{\text{obs}}$, s^{-1}
0.6679	*p*-F	1.0	1.0	1.0	248
		1.5	1.0	1.0	250
		2.0	1.0	1.0	247
		2.5	1.0	1.0	248
	H	1.0	1.0	1.0	246
		1.5	1.0	1.0	245
		2.0	1.0	1.0	242
		2.5	1.0	1.0	245
0.6679	H	1.0	1.0	1.0	246
		1.0	1.25	1.0	243
		1.0	1.50	1.0	240
		1.0	1.75	1.0	242
0.4192	H	1.0	1.0	1.0	196
		1.0	1.0	2.0	235
		1.0	1.0	3.0	253
		1.0	1.0	4.0	297

ture is zero for an isoenthalpic series and the reactivity is determined by the entropy of activation [9]. In the present study for all the anilines, at varying mole fractions of benzene in 2-methylpropan-2-ol, the activation enthalpy is linearly related to the activation entropy ($N = 8$, $0.965 < r < 0.999$, $0.25 < sd < 1.67$, $0.02 < \Psi < 0.30$, $272 \pm 4 > \beta > 212 \pm 23$) and a representative plot is given in Fig. 1. The operation of an isokinetic relationship reveals that a single mechanism is operating in all the solvent systems studied. Likewise in a given mole fraction of benzene in 2-methyl-propan-2-ol, all the substituted anilines are oxidized through a common mechanism as evidenced by linear plots of $\Delta H^{\#}$ *versus* $\Delta S^{\#}$ ($N = 15$, $0.968 < r < 0.990$, $0.95 < sd < 1.03$, $0.15 < \Psi < 0.27$, $255 \pm 13 < \beta < 292 \pm 14$).

Since the reactions are of ion-dipolar type, it is expected that the entropy of the activated complex for all these anilines should be nearly of the same order of magnitude. However, because of the difference in the polarity of different anilines, the extent of solvation should be different and hence the experimental value $\Delta S^{\#}$ may be different for different anilines [10], as observed in the present investigation.

The data in Table 2 indicates that values of $\Delta S^{\#}$ vary from 0.1305 to 0.8599 mole fraction of benzene in 2-methylpropan-2-ol which clearly suggests that the extent of solvation of the activated complex is different in different solvent systems. A solvent change from 0.1305 to 0.8599 mole fraction of benzene in 2-methylpropan-2-ol causes a maximum of about 25 fold

Substituent in aniline moiety	TP[a]	Mole fraction of benzene in 2-methylpropan-2-ol							
		0.1305	0.1465	0.1766	0.3170	0.4192	0.5199	0.6679	0.8599
H	E_a	13.6	15.1	9.6	27.8	23.4	32.7	45.3	50.8
	$\Delta H^{\#}$	11.5	13.0	7.6	25.8	21.4	30.7	43.3	48.8
	$\Delta S^{\#}$	−289	−283	−299	−231	−243	−211	−167	−148
	$\Delta G^{\#}$	98.1	97.9	97.2	94.9	94.3	94.0	93.4	93.1
p-Me	E_a	9.9	10.0	14.1	14.6	19.9	21.5	24.8	32.9
	$\Delta H^{\#}$	7.9	7.9	12.0	12.6	17.8	19.4	22.7	30.9
	$\Delta S^{\#}$	−300	−299	−285	−282	−263	−255	−245	−216
	$\Delta G^{\#}$	97.7	97.6	97.4	97.0	96.6	95.9	95.9	95.6
p-OMe	E_a	8.8	9.0	11.7	10.7	21.5	31.9	31.1	40.0
	$\Delta H^{\#}$	6.7	7.0	9.7	8.6	19.5	29.8	29.0	37.8
	$\Delta S^{\#}$	−295	−294	−284	−285	−247	−211	−211	−178
	$\Delta G^{\#}$	95.1	94.9	94.7	93.8	93.6	93.1	92.4	91.1
p-COMe	E_a	5.4	5.5	6.7	21.5	26.1	23.3	28.8	44.3
	$\Delta H^{\#}$	3.3	3.4	4.6	19.4	24.1	21.2	26.8	42.2
	$\Delta S^{\#}$	−311	−310	−304	−251	−227	−235	−214	−161
	$\Delta G^{\#}$	96.4	96.1	95.6	94.4	92.0	91.6	91.1	90.5
p-NHCOMe	E_a	11.4	8.4	11.5	15.7	23.0	23.9	27.7	49.6
	$\Delta H^{\#}$	9.3	6.4	9.4	13.6	20.9	21.9	25.6	47.6
	$\Delta S^{\#}$	−288	−297	−286	−269	−242	−236	−219	−141
	$\Delta G^{\#}$	95.7	95.3	95.2	94.1	93.3	92.7	91.4	89.9
p-NO$_2$	E_a	5.8	6.8	7.4	8.5	16.2	32.2	1.8	38.0
	$\Delta H^{\#}$	3.8	4.7	5.3	6.5	14.2	30.2	33.5	35.9
	$\Delta S^{\#}$	−310	−306	−304	−299	−265	−206	−191	−179
	$\Delta G^{\#}$	96.6	96.5	96.4	96.0	93.7	92.0	90.8	89.5
p-Cl	E_a	4.6	13.7	15.5	20.5	19.3	15.7	12.5	14.6
	$\Delta H^{\#}$	10.6	11.6	13.5	18.5	17.2	13.6	10.5	12.5
	$\Delta S^{\#}$	−287	−284	−277	−257	−254	−263	−270	−262
	$\Delta G^{\#}$	96.7	96.6	96.5	95.3	93.4	92.5	91.4	90.9
p-Br	E_a	6.1	5.3	5.7	16.4	20.7	30.3	12.3	13.5
	$\Delta H^{\#}$	4.0	3.2	3.6	14.3	18.6	28.3	10.2	11.5
	$\Delta S^{\#}$	−312	−314	−312	−268	−249	−215	−269	−263
	$\Delta G^{\#}$	97.4	97.3	97.2	94.5	93.3	92.7	90.8	90.2
p-F	E_a	7.6	8.6	9.3	13.5	17.7	29.2	31.1	32.2
	$\Delta H^{\#}$	5.5	6.6	7.3	11.5	15.7	27.1	29.0	30.1
	$\Delta S^{\#}$	−306	−302	−299	−283	−265	−223	−215	−208
	$\Delta G^{\#}$	97.3	97.1	96.8	96.1	95.1	93.9	93.3	92.4
m-Me	E_a	8.1	9.4	11.8	15.3	17.5	33.0	25.2	33.8
	$\Delta H^{\#}$	6.0	7.3	9.8	13.3	15.4	31.0	23.3	31.8
	$\Delta S^{\#}$	−305	−300	−289	−273	−263	−205	−245	−193
	$\Delta G^{\#}$	97.3	97.1	96.5	95.0	94.2	92.3	90.2	89.6
m-COOH	E_a	6.1	6.8	9.3	9.3	14.4	30.8	40.7	39.2
	$\Delta H^{\#}$	4.0	4.7	7.2	7.3	12.4	28.8	38.6	37.2
	$\Delta S^{\#}$	−313	−310	−299	−293	−265	−209	−173	−175
	$\Delta G^{\#}$	97.8	97.6	96.9	95.1	91.8	91.6	90.4	89.6
m-NO$_2$	E_a	11.3	15.4	18.1	16.5	12.1	16.7	18.6	30.5
	$\Delta H^{\#}$	9.2	13.3	16.1	14.4	10.1	14.6	16.6	28.5
	$\Delta S^{\#}$	−291	−277	−267	−267	−276	−257	−246	−203
	$\Delta G^{\#}$	96.5	96.2	96.9	94.3	92.7	91.5	90.2	89.1
m-Et	E_a	11.4	13.5	15.4	9.5	21.5	7.3	22.6	11.6
	$\Delta H^{\#}$	9.4	11.4	13.3	7.5	19.4	5.3	20.5	9.5
	$\Delta S^{\#}$	−293	−286	−277	−292	−251	−295	−242	−272
	$\Delta G^{\#}$	97.2	97.1	96.4	94.9	94.7	93.6	93.0	91.1
m-OMe	E_a	1.8	2.3	3.8	5.3	3.0	15.0	22.0	34.6
	$\Delta H^{\#}$	0.17	0.29	1.8	3.2	1.4	13.0	19.9	32.5
	$\Delta S^{\#}$	−329	−328	−322	−317	−322	−280	−254	−208
	$\Delta G^{\#}$	98.8	98.6	98.3	98.1	97.8	96.9	96.1	94.9
m-COMe	E_a	6.6	9.8	9.2	5.5	4.3	15.3	21.5	30.3
	$\Delta H^{\#}$	4.6	7.7	7.1	3.4	2.2	13.2	19.4	28.3
	$\Delta S^{\#}$	−311	−300	−301	−311	−313	−275	−253	−222
	$\Delta G^{\#}$	97.7	97.5	97.4	96.6	96.1	95.6	95.2	94.7

Table 2. Thermodynamic and activation parameters for the oxidation of anilines by nicotinium dichromate in benzene/2-methylpropan-2-ol mixtures.
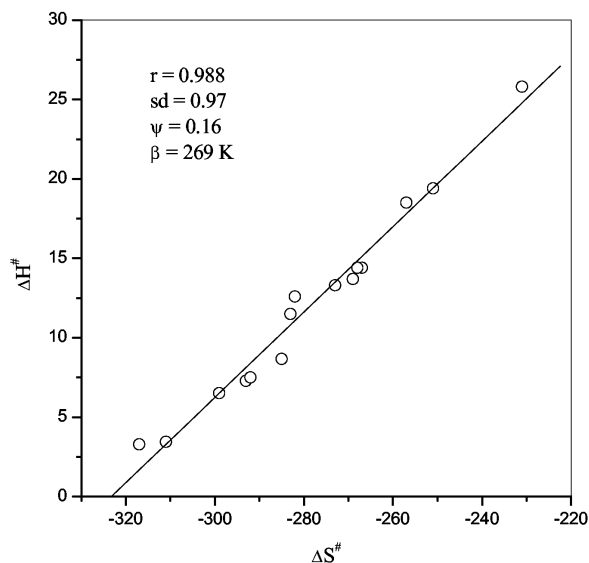
[a] Thermodynamic parameters.

Fig. 1. The isokinetic plot for the oxidation of anilines by NDC in 0.3170 mole fraction of benzene in 2-methylpropan-2-ol.

rate acceleration for the reaction which corresponds to a decrease in $\Delta G^{\#}$ of about 8 kJ mol^{-1}. Negative entropy of activation indicates a greater degree of ordering in the transition state than in the initial state, due to an increase in solvation during the activation process.

Solvent-reactivity correlation

The title reaction has been studied in varying mole fractions of benzene (typical non-HBD solvent) in 2-methylpropan-2-ol (typical HBD solvent) with a view to understand the effect of preferential solvation on the thermodynamics of the reaction. Such mixtures are very useful for studying solvent effects upon reactions since the properties can be adjusted continuously by changing the composition of the mixture. The separation of solvent effects on rate (as $\log k$ or $\Delta G^{\#}$ values) into initial-state and transition-state contributions and also the rationalization of various solvent-solvent-solute interactions has been done, by adopting the technique of correlation analysis, using the values of $\Delta G^{\#}$, which are rather more convenient to use than $\log k$ values [11].

The correlation of $\Delta G^{\#}$ values with the inverse of the relative permittivity through the Laidler-Eyring [12] equation is just satisfactory with an explained variance $100r^2 < 95\%$ ($0.762 < r < 0.974$, $0.34 < sd < 1.42$, $0.26 < \Psi < 0.75$). The slope of these plots is negative indicating a decrease in free

energy of activation with a decrease in relative permittivity of the medium. Similarly, the correlation of the values of $\Delta G^{\#}$ with one of the more successful solvent polarity indices, Reichardt's [8] E_T^N, is also satisfactory ($0.897 < r < 0.997$, $0.18 < sd < 0.71$, $0.09 < \Psi < 0.37$) with a positive slope (explained variance $< 99\%$). The results of these correlations reveal the operation of selective or preferential solvation which includes both non-specific solute-solvent association caused by dielectric enrichment in the solvation shell of solute ions or dipolar solute molecules and specific solute-solvent association such as hydrogen bonding or EPD/EPA interactions [8].

From idealized theories, the solvent parameters ε_r and E_T^N are often predicted to serve as a quantitative measure of solvent polarity. However, this approach is often inadequate since these theories regard solvents as a non-structured continuum, not composed of individual solvent molecules with their own solvent-solvent interactions, and they do not take into account specific solute-solvent interactions, such as hydrogen bonding and electron pair donor-acceptor interactions, which often play a dominating role in solute-solvent interactions. No single macroscopic physical parameter could possibly account for the multitude of solute-solvent interactions on the molecular level. Thus, bulk solvent properties like ε_r and E_T^N will poorly describe the microenvironment around the reacting species, which governs the stability of the transition state and hence the rate of the reaction. Hence, there have been a variety of attempts to quantify different aspects of solvent polarity and then use the resultant parameters to interpret solvent effects on reactivity through multiple regressions. Various treatments for the above solvent-solvent-solute interactions based on Linear Solvation Energy Relationships (LSER) have been developed [7].

In order to obtain a deeper insight into the various solvent-solvent-solute interactions, which influence reactivity, we have tried to adopt the solvatochromic comparison method developed by Kamlet and Taft [13]. This method may be used to unravel, quantify, correlate, and rationalize multiple interacting solvent effects on reactivity. The kinetic data were correlated with the solvatochromic parameters α, β and π^* characteristic of the different solvents in the form of the following LSER.

$$\log k = A_o + s\pi^* + a\alpha + b\beta$$

where π^* is an index of solvent dipolarity/polar-

Table 3. Statistical results and weighted percentage contributions for the correlation of $\Delta G^{\#}$ for the oxidation of substituted anilines by NDC with Kamlet-Taft's solvatochromic parameters α, β and π^*.

Sudstituent in aniline moiety	R^2	sd	ψ	a	b	s	P_α	P_β	P_{π^*}
H	0.980	0.38	0.18	43.7	−2.4	6.1	84	05	11
p-Me	0.948	0.24	0.29	9.2	0.3	−5.4	62	02	36
p-OMe	0.993	0.15	0.10	7.8	5.5	2.4	50	35	15
p-COMe	0.984	0.40	0.16	34.5	−3.2	−25.6	55	05	40
p-NHCOMe	0.999	0.06	0.03	11.3	6.4	−4.8	50	29	21
p-NO$_2$	0.988	0.42	0.14	10.7	4.8	−36.6	21	09	70
p-Cl	0.991	0.31	0.12	24.4	0.2	−25.2	49	00	51
p-Br	0.997	0.22	0.07	41.6	1.8	−1.8	92	04	04
p-F	0.982	0.33	0.17	12.8	2.6	−16.7	40	08	52
m-Me	0.978	0.59	0.18	23.1	6.5	−11.7	56	16	28
m-COOH	0.988	0.48	0.13	47.9	−3.2	−28.5	60	04	36
m-NO$_2$	0.994	0.29	0.09	27.3	3.1	−17.5	57	06	37
m-Et	0.979	0.42	0.18	17.7	7.5	8.6	52	22	26
m-OMe	0.988	0.20	0.14	−3.1	7.0	−5.8	20	44	36
m-COMe	0.993	0.13	0.11	13.3	1.5	−2.4	77	09	14

izability, which measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect, α is the solvent HBD (hydrogen bond donor) acidity, β is the solvent HBA (hydrogen bond acceptor) basicity of the solvent in a solute to solvent hydrogen bond and A_o is the regression value of the solute property in the reference solvent cyclohexane. The regression coefficients s, a and b measure the relative susceptibilities of the solvent dependent solute property $\log k$ ($\Delta G^{\#}$ in the present case) to the indicated solvent parameter. The solvatochromic parameters employed in the present study were taken from the literature and are estimated based on the preferential solvation model [1]. The $\Delta G^{\#}$ values show an excellent correlation (Table 3) with solvent *via* the above LSER with a variance of *ca.* 98%. Such an excellent correlation indicates the existence of both specific and non-specific solute-solvent-solvent interactions in the present system. It is interesting to note that the correlation of enthalpy ($28 < 100R^2 < 97$, $1.62 < sd < 6.12$, $0.19 < \psi < 1.07$) and entropy ($27 < 100R^2 < 98$, $5.7 < sd < 47.5$, $0.18 < \psi < 1.08$) of activation of the oxidation process with the Kamlet-Taft's solvatochromic parameters is poor.

The statistical results of the correlation and weighted percentage contributions of the solvatochromic parameters are presented in Table 3. The observation of this multiple regression analysis leads to the following conclusions. i) The weighted percentage contributions of the solvatochromic parameters indicate that the specific solvent-solvent-solute interactions, as indicated by P_α and P_β, play a major role in governing the activation free energy of the oxidation process. ii) The sign of the coefficient of α and β terms are positive suggesting better solvation of the transition state, through hydrogen bonding, as compared to the reactants. Further, decrease in HBD and HBA properties of the medium will decrease the activation free energy and consequently accelerate the reaction rate. iii) The contribution of the solvent HBD acidity, α, to the total solvent effects is dominant. Based on the two-step preferential solvation model, proposed by Skwierczynski and Connors [14], it was established that the properties of 2-methylpropan-2-ol/benzene mixtures are very close to the average of the properties of the two solvents, expect for the hydrogen bond acidity α, which seems to be equal to that of pure benzene (*i.e. ca.* zero) [1]. Hence with increase in mole fraction of benzene in the mixture there is a drastic decrease in the hydrogen bond acidity, α, of the medium and hence decrease in the activation free energy, and consequently increase in rate of the reaction. iv) Likewise, as benzene has no hydrogen bonding properties, with increase in mole fraction of benzene in the mixture the hydrogen bond basicity, β, decreases [1], which in turn decreases the activation free energy and consequently enhances the rate of the oxidation. v) As indicated by $P\pi^*$, the contribution of solvent dipolarity/polarizabilty also contributes to the activation free energy to an appreciable extent. The sign of the coefficients of this term is negative indicating a decrease in free energy of activation with increase in the dipolarity/polarizability of the medium. Since benzene is a more polarizable solvent ($\delta = 1$) than 2-methylpropan-2-ol ($\delta = 0$), an increase in its mole fraction in the mixture increases the polarizability of the medium and consequently increases the rate of the reaction by decreasing $\Delta G^{\#}$.

Structure-reactivity correlation

The effect of substituents on the activation free energy of the oxidation was studied with 15 *para*- and *meta*-substituted anilines in varying mole fractions of benzene in 2-methylpropan-2-ol (Table 2). The results in Table 2 reveal that the $\Delta G^{\#}$ values vary with substrate in a particular mole fraction of benzene, though the rate of the reaction is independent of [substrate]. This may be due to the fact that because of the difference in polarity of different anilines, the extent of

Table 4. Results of simple and multiple linear correlations of the rate data of NDC oxidation anilines at 299 K in all mole fractions of benzene/2-methylpropan-2-ol mixtures.

Explanatory variable	$100\,R^{2a}$	n
para- and *meta-*substituents		
σ	00-19	15
σ^+	01-36	12
σ_p^- and σ_m	00-15	15
*para-*substituents only		
σ	00-48	9
σ^+	01-33	8
σ^-	01-32	9
σ_I, σ_R	05-56	9
F, R	68-69	9
F, R^b	65-67	9
*meta-*substituents only		
σ	01-19	7
σ^+	67-83	5
σ_I, σ_R	69-70	7
F, R	50-60	7
F, R^b	55-56	7

[a] $100R^2$ in the case of multiple linear regression analysis (ref. [7]); [b] improved F and R from ref. [16].

solvation should be different and hence the experimental values of rate constants may be different for different anilines as observed in the present study. The rate data fail to conform to the usual Hammett equation; the $\Delta G^{\#}$ (*para-* and *meta-*collectively and separately) *versus* σ plot is a scatter plot (Table 4). The oxidation rates of *para-* and *meta-*substituted anilines were correlated separately with Hammett σ^- and Brown-Okamoto σ^+ values, but also without success (Table 4). The failure of the single parameter equation to correlate the rate data leads to the possibility of operation of dual substituent parameter (DSP) equations. The biparametric equations fail to correlate the rate data with the substituent (Table 4). The σ_I and σ_R values used are those reported by Dayal *et al.* [15]. The F and R values are those of Swain *et al.* [16]. The possible reason for the lack of any Linear Free Energy Relationship is that the isokinetic temperature falls within the experimental temperature. It is pertinent to note that the compensation law may lead to artifacts [17, 18].

Mechanism

Under the reported anhydrous condition hydrolysis of the dichromate to the chromate anion is unlikely. A perusal of data in Table 2 indicates that the energy of activation of the oxidation is susceptible to the substituent present in the benzene ring.
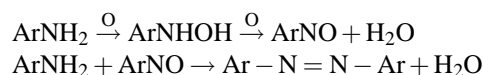
This indicates the involvement of substrate in or prior to the rate-limiting step in such a way that the rate is independent of [substrate]. In non-aqueous media chromium(VI) reagents complex with the aniline and the reaction exhibits Michaelis-Menten kinetics with respect to the substrate. If the formation constant (K) of the oxidant-substrate complex is large the oxidation is to exhibit zero order dependence on [substrate] [17]:

$$\text{NDC} + \text{Substrate} \leftrightarrows \text{NDC-Substrate} \quad K, \text{ rapid}$$
$$\text{NDC-Substrate} + \text{TsOH} \rightarrow \text{Product} \quad k, \text{ slow}$$

This mechanism leads to, under the condition that the formation constant (K) of the oxidant-substrate complex is large, the rate law

$$-d[\text{NDC}]/dt = k[\text{NDC}][\text{TsOH}]$$

The above scheme accounts for the observed orders. The formation of the reaction product azobenzene may follow, through N-attack:

$$\text{ArNH}_2 \xrightarrow{\text{O}} \text{ArNHOH} \xrightarrow{\text{O}} \text{ArNO} + \text{H}_2\text{O}$$
$$\text{ArNH}_2 + \text{ArNO} \rightarrow \text{Ar}-\text{N}=\text{N}-\text{Ar} + \text{H}_2\text{O}$$

Experimental Section

All the chemicals and solvents used were of analytical grade. The solvents 2-methylpropan-2-ol and benzene were purified by reported methods [8]. The solid anilines were used as such and the liquid anilines were used after vacuum distillation. Nicotinium dichromate was prepared by a reported method [19] and its purity was checked by an iodometric method.

The reactions were carried out under pseudo-first-order conditions by keeping an excess of substrate over NDC. The progress of the reaction was followed by estimating the unconsumed oxidant iodometrically at 26, 34, 42, 49 (± 0.1) °C. The rate constants were determined by a least squares method, from the linear plots ($r \geq 0.96$) of log [NDC] *versus* time. Replicate runs showed that the rate constants were reproducible to within $\pm 3\%$. The stoichiometry of the reaction was determined by carrying out several sets of experiments with varying amounts of [NDC] largely in excess over [substrate]. The estimation of unconsumed NDC showed that three moles of the substrate react with two moles of NDC. For product analysis NDC was allowed to react with aniline, under kinetic conditions, for 24 h. After completion of the reaction the oxidation product was analyzed using preparative TLC on silica gel, which yielded azobenzene. The product azobenzene was identified by its melting

point [66 ℃ (lit. 68 ℃)], IR and UV spectra. The spectra are superimposable with those of the authentic sample; UV (EtOH): $\lambda_{\max} = 320$ nm.

Correlation analyses were carried out using Microcal Origin (version 6) computer software. The goodness of the fit was discussed using correlation coefficient (r in the case of simple linear regression and R in the case of multiple linear regression), standard deviation, sd, and Exner's statistical parameter, ψ [7]. The percentage contribution (P_X) of a parameter to the total effect on reactivity was computed using the regression coefficient of each parameter as reported earlier [20].

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