Studies on the Kinetics of Imidazolium Fluorochromate Oxidation of Some *meta-* and *para-*Substituted Anilines in Nonaqueous Media

D. S. BHUVANESHWARI, K. P. ELANGO

Department of Chemistry, Gandhigram Rural Institute (Deemed University), Gandhigram 624 302, India

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> ABSTRACT: The imidazolium fluorochromate (IFC) oxidation of *meta*- and *para*-substituted anilines, in seven organic solvents, in the presence of *p*-toluenesulfonic acid (TsOH) is first order in IFC and TsOH and is zero order with respect to substrate. The IFC oxidation of 15 *meta*- and *para*-substituted anilines at 299–322 K complies with the isokinetic relationship but not to any of the linear free energy relationships; the isokinetic temperature lies within the experimental range. The specific rate of oxidizing species-anilines reaction (k_2) correlates with substituent constants affording negative reaction constants. The rate data failed to correlate with macroscopic solvent parameters such as ε_r and E_T^N . A correlation of rate data with Kamlet–Taft solvatochromic parameters (α , β , π^*) suggests that the specific solute–solvent interactions play a major role in governing the reactivity, and the observed solvent effects have been explained on the basis of solute–solvent complexation. © 2006 Wiley Periodicals, Inc. Int J Chem Kinet 38: 166–175, 2006

INTRODUCTION

The kinetics of oxidation of organic compounds in nonaqueous and aquo-organic solvent media have revealed the important role of nonspecific and specific solvent effects on the reactivity. It has been shown that the reactivity is influenced by the preferential solvation of the reactants and/or the transition state through nonspecific and specific solvent–solvent–solute interactions. Furthermore, it has been established that the technique of correlation analysis may well be used to separate, quantify, and rationalize such solvent–solvent–solute interactions on reactivity [1–5].

Further, 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 [6], all known as linear free energy relationships (LFER), have been found

Correspondence to: K. P. Elango; E-mail: drkpelango@ rediffmail.com.

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useful for correlating reaction rates and equilibrium constants for side chain reactions for *meta-* and *para*-substituted derivatives. 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 being followed in the imidazolium fluorochromate (IFC, a mild and selective oxidant, reported only recently [7]) oxidation of some *meta-* and *para-*substituted anilines.

This article focuses on the study of kinetics and mechanism of oxidation of substituted anilines by IFC in nonaqueous media. Anilines (aromatic amines) are the most widespread and principal contaminants of industrial wastewaters. These comprise an important class of environmental contaminants—they are the building blocks for many textile dyes, agrochemicals, and other class of synthetic chemicals. The reaction pathways of aromatic amines in natural systems are dominated by redox reactions with soil and sediment constituents. Better understanding of the mechanism of oxidation of such compounds/contaminants to harmless products is the important goal for basic research and industrial applications, hence, the present study.

EXPERIMENTAL SECTION

Materials

All the chemicals and solvents used were of analytical grade. The solvents *tert*-butanol (*t*-BuOH), dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), acetonitrile (MeCN), nitrobenzene (NB), chlorobenzene (CB), and 1,4-dioxane (Diox) are of analytical grade and were purified by conventional methods. The anilines used were with substituents H, *p*-Me, *p*-OMe, *p*-COMe, *p*-NHCOMe, *p*-NO₂, *p*-Cl, *p*-Br, *p*-F, *m*-Me, *m*-COOH, *m*-NO₂, *m*-Et, *m*-OMe, and *m*-COMe. The solid anilines were used as such, and the liquid anilines were used after vacuum distillation. Imidazolium fluorochromate (IFC) was prepared by the reported method [7], and its purity was checked by the iodometric method.

Kinetic Measurements

The reactions were carried out under pseudo-first-order conditions by keeping an excess of substrate over IFC. The progress of the reactions was followed by estimating the unreacted oxidant iodometrically at 26, 34, 42, and $49(\pm 0.1)^{\circ}$ C. The rate constants were determined by the least squares' method, from the linear

plots (r > 0.97) of log [IFC] versus time. Replicate runs showed that the rate constants were reproducible to within $\pm 3\%$.

Data Analysis

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 . The percentage contribution (\mathbf{P}_x) of a parameter to the total effect on reactivity was computed using the regression coefficient of each parameter as reported earlier [8].

Stoichiometry

The stoichiometry of the reaction was determined by carrying out several sets of experiments with varying amounts of [IFC] largely in excess over [aniline]. The estimation of unreacted IFC showed that 1 mol of aniline reacts with 1 mol of IFC.

Product Analysis

The oxidation product was analyzed using preparative TLC on silica gel, which yielded the following fractions:

- (1) Azobenzene mp 66°C (lit. 68°C), UV (EtOH) λ_{max} 320 nm.
- (2) *p*-Benzoquinone mp 111°C (lit. 114°C), UV (EtOH) λ_{max} 246 nm.

RESULTS AND DISCUSSION

The kinetic studies were carried out under pseudo-firstorder conditions with the [substrate] \gg [IFC]. The firstorder dependence of the reaction on IFC is obvious from the linearity of the plots of log [IFC] versus time. Further, the pseudo-first-order rate constants, k_{obs} , do not depend on the initial concentration of IFC (Table I). The oxidation is zero order in the substrate, both in the presence and absence of acid; the pseudo-first-order rate constant remains constant at different [substrate]₀. The oxidation of anilines by IFC in acetonitrile is remarkably slow, but is catalyzed in the presence of ptoluene sulfonic acid, and the reaction proceeds at a comfortable rate. The k_{obs} values varied with variation in the initial concentration of TsOH and dependence on acid was also observed to be unity, as seen from linear plot (r = 0.996, sd = 0.02, $\Psi = 0.12$, slope = 0.99 ± 0.05) of log k_{obs} versus log [TsOH]. Catalysis

10 ² [aniline]	10 ³ [IFC]	$10^{2}[H^{+}]$	
(M)	(M)	(M)	$10^5 k_{\rm obs} ({\rm s}^{-1})$
3.0	1.0	2.0	13.7
4.0	1.0	2.0	13.3
5.0	1.0	2.0	13.6
6.0	1.0	2.0	13.5
3.0	1.0	2.0	63.2 ^{<i>a</i>}
4.0	1.0	2.0	58.9 ^a
5.0	1.0	2.0	63.8 ^{<i>a</i>}
6.0	1.0	2.0	62.5 ^a
3.0	1.0	2.0	14.2^{b}
4.0	1.0	2.0	13.5^{b}
5.0	1.0	2.0	13.8 ^b
6.0	1.0	2.0	13.6 ^b
5.0	1.0	2.0	13.6
5.0	1.5	2.0	12.9
5.0	2.0	2.0	13.4
5.0	2.5	2.0	13.3
5.0	1.0	1.0	6.3
5.0	1.0	1.5	10.0
5.0	1.0	2.0	13.6
5.0	1.0	2.5	15.5
5.0	1.0	3.0	18.9
4.0	1.0	_	0.69
5.0	1.0	-	0.66
6.0	1.0	_	0.66
7.0	1.0	_	0.68
3.0	1.0	2.0	10.3 ^c

Table IPseudo-First-Order Rate Constants for theOxidation of Aniline by IFC at 299 K in AcetonitrileMedium

^{*a*} *p*-Me-substituted aniline.

^bIn DMF.

^cIn the presence of 0.003 M Mn(II).

by *p*-toluene sulfonic acid suggests protonation of the IFC (pH of a 0.01 M solution; IFC 2.62, PCC 1.75, PFC 2.45 [7]) species rather than the aniline molecule, which would have resulted in retardation. The protonated IFC species is probably difficult to visualize, but participation of protonated chromium species in Cr(VI) oxidations is well known [9].

The reaction did not promote polymerization of acrylonitrile indicating absence of free radicals. However, addition of Mn(II) retards the rate of the oxidation process indicating two electron oxidation [10].

Activation Parameters

The activation parameters were calculated from k_{obs} at 299, 307, 315, and 322 K using the Eyring relationship by the method of least squares and are collected in Table II. The oxidation is neither isoenthalpic nor isoentropic but complies with the compensation law

also known as isokinetic relationship (Eq. (1)):

$$\Delta H^{\#} = \Delta H^0 + \beta \Delta S^{\#} \tag{1}$$

The isokinetic temperature 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 temperature is zero for an isoenthalpic series, and the reactivity is determined by the entropy of activation [11]. In the present oxidation, the activation enthalpy is linearly related to activation entropy (in acetonitrile medium, r = 0.993, sd = 3.16, $\Psi = 0.13$, isokinetic temperature = 314 ± 0.01 K). The operation of isokinetic relationship reveals that all the substituted anilines examined are oxidized through a common mechanism.

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 difference in the polarity of different anilines, the extent of solvation should be different and hence the experimental value of $\Delta S^{\#}$ may be different for different anilines, as observed by us in the present case.

The activation energies and the entropies and enthalpies of activation were also calculated for the oxidation of p-COMe-substituted aniline in the seven organic solvent media (Table III). The existence of a linear relationship (r = 0.998, sd = 2.29, $\psi = 0.07$, isokinetic temperature = 315 ± 0.01 K) between $\Delta H^{\#}$ and $\Delta S^{\#}$ indicates that a single mechanism is operating in all the solvent systems studied. A perusal of data in Table III indicates that values of $\Delta S^{\#}$ vary from 201 to $-173 \text{ J K}^{-1} \text{ mol}^{-1}$ which clearly suggests that the extent of solvation of the activated complex is different in different solvents. A solvent change from tert-butanol to 1,4-dioxane causes a 66-fold rate acceleration for the reaction which corresponds to a decrease in $\Delta G^{\#}$ of 10.2 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. The results in Table III show that the largest k_{obs} values are obtained in the apolar solvents correspond to the largest decrease in activation entropy. This observation can be rationalized because polar solvents will have some structure corresponding to the orientation of the dipolar solvent molecules due to intermolecular solvent-solvent interactions. In less polar solvents, however, which have only a small or no dipole moment, the solvent molecules will be relatively unoriented and consequently have higher entropy.

Substituents	I	Rate Cons	tants 10 ⁵ k _{ot}	(s^{-1})	Ea	$\Delta H^{\#}$	$-\Delta S^{\#}$	$\Delta G^{\#}$
in Aniline	299 K	307 K	315 K	322 K	$(kJ mol^{-a} K^{-1})$	$(kJ mol^{-1})$	$(J K^{-1} mol^{-1})$	$(kJ mol^{-1})$
Н	13.6	54.6	69.5	106	052	51	142	93.8
<i>p</i> -Me	63.6	103	274	452	057	55	120	90.8
<i>p</i> -OMe	1000	1150	1970	fast	028	26	195	84.5
<i>p</i> -COMe	5.96	27.3	89.1	183	095	93	007	95.4
<i>p</i> -NHCOMe	1.55	25.2	59.9	194	128	67	093	94.3
$p-NO_2$	1.54	10.5	30.4	111	116	56	131	95.4
<i>p</i> -Cl	6.88	29.1	75.1	180	089	80	053	95.6
<i>p</i> -Br	3.48	14.2	17.6	38.3	062	60	126	97.2
<i>p</i> -F	24.0	46.3	94.4	187	057	56	127	93.1
<i>m</i> -Me	19.9	25.8	59.9	82.8	043	41	179	94.0
<i>m</i> -COOH	2.00	18.6	27.5	33.9	074	72	086	97.5
$m-NO_2$	1.44	11.0	22.2	36.4	086	84	047	98.5
<i>m</i> -Et	20.5	26.1	29.4	32.6	126	11	280	94.1
<i>m</i> -OMe	22.2	29.4	47.2	64.3	030	28	219	93.8
m-COMe	20.3	21.4	23.5	25.4	006	04	301	94.3

Table IIEffect of Temperature on the Rate of Oxidation of Substituted Anilines by IFC in Acetonitrile and ActivationParameters for the Oxidation

[Substrate] = 5×10^{-2} M; [IFC] = 1×10^{-3} M; [H⁺] = 2×10^{-2} M.

Table III Thermodynamic Parameters and Relative Rate Constants at 299 K for the Oxidation of *p*-COMe-Substituted Aniline by IFC in Different Solvents

Solvent	$\varepsilon_{ m r}$	$\frac{10^5 k_{\rm obs}}{({\rm s}^{-1})}$	$k_{\rm obs}^{\rm rel}$	$\Delta H^{\#}$ (kJ mol ⁻¹)	$\frac{\Delta S^{\#}}{(\mathrm{J}\mathrm{K}^{-1}\mathrm{mol}^{-1})}$	$\Delta G^{\#}$ (kJ mol ⁻¹)
t-BuOH	12.47	1.33	1	161	201	101
DMF	36.71	2.55	2	107	36	96.9
DMSO	46.68	5.33	4	50	-154	96.3
MeCN	37.50	5.96	4.5	93	-7	95.4
NB	34.82	38.4	29	41	-173	92.7
CB	5.62	42.2	32	72	-66	91.3
Diox	2.209	88.1	66	43	-161	90.8

Thus, nonpolar solvents will have a greater entropy loss as a result of increased solvation during activation process. Hence, it is presumed that, in the present study, solvent–solvent interactions play a significant role, in addition to, solute–solvent interactions in governing the rate of the reaction [12].

Structure–Reactivity Correlation

The effect of substituents on the oxidation rate was studied with 15 *para-* and *meta-substituted* anilines in seven organic solvent media (Table IV). The results in Table IV reveal that the rate constants vary with substrate in a particular solvent, though the rate of the reaction is independent of [substrate]. This may be due to the fact that because of difference in polarity of different anilines, the extent of solvation should be different and hence the experimental values of rate

constants may be different for different anilines as observed by us in the present studies. The rate data fail to conform to the usual Hammett equation; $\log k_{obs}$ (para- and meta-collectively and separately) versus σ plot is a scatter gram (Table V). The oxidation rates of para- and meta-substituted anilines are correlated separately with Hammett σ^- and Brown–Okamoto σ^+ but also without success (Table V). A typical representative plot is shown in Fig. 1. 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 V). The $\sigma_{\rm I}$ and $\sigma_{\rm R}$ values used are those reported by Dayal et al. [13]. The F and R values are those of Swain et al. [14]. The possible reason for the lack of any linear free energy relationship is that the isokinetic temperature falls within the experimental temperature (299-322 K); the isokinetic temperature calculated from the

		Substituents in Aniline Moiety													
					para-Positi	on				meta-Position					
Solvents	Н	Me	OMe	COMe	NHCOMe	NO ₂	Cl	Br	F	Me	СООН	NO ₂	Et	OMe	COMe
DMSO	0.61	3.22	8.62	5.33	5.43	6.21	3.98	0.77	0.61	0.32	0.16	1.97	5.59	23.7	15.7
MeCN	13.6	63.6	1000	5.96	1.55	1.54	6.88	3.48	24.0	19.9	2.00	1.44	20.3	22.2	20.3
DMF	13.8	1.59	10.7	2.55	10.2	2.51	0.93	1.15	0.43	9.97	2.47	0.48	440	29.6	119
NB	117	520	65.2	38.4	42.9	143	29.6	43.0	41.2	62.4	50.3	272	30.0	322	75.7
t-BuOH	1.54	15.0	102	1.33	97.6	80.5	0.44	3.09	2.98	5.38	0.59	267	96.2	377	5.64
CB	12.2	248	101	42.2	1,052	108	25.8	242	81.2	172	91.8	21.4	24.7	412	18.8
Diox	5.65	242	253	88.1	141	169	91.9	36.3	204	109	31.4	24.7	64.5	94.2	25.8

Table IV Pseudo-First-Order Rate Constants $[10^5 k_{obs}, (s^{-1})]$ for the oxidation of *meta-* and *para-*substituted anilines by IFC at $26 \pm 0.1^{\circ}$ C

[Substrate] = 5 × 10⁻² M; [IFC] = 1 × 10⁻³ M; [H⁺] = 2 × 10⁻² M.

Table VResults of Simple and Multiple LinearCorrelation of the Rate Data (k_{obs}) of IFC–AnilineReaction at 299 K in All the Organic SolventsInvestigated

Explanatory Variable	$100 r^{2a}$	п
para- and m	eta-Substituents	
σ	3-72	15
σ^+	3–68	12
$\sigma_{\rm p}^{-}$ and $\sigma_{\rm m}$	6–52	15
para-Sub	stituents Only	
σ	5-71	9
σ +	7-62	8
σ -	1–46	9
meta-Sub	stituents Only	
σ	6–78	7
σ +	17–95	5
para-S	ubstituents	
σ_{I}, σ_{R}	2-47	9
F, R	3-52	9
F, R^*	8–46	9
meta-S	ubstituents	
$\sigma_{\rm I}, \sigma_{\rm R}$	25-80	7
F, R	62-79	7
F, R^*	57-72	7

^{*a*} 100 R^2 in the case of multiple linear regression analysis. *Improved *F* and *R*.

isokinetic plot is 314 ± 0.01 K. It is pertinent to note that the compensation law may lead to artifact [15].

Anilines in basic and neutral medias are present as free bases but in acid medium exist in dual forms: the free bases and the conjugate acids. And the ratio of the concentrations of the free bases to the conjugate acid ($[XC_6H_4NH_2]/[XC_6H_4NH_3^+]$) depends on the p K_a of the aniline and the acidity of the medium. The reported oxidations of anilines, in the present



Figure 1 Plot of log k_{obs} (DMF) versus σ^+ .

study, were carried out under pseudo-first-order conditions ([anilines] \gg [IFC]), and the concentration of IFC at different reaction times was determined by titrimetry. The pseudo-first-order rate constants (k_{obs}) were obtained from the least-squares slopes of log [IFC] versus time plots, and the second-order rate constants are $k' = k_{obs}/[aniline]_T$, where [aniline]_T is the total concentration of aniline. Since the p K_a varies from 5.35 (*p*-OMe) to 1.01 (*p*-NO₂) and molecular anilines are the reactive species (nucleophile), the reported $k_{obs}/[aniline]_T$ values are not the rate constants of the oxidant-molecular aniline reactions. And the analysis of k_{obs} and $k_{obs}/[aniline]_T$ in terms of the Hammett and modified Hammett equations is erroneous.

Hence, the specific reaction rates of molecular anilines with the oxidant $\{k_2 = k'(K_a + [H^+])/K_a\}$ have

		Substituents in Aniline Moiety												
			раг	a-Position	meta-Position									
Solvents	Н	Me	OMe	COMe	NO ₂	Cl	Br	Me	СООН	NO ₂	OMe	COMe		
DMSO	17	282	1,469	5	2	45	7	12	0.4	3	408	92		
MeCN	369	5,564	170,491	5,824	0.5	79	31	779	6	2	382	118		
DMF	374	139	1,815	2	0.9	11	10	391	7	0.7	509	695		
NB	3,186	45,542	11,111	38	51	338	384	2,446	140	413	5,553	442		
t-BuOH	42	1,311	17,378	1	29	5	28	211	2	406	6,487	33		
CB	331	21,718	17,188	41	38	296	2,160	6,741	255	33	7,088	110		
Diox	153	21,185	43,132	86	60	10,524	324	4,254	2	38	1,623	150		

Table VI Specific Rate ($\times 10^3 k_2$, dm³ mol⁻¹ s⁻¹) of the Oxidant–Molecular Aniline Reaction at 299 K

been obtained, as reported earlier for the oxidation of anilines by percarbonate [16] and perborate [11], and correlated in terms of the structure–reactivity relationships. In the reactions of anilines in acid medium, as the free bases are the nucleophiles, the specific reaction rates of anilines are to be obtained using the concentrations of the free bases but not the total concentrations of anilines. The concentrations of the free bases, in the present study, have been deduced as reported earlier by adopting the similar approximations. The specific rates of the oxidant-molecular aniline reactions are collected in Table VI. *p*-NHCOMe, *p*-F, and *m*-Et are not included due to nonavailability of their pK_a values.

The specific rates of the rate-limiting step of *para*and *meta*-substituted anilines correlate satisfactorily with the Brown–Okamoto equation (Table VII), and a representative plot is given in Fig. 2. Regression analysis of *para*- and *meta*-substituents, both collectively and separately, shows an improved correlation with various substituent constants (Table VII), when compared to the same using k_{obs} . Multiple correlation analysis reveals that dual substituent parameter (DSP) equation with explanatory variables σ_I and σ_R^+ governs fairly the variation of k_2 with *meta* substituents. The reaction coefficients of field and resonance effects are negative, and the percentage contributions of these two terms are almost equal [11]. Parallel to simple linear correlation results, the correlation of k_2 with substituent constants, through multiple correlation equations, are better than those with k_{obs} (Table VII).

Table VII Results of Simple and Multiple Linear Correlation of the specific Rate (k_2) of Oxidant–Molecular Aniline Reaction at 299 K in All the Organic Solvents Investigated



Figure 2 Correlation of log k_2 (DMF) with σ^+ .

Explanatory Variable	$100 r^{2a}$	n
para- and me	eta-Substituents	
σ	29-80	12
σ^+	47-85	10
$\sigma_{\rm p}^{-}$ and $\sigma_{\rm m}$	27-80	12
para-Subs	tituents Only	
σ	56-92	7
σ +	64–99	6
σ –	41-81	7
meta-Subs	tituents Only	
σ	14-82	5
σ^+	27-79	5
para-Su	ubstituents	
$\sigma_{\rm I}, \sigma_{\rm R}$	53-87	7
$\sigma_{\rm I}, \sigma_{\rm R}^+$	66–90	7
$\sigma_{\rm I}, \sigma_{\rm R}^{\rm R}$	44-83	7
F, R	58–93	7
meta-Su	ubstituents	
$\sigma_{\rm I}, \sigma_{\rm R}$	38-83	6
$\sigma_{\rm I}, \sigma_{\rm R}^+$	61–91	6
F, R	41-88	6

^{*a*} 100 R^2 in the case of multiple linear regression analysis.

Solvent-Reactivity Correlation

The reaction has been studied in seven organic solvents viz. DMF, DMSO, MeCN, NB (all hydrogen bond acceptor (HBA), aprotic, and dipolar), CB, Diox (both HBA, aprotic, and apolar) and t-BuOH (hydrogen bond donor (HBD) and protic) with a range of ca. 44 units of relative permittivity. The pseudo-firstorder rate constants are given in Table IV. The correlation of these rate constants with inverse of relative permittivity through Laidler-Eyring [17] equation $(0.663 > r > 0.074, 1.17 > \text{ sd} > 0.48, 1.18 > \Psi >$ 0.80) and with Reichardt's [12] normalized micropolarity parameter $E_{\rm T}^{\rm N}$ (0.885 > r > 0.074, 1.11 > sd > $0.45, 1.18 > \Psi > 0.61$) does not yield any meaningful equation. Khurana et al. made parallel observation for the oxidation of formic and oxalic acid by quinolinium fluorochromate, QFC, in organic solvent media, and the effect of solvent on the reaction was satisfactorily explained by multiparameter equations [18].

From idealized theories, the solvent parameters ε_r and $E_{\rm T}^{\rm N}$ 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 nonstructured continuum, not composed of individual solvent molecules with their own solventsolvent interactions and they do not take into account specific solute-solvent interactions, such as hydrogen bonding and electron pair donor-electron pair 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 microscopic level. Thus, bulk solvent properties like

 $\varepsilon_{\rm r}$ and $E_{\rm T}^{\rm N}$ 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 regression. Various treatments for the above solvent-solvent-solute interactions based on linear solvation energy relationships (LSER) have been developed [6].

Swain et al. [19] believed that the specific solvation is determined principally by the acidity and basicity of the solvent. The rate data are analyzed using a twoparameter equation involving anion-solvating tendency (A) and cation-solvating tendency (B).

$$\log k_{\rm obs} = aA + bB + c \tag{2}$$

where the regression coefficients a and b measure the susceptibility of the solvent-dependent solute property $\log k_{obs}$ to the indicated solvent parameter and c is the regression value of the solute property in the reference solvent. The rates of oxidation for all the compounds investigated show a satisfactory correlation in the above LSER (Eq. (2)) with an explained variance of over 90%. Results in Table VIII suggest that the contribution of anion-solvating tendency to reactivity was found to be dominant, as indicated by P_A . The sign of the coefficients of both these terms are negative indicating that the reactants are solvated, through specific anion- and cation-solvating tendencies, to a greater extent than the transition state and further may be the operation of appreciable solvent-solvent interactions.

$k_{ m obs}$) of Substituted Anilines by IFC with Swain's Specific Solvatochromic Parameters A and B										
Substituent	R^2	sd	Ψ	а	b	P_{A}	$P_{\rm B}$			
Н	0.877	0.83	0.41	-6.795	-2.190	76	24			
<i>p</i> -Me	0.890	0.69	0.39	-5.374	-2.214	71	29			
<i>p</i> -OMe	0.881	0.63	0.41	-2.069	-2.947	41	59			
p-COMe	0.967	0.41	0.21	-8.514	-1.529	85	15			
p-NHCOMe	0.955	0.44	0.25	-4.282	-2.838	60	40			
$p-NO_2$	0.939	0.53	0.29	-3.962	-3.020	57	43			
p-Cl	0.949	0.55	0.27	-9.593	-1.329	88	12			
<i>p</i> -Br	0.966	0.44	0.22	-7.032	-2.414	74	26			
<i>p</i> -F	0.931	0.63	0.31	-6.586	-2.524	72	28			
<i>m</i> -Me	0.954	0.48	0.25	-6.287	-2.363	73	27			
<i>m</i> -COOH	0.961	0.50	0.23	-8.968	-1.972	82	18			
$m-NO_2$	0.891	0.78	0.39	-0.782	-4.479	15	85			
<i>m</i> -Et	0.881	0.67	0.41	-3.057	-2.775	52	48			
<i>m</i> -OMe	0.951	0.39	0.26	-2.104	-2.883	42	58			
<i>m</i> -COMe	0.685	0.42	0.66	-3.701	-0.214	95	05			

Table VIII Statistical Results and Weighted Percentage Contributions for the Correlation of Rate of Oxidation (log

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 [20]. 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:

$$\log k = A_0 + s\pi^* + a\alpha + b\beta \tag{3}$$

where π^* in an index of solvent dipolarity/ polarizability, 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_0 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_{obs} to the indicated solvent parameter. The rates of oxidation for all the compounds studied show a satisfactory correlation with solvent via the above LSER (Eq. (3)) with an explained variance of about 92%. Such a correlation indicates the existence of both specific and nonspecific solute-solvent interactions in the present study.

From the values of the regression coefficients, the contribution of each parameter, on a percentage basis, to reactivity was calculated and listed in Table IX.

The observation of this systematic multiple regression analysis leads us to the following preliminary conclusions: (i) The rate of the reaction is strongly influenced by specific solute-solvent interactions as indicated by the percentage contributions of α and β parameters. (ii) The negative sign of the coefficients of α and β terms suggests that the specific interactions between the reactants and the solvent, through HBD and HBA properties, are more than that between the transition state and the solvent. (iii) tert-Butanol, a typical hydroxylic solvent, can form relatively strong complexes with solutes by hydrogen bonding, and such a complexing solvent acts as a very mild form of blocking reagent [21]; hence, the approach of the oxidizing species during activation is relatively difficult, consequently the rate of the reaction is very slow in t-BuOH. On the basis of complex formation between the anilines and solvents, it would be expected that the oxidation would be faster in nonpolar solvents than in polar solvents and the observed results (Table IV, a solvent change from tert-BuOH to Diox causes a 66-fold rate acceleration) are in the same lines. (iv) The negative sign of the coefficient of this term suggests that with decrease in polarizability/dipolarity of the medium, the rate of the oxidation process will increase and the rate is maximum in apolar solvents as observed from Table IV.

Mechanism

The correlations of log k_{obs} versus pK_a [22] and log k_{obs} versus ΔpK_a (= pK_a -substituted aniline – pK_a aniline) [23] are nonlinear. This observation along with the results of structure–reactivity correlation indicates that

Table IX Statistical Results and Weighted Percentage Contributions for the Correlation of Rate of Oxidation (log k_{obs}) of Substituted Anilines by IFC with Kamlet–Taft's Solvatochromic Parameters α , β , and π^*

Substituent	R^2	sd	Ψ	а	b	S	P_{α}	P_{eta}	$P_{\pi*}$
Н	0.860	0.95	0.44	-3.011	-1.976	-3.185	37	24	39
<i>p</i> -Me	0.936	0.57	0.29	0.264	-3.282	-2.124	05	58	45
<i>p</i> -OMe	0.934	0.51	0.30	1.086	-2.067	-2.612	19	36	45
<i>p</i> -COMe	0.960	0.49	0.23	-4.799	-1.368	-3.491	50	14	36
<i>p</i> -NHCOMe	0.911	0.67	0.35	-2.749	-0.988	-3.573	37	14	49
p-NO ₂	0.889	0.77	0.39	-2.739	-0.891	-3.687	38	12	50
<i>p</i> -Cl	0.951	0.58	0.26	-4.887	-1.757	-3.457	49	17	34
<i>p</i> -Br	0.967	0.47	0.21	-1.932	-2.763	-3.098	25	35	40
<i>p</i> -F	0.969	0.45	0.20	-0.660	-3.169	-2.954	10	47	43
<i>m</i> -Me	0.968	0.44	0.21	-1.365	-2.673	-2.912	20	38	42
<i>m</i> -COOH	0.961	0.54	0.23	-3.231	-2.828	-3.219	35	30	35
$m-NO_2$	0.817	1.09	0.50	-0.037	-1.449	-3.771	01	28	71
<i>m</i> -Et	0.890	0.69	0.39	-4.327	0.772	-4.141	47	08	45
<i>m</i> -OMe	0.892	0.62	0.38	-1.092	-1.026	-2.892	22	20	58
<i>m</i> -COMe	0.872	0.78	0.42	-5.685	0.035	-3.576	61	00	39

molecular anilines are the reactive species [24]. A perusal of data in Table II 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 nonaqueous 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] [25] (Scheme 1).

$$IFC + H^{+} \stackrel{K'}{\hookrightarrow} IFCH^{+}$$
$$IFCH^{+} + Substrate \stackrel{K}{\hookrightarrow} Complex \quad (rapid)$$
$$Complex \stackrel{k}{\to} Product \qquad (slow)$$

Scheme 1 In the presence of acid.

The mechanism shown in Scheme 1 leads to, under the condition that the formation constant (K) of the oxidant–substrate complex is large, the following rate law:

$$-d[IFC]/dt = kK'[IFC][H^+]$$

The above scheme accounts for the observed orders. The products separated suggest the formation of phenylhydroxylamine, indicating N attack. Formation of azobenzene and benzoquinone from phenylhydroxylamine and the subsequent oxidation products follow Scheme 2.

$$ArNH_2 \xrightarrow{O} ArNHOH \xrightarrow{O} ArNO$$
$$ArNH_2 + ArNO \rightarrow Ar-N=N-Ar$$
Rearrangement, H⁺
$$ArNHOH \rightarrow p-Aminophenol$$

p-Aminophenol \xrightarrow{O} Benzoquinone

Scheme 2

In the absence of p-TsOH, the rate of the reaction is very slow and the order with respect to [substrate] is zero (see Scheme 3). This suggests that protonated IFC is the active species and better electrophile.

IFC + Substrate
$$\stackrel{K}{\hookrightarrow}$$
 Complex (rapid)
Complex $\stackrel{k}{\rightarrow}$ Product (slow)

scheme 3 In the absence of acid.

The mechanism shown in Scheme 3 yields, if the formation constant (K) of the oxidant–substrate complex is large, the following rate law:

$$-d[IFC]/dt = k[IFC]$$

The rate law in its final form accounts for the observed kinetics.

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