Linear Free-Energy Relationships in Chromium(VI) Oxidation of Substituted Benzylamines in Nonaqueous Media

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ABSTRACT: The kinetics of oxidation of 11 para- and meta-substituted benzylamines by imidazolium fluorochromate (IFC) in different organic solvent media has been investigated in the presence of p-toluenesulfonic acid (TsOH). The reaction was run under pseudo-first-order conditions. The rate of the reaction was found to be first order in IFC and found to increase with increase in [TsOH]. Solution IR studies in combination with kinetic measurements were used to get a better insight into the mechanism of the oxidation process. The product analysis was carried out using GC–MS. Various thermodynamic parameters for the oxidation have been reported and discussed along with the validity of the isokinetic relationship. The specific rate of oxidizing species benzylamines reaction (k_2) correlates with Hammett's substituent constants affording positive reaction constants. The rate data failed to correlate with macroscopic solvent parameters, such as ε_r and E_T^N, while showing satisfactory correlation with Kamlet–Taft's solvatochromic parameters (α, β, and π^*) which 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. © 2007 Wiley Periodicals, Inc. Int J Chem Kinet 39: 362–369, 2007

INTRODUCTION

The kinetics of oxidation of aromatic primary amines by many reagents has been studied [1–7]. The oxidation of benzylamines presents interesting possibilities. It is known to yield a number of products, including those resulting from condensation of the intermediate

products of oxidation, with the parent amine [7]. Usually, oxidation may be effected in many ways to yield different products depending upon which reactant is used in excess [7]. However, the scope, utility, and mechanisms of such reactions have not been systematically investigated; hence, we undertook the present study.

Further, the oxidation of organic compounds in non-aqueous and aquo-organic solvent media has 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 [8–12].

The Hammett equation and its modified forms [13], 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. 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 [14]) oxidation of 11 meta- and para-substituted benzylamines in nonaqueous media.

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), chlorobenzene (CB), acetone (Me$_2$CO), and ethyl acetate (EA) are of analytical grade and were purified by conventional methods. Benzylamines (Aldrich or Merck, Bangalore, India) were used with substituents H, *p*-Me, *p*-OMe, *p*-Ph, *p*-Cl, *p*-F, *p*-COOH, *m*-Me, *m*-F, *m*-Cl, and *m*-OMe. Solid benzylamines were used as such, and Liquid benzylamines were used after vacuum distillation. IFC was prepared by using the reported method [14], 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 unconsumed oxidant iodometrically at 26, 34, 42, and 49 (± 0.1)°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 $\pm 3\%$. The solution IR experiment was done with a horizontal attenuated total reflectance ZnSe flat prism plate, in a JASCO FT-IR 460 Plus spectrometer.

Data Analysis

Correlation analyses were carried out using Microcal origin (version 6) computer software. The goodness of the fit was discussed using the correlation coefficient (r in the case of simple linear regression and R in the case of multiple linear regression) and standard deviation (SD). The percentage contribution (P_x) of a parameter to the total effect on the reactivity was computed using the regression coefficient of each parameter as reported earlier [15].

Product Analysis

The product analysis was carried out, under kinetic conditions, by employing GC–MS. The results reveal that the oxidation products were benzaldehyde (m/z 106, 78) and *N*-benzylidene(phenyl)methanamine (m/z 195, 165, 118, 104, 89, 77, 63). In addition to these, as reported earlier [16], two more fractions corresponding to complex intermediates were also obtained.

RESULTS AND DISCUSSION

The kinetic studies were carried out under pseudo-first-order conditions with the [substrate] > [IFC]. The first-order dependence of the reaction on IFC is obvious from the linearity of the plots of log [IFC] versus time. Furthermore, 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]$_o$. The oxidation of benzylamine by IFC in DMF is remarkably slow but is catalyzed in the presence of *p*-toluenesulfonic acid, and the reaction proceeds at a comfortable rate. Catalysis by *p*-toluenesulfonic acid suggests protonation of the IFC species rather than the benzylamine molecule, which would have resulted in retardation. Parallel observations were made in the oxidation of substituted anilines by the same oxidant [17]. The participation of protonated chromium species in Cr(VI) oxidations is
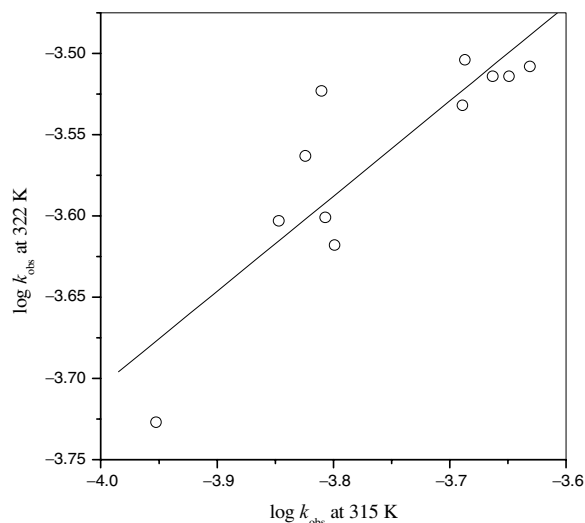
Table I Pseudo-First-Order Rate Constants for the Oxidation of Benzylamine by IFC at 299 K in DMF Medium

10^2 [BA] (M)	10^3 [IFC] (M)	10^2 [TsOH] (M)	10^5 k_{obs} (s^{-1})
3.0	2.0	2.0	8.96
4.0	2.0	2.0	9.10
5.0	2.0	2.0	9.05
6.0	2.0	2.0	8.98
4.0	1.0	2.0	9.21
4.0	1.5	2.0	9.11
4.0	2.0	2.0	9.10
4.0	2.5	2.0	9.12
4.0	2.0	1.0	7.85
4.0	2.0	2.0	9.10
4.0	2.0	3.0	12.52
4.0	2.0	4.0	15.23
3.0	2.0	–	4.25
4.0	2.0	–	4.18
5.0	2.0	–	4.22
6.0	2.0	–	4.19

Figure 1 The isokinetic plot for substituted benzylamines in DMF.

well known [18]. The reaction did not promote polymerization of acrylonitrile indicating the absence of free radicals.

Activation Parameters

The activation parameters were calculated from k_{obs} at 299, 307, 315, and 322 K using the van't Hoff plot by the method of least squares and are presented in Table II. The operation of isokinetic relationship is tested by plotting the logarithms of rate constants at two temperatures ($T_2 > T_1$) against each other according to Eq. (1) as suggested by Exner [19].

$$\log k(\text{at } T_2) = a + b \log k(\text{at } T_1) \qquad (1)$$

In the present study, fairly linear plots imply the validity of isokinetic relationship. A representative plot is shown in Fig. 1 (in DMF medium, $r = 0.901$, SD $= 0.035$, isokinetic temperature $= 340 \pm 22$ K). The operation of isokinetic relationship reveals that all the substituted benzylamines examined are oxidized through a common mechanism.

The thermodynamic parameters were also calculated for the oxidation of benzylamine in the seven neat organic solvents (Table III). Negative entropy of

Table II Effect of Temperature on the Rate of Oxidation of Substituted Benzylamines by IFC in DMF and Activation Parameters for the Oxidation

Substituents in Benzylamine	Rate Constants 10^5 k_{obs} (s^{-1})				E_a	$\Delta H^{\#}$	$-\Delta S^{\#}$	$\Delta G^{\#-}$(299 K)
	299 K	307 K	315 K	322 K				
H	09.1	09.5	11.2	18.7	23	21	253	96.6
m-OMe	10.3	11.1	15.6	25.0	31	28	228	96.3
m-Me	10.5	14.9	15.9	24.1	26	24	241	95.9
m-F	13.3	15.5	22.4	30.6	30	27	229	95.5
m-Cl	13.9	15.1	21.7	30.6	28	25	234	95.4
p-OMe	10.5	10.6	14.2	24.9	29	27	233	96.3
p-Me	09.8	13.4	15.0	27.4	33	30	221	96.2
p-F	13.9	15.8	23.3	31.1	29	26	231	95.4
p-Cl	15.5	17.3	19.9	29.9	21	19	255	95.2
p-Ph	15.4	17.9	20.4	29.3	21	18	256	95.1
p-COOH	13.6	13.9	20.6	31.3	30	27	229	95.5

[Substrate] $= 4 \times 10^{-2}$ M; [IFC] $= 2 \times 10^{-3}$ M; [TsOH] $= 2 \times 10^{-2}$ M.
E_a in kJ mol^{-1}; $\Delta H^{\#}$ in kJ mol^{-1}; $\Delta S^{\#}$ in J K^{-1} mol^{-1}; $\Delta G^{\#}$ in kJ mol^{-1}.

Table III Thermodynamic Parameters for the Oxidation of Benzylamine by IFC in Different Solvents and Their Relative Permittivity Values

Solvent	ε_r	Rate Constants $10^5 \, k_{obs}$ (s^{-1})				E_a	$\Delta H^\#$	$-\Delta S^\#$	$\Delta G^\#$ (299 K)
		299 K	307 K	315 K	322 K				
CB	5.62	37.4	65.2	79.9	139.0	43	40	175	92.6
EA	6.02	59.0	78.6	108.0	155.0	33	31	204	91.6
t-BuOH	12.47	4.99	5.13	5.63	7.79	14	12	288	97.9
Me$_2$CO	20.7	11.5	11.6	16.3	19.8	20	18	262	96.0
DMF	36.71	09.1	09.5	11.2	18.7	23	21	253	96.6
MeCN	37.5	4.90	5.31	5.67	7.34	13	10	293	98.0
DMSO	46.68	6.69	6.84	7.35	8.33	07	05	308	96.9

[Substrate] = 4×10^{-2} M; [IFC] = 2×10^{-3} M; [TsOH] = 2×10^{-2} M.
E_a in kJ mol^{-1}; $\Delta H^\#$ in kJ mol^{-1}; $\Delta S^\#$ in J K^{-1} mol^{-1}; $\Delta G^\#$ in kJ mol^{-1}.

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 existence of a linear relationship (Fig. 2, r = 0.991, SD = 0.085, isokinetic temperature = 246 ± 15 K) between log k_{obs} at 322 K and log k_{obs} at 299 K indicates that a single mechanism is operating in all the solvent systems studied.

Structure-Reactivity Correlation

The effect of substituents on the oxidation rate was studied with 11 para- and meta-substituted benzylamines in seven organic solvents (Table IV). The results in Table IV reveal that the rate constants vary with substrate in a particular solvent, though the rate
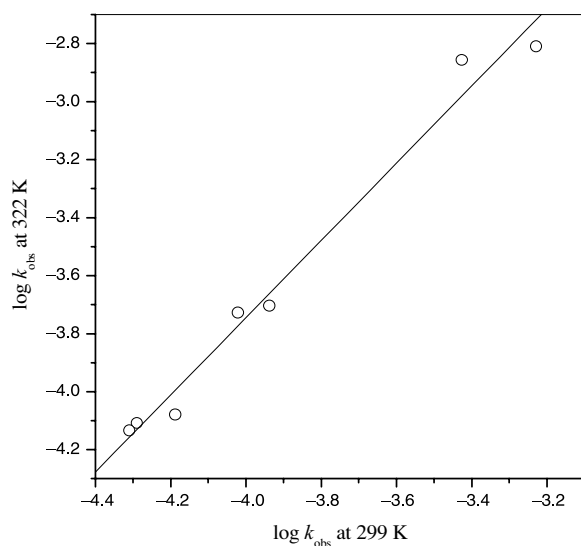

Figure 2 The isokinetic plot for the oxidation of unsubstitued benzylamine in all solvents.

of the reaction is independent of [substrate]. This may be because of difference in polarity of different benzylamines, the extent of solvation should be different and hence the experimental values of rate constants (as well as the values of $\Delta S^\#$) may be different for different benzylamines as observed in the present study. The rate data failed to conform to either the usual Hammett equation or its modified ones; plots of log k_{obs} versus substituent constants [20] are nonlinear (not shown). The dual substituent parameter (DSP) equations [21,22] also failed to correlate the rate data with the substituent.
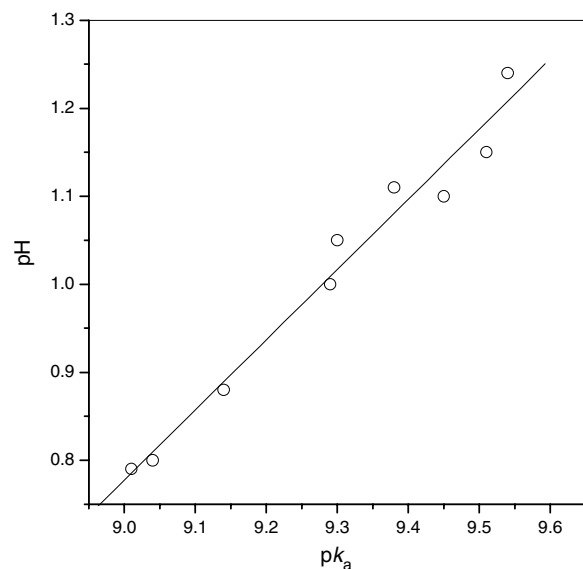
Benzylamine in basic and neutral media is present as free bases but in acid medium exists in dual forms: the free bases and the conjugate acids. And, the ratio of concentrations of the free bases to the conjugate acid [XC$_6$H$_4$CH$_2$NH$_2$]/[XC$_6$H$_4$CH$_2$NH$_3^+$]) depends on the pK_a of the benzylamine and the acidity of the medium. The reported oxidations of benzylamine, in the present study, were carried out under pseudo-first-order conditions ([benzylamine] > [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}/[benzylamine]$_T$, where [benzylamine]$_T$ is the total concentration of benzylamine. Since the molecular benzylamine is the reactive species (nucleophile), the reported k_{obs}/[benzylamine]$_T$ values are not the rate constants of the oxidant-molecular benzylamine reactions. And the analysis of k_{obs} and k_{obs}/[benzylamine]$_T$ in terms of the Hammett and modified Hammett equations is erroneous.

Hence, the specific reaction rates of molecular benzylamine with IFC $\{k_2 = k'(K_a + [H^+])/[H^+]\}$ have been obtained from the measured pH and the reported pK_a values [23]. The measured pH varies linearly

Table IV   Pseudo-First-Order Rate Constants ($10^5 \, k_{obs}$, s^{-1}) for the Oxidation of Meta- and Para-Substituted Benzylamines by IFC at $26 \pm 0.1°$C

Substituents in Benzylamine	Solvents						
	DMF	Me$_2$CO	DMSO	t-BuOH	MeCN	EA	CB
H	09.1	11.5	6.69	4.99	4.90	059	37.4
m-OMe	10.3	12.0	5.75	6.78	7.62	216	69.5
m-Me	10.5	11.2	6.54	9.43	6.59	272	70.0
m-F	13.3	14.7	8.22	8.40	10.2	210	92.8
m-Cl	13.9	14.9	8.27	9.14	9.03	187	79.1
p-OMe	10.5	10.5	6.83	6.22	7.84	160	67.0
p-Me	09.8	11.2	8.61	9.43	9.08	182	77.3
p-F	13.9	14.1	7.51	8.72	8.13	193	91.3
p-Cl	15.5	14.1	7.49	9.21	9.79	193	76.5
p-Ph	15.4	14.3	1.98	15.4	11.6	263	56.0
p-COOH	13.6	18.9	7.58	8.43	10.6	233	46.8

with the pK_a of benzylammonium ion (Fig. 3). This clearly reveals the operation of a linear free-energy relationship in the dissociation of benzylammonium ions in nonaqueous media. The p-Ph and p-COOH substituents are not included because of the nonavailability of pK_a values. In the reactions of benzylamine in acid medium, as the free bases are the nucleophiles, the specific reaction rates of benzylamines are to be obtained using the concentrations of the free bases but not the total concentrations of benzylamines. The specific rates of the oxidant-molecular benzylamine reactions are presented in Table V. The existence of isokinetic and Exner relationships in the title study and the linear correlation between pH and pK_a clearly points out the

linear free-energy relationship in the IFC-molecular benzylamine reaction. Hence, the rate constants (k_2) calculated through the modified method are analyzed using the usual Hammett equations.

The specific rates of the rate-limiting step of para- and meta-substituted benzylamines correlate satisfactorily with the Hammett's substituent constants, and a representative plot is given in Fig. 4. The small magnitude $(0.074 \pm 0.009 - 0.262 \pm 0.10)$ of the reaction constant obtained indicates that the reaction is less susceptible to substituent effects, as expected. Furthermore, positive reaction constant suggests that there may be a disappearance of positive charge at the reaction center.

It is clear that ρ values, like rate constant values for given reactants, are influenced by solvent effects. Hammett predicted that, in general, the reaction constant appears to increase with decreasing relative permittivity of the medium. In the present study, however, there is a very marked deviation from the relationship between ρ and ε_r. This suggests that ρ values are influenced both by nonspecific and by specific solvent effects [13].

Solvent-Reactivity Correlation

The reaction has been studied in seven organic solvents, viz. DMF, DMSO, MeCN, Me$_2$CO, EA (all hydrogen bond acceptor (HBA), aprotic, and dipolar), CB (HBA, aprotic, and apolar), and t-BuOH (hydrogen bond donor (HBD) and protic) with a range of ca. 41 units of relative permittivity. The pseudo-first-order rate constants are given in Table IV. The correlation of these rate constants with inverse of relative permittivity [24] through Laidler–Eyring [25] equation $(0.905 > r > 0.751, 0.25 > SD > 0.52)$ and with Reichardt's

Figure 3   The plot of pH versus pK_a.

Table V   Specific Rate ($10^3 \, k_2$, dm^3 mol^{-1} s^{-1}) of the Oxidant-Molecular Benzylamine Reaction at 299 K

Substituents in Benzylamine	Solvents						
	DMF	Me$_2$CO	DMSO	t-BuOH	MeCN	EA	CB
H	2.270	2.870	1.672	1.247	1.225	14.75	9.350
m-OMe	2.570	3.000	1.437	1.695	1.905	54.00	17.40
m-Me	2.625	2.800	1.635	2.357	1.647	68.00	17.50
m-F	3.325	3.675	2.055	2.100	2.550	53.00	23.20
m-Cl	3.475	3.725	2.068	2.285	2.258	47.00	19.80
p-OMe	2.630	2.625	1.707	1.555	1.960	40.00	16.70
p-Me	2.450	2.800	2.152	2.357	2.270	46.00	19.30
p-F	3.475	3.525	1.877	2.180	2.032	48.00	22.80
p-Cl	3.875	3.525	1.873	2.303	2.448	48.00	19.10

[26] normalized micropolarity parameter E_T^N (0.974 > r > 0.797, 0.38 > SD > 0.10) does not yield any meaningful equation.

Swain et al. [27] believed that the specific solvation is determined principally by the acidity and the basicity of the solvent. The rate data are analyzed using a two-parameter equation involving anion-solvating tendency (A) and cation-solvating tendency (B).

$$\log k_{obs} = aA + bB + c \qquad (2)$$

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
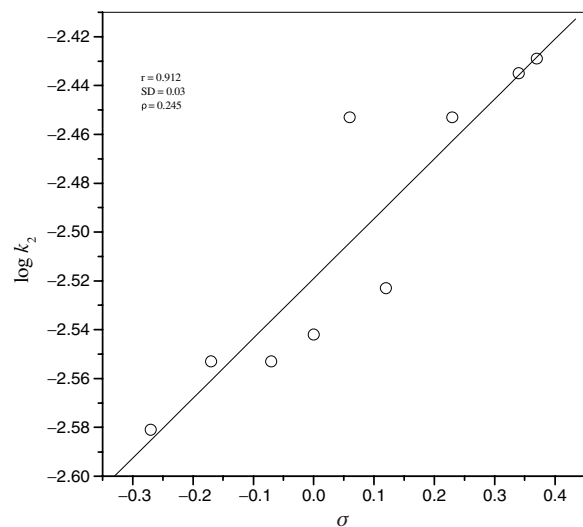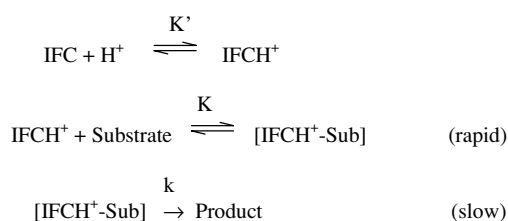
the above linear solvation energy relationship (Eq. (2)) with an explained variance of ca. 80%. The contribution of anion-solvating tendency to reactivity was found to be dominant (∼80%). The sign of the coefficients of both these terms is negative, indicating that the reactants are solvated, through specific anion- and cation-solvating tendencies, to a greater extent than the transition state and further may be due to appreciable solvent–solvent interactions.

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 [28]. This method may be used to unravel, quantify, correlate, and rationalize multiple interacting solvent effects on the 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:

$$\log k = A_o + s\pi^* + a\alpha + b\beta \qquad (3)$$

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 acidity, β is the solvent HBA 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 $\log k_{obs}$ 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 ca. 92%. Such a correlation indicates the existence of both specific and nonspecific solute–solvent interactions in the present study.

Figure 4   Hammett plot for the oxidation of benzylamine in acetone at 299 K.

$$IFC + H^+ \underset{}{\overset{K'}{\rightleftharpoons}} IFCH^+$$

$$IFCH^+ + Substrate \overset{K}{\rightleftharpoons} [IFCH^+\text{-}Sub] \qquad (rapid)$$

$$[IFCH^+\text{-}Sub] \overset{k}{\rightarrow} Product \qquad (slow)$$

Scheme 1

From the values of the regression coefficients, the contribution of each parameter, on a percentage basis, to reactivity was calculated and is listed in Table VI. 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 interaction between the reactants and the solvent, through HBD and HBA properties, is more than that between the transition state and the solvent. (iii) The solvent HBD acidity, as indicated by the α term, plays a dominant role in governing the reactivity. It alone explains over 50% of the observed solvent effect. (iv) The solvent polarizability/dipolarity, as indicated by P_{π^*}, also plays an appreciable role in governing the reactivity. 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. On the basis of complex formation between the benzylamines and solvents, it would be expected that the oxidation would be faster in nonpolar solvents than in polar solvents and the observed results are on the same lines. Parallel observations were
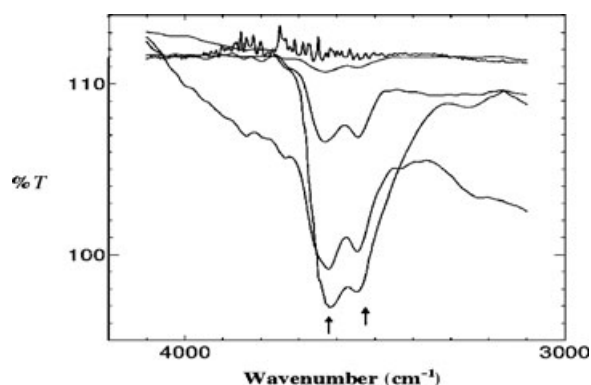
Figure 5 FT-IR spectra of the reaction mixture in acetonitrile with increase in time.

recorded by us in IFC [17] and nicotinium dichromate [29] oxidation of anilines in neat organic solvents.

Mechanism

Figure 5 shows the solution FT-IR spectrum of the reaction mixture at different time intervals. The doublet around 3500–3600 cm^{-1} corresponds to asymmetric and symmetric stretching vibrations of the two N–H bonds of the aromatic primary amine. It is evident from the figure that with increase in time the intensity of the peak decreases which indicates the participation of the amine group in the reaction. The result of structure–reactivity correlation indicates that molecular benzylamines are the reactive species [30]. 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] [17]. In nonaqueous media, chromium(VI) reagents complex

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

Substituent	R^2	SD	a	b	s	P_α	P_β	P_{π^*}
H	0.934	0.17	−3.74	0.02	−2.68	58	01	41
m-OMe	0.929	0.23	−4.24	−0.20	−3.31	55	02	43
m-Me	0.932	0.22	−4.66	0.08	−3.63	56	01	43
m-F	0.879	0.37	−6.68	0.77	−4.37	56	07	37
m-Cl	0.940	0.18	−3.99	−0.07	−2.89	57	02	41
p-OMe	0.941	0.19	−3.84	−0.28	−2.88	55	04	41
p-Me	0.902	0.24	−3.80	−0.18	−2.86	55	03	42
p-F	0.931	0.21	−4.18	−0.10	−3.01	57	02	41
p-Cl	0.934	0.19	−3.89	−0.12	−2.93	56	02	42
p-Ph	0.851	0.26	−3.98	0.37	−2.79	56	05	39
p-COOH	0.945	0.24	−6.82	1.02	−4.53	55	08	37

with the substrate 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] [31] (Scheme 1).

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:

$$-d[IFC]/dt = k[IFCH^+\text{-Sub}]$$

$$[IFCH^+\text{-Sub}] = K[IFCH^+][Sub]/(1 + K[Sub])$$

If $K[Sub] \gg 1$

$$[IFCH^+\text{-Sub}] = [IFCH^+] = K'[IFC][H^+]$$

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

The above scheme accounts for the observed orders.

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