Preferential Solvational Effects on the Cr(VI) Oxidation of Benzylamines in Benzene/2-Methyl-propan-2-ol Mixtures

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ABSTRACT: Imidazolium fluorochromate (IFC) oxidation of 11 meta- and para-substituted benzylamines, in varying mole fractions of benzene/2-methylpropan-2-ol binary mixtures, is first order in IFC and acid and zero order in substrate. The Hammett correlation yielded a U-shaped curve, indicating a change in the relative importance of bond formation and bond fission in the transition state. The rate data failed to correlate with macroscopic solvent parameters such as ε_r and E_T^N. The correlation of k_{obs} with Kamlet–Taft solvatochromic parameters suggests that H-bonding between the reacting species and the solvent plays a major role in governing the reactivity. © 2010 Wiley Periodicals, Inc. Int J Chem Kinet 42: 159–167, 2010

INTRODUCTION

The study of solute–solvent interactions in binary solvent mixtures is more complex than in pure solvents. In a pure solvent, the composition of the microsphere of a solvated solute, the so-called cybotatic region, is the same as in the bulk solvent, whereas in binary mixtures this can be distinct which leads to preferential solvation phenomena. This is due to the interactions of the solute to a different extent with each of the mixture components, which in turn affect the composition of the microsphere of solvation [1].

Studies on the kinetics of oxidation of organic compounds in nonaqueous and aquo-organic solvent mixtures have revealed the important role of nonspecific and specific solvent effects on reactivity [2–9]. It has been shown that the reactivity is influenced by the preferential solvation of the reactants and/or transition state through such effects, and has been established that the technique of correlation analysis may be well applied to separate and quantify these effects on the reactivity.

Furthermore, the important tool in deciding the mechanism of reactions is the study of substituent effects and thermodynamic parameters. The Hammett equation and its modified forms [10], all known as linear free energy relationships (LFER), have been found to be useful for correlating reaction rates and equilibrium constants for side chain reactions of meta- and

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para-substituted derivatives. Thus, a systematic study of various LFERs and 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 oxidation of several meta- and para-substituted benzylamines by imidazolium fluorochromate (IFC, a mild and selective oxidant, reported only recently [11]) in benzene/2-methylpropan-2-ol mixtures of varying compositions. This mixture is chosen since by varying the mole fraction of the constituent solvents, the hydrogen bonding properties of the medium can be varied gradually 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 [12].

EXPERIMENTAL

Materials

All the chemicals and solvents used were of analytical grade. The solvents 2-methylpropan-2-ol and benzene are of analytical grade and were purified by conventional methods. The benzylamines (Aldrich or Merck, Bangalore, India) used were with substituents H, *p*-Me, *p*-OMe, *p*-Ph, *p*-Cl, *p*-F, *p*-COOH, *m*-Me, *m*-F, *m*-Cl, and *m*-OMe. The solid benzylamines were used as such, and the liquid benzylamines were used after vacuum distillation. IFC was prepared by the reported method [11], and its purity was checked by the iodometric method.

Kinetic Measurements

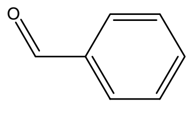
The reactions were carried out under pseudo-first-order conditions by keeping an excess of substrate over IFC. The progress of the reactions was followed by estimating the unconsumed oxidant iodometrically at 299, 307, 315, and 322 K. The rate constants were determined by the least-squares method, from the linear plots ($r > 0.97$) of log [IFC] versus time. Replicate runs showed that the rate constants were reproducible to within ±3%.

Data Analysis

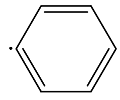
Correlation analyses were carried out using Microcal origin (version 6) computer software. The goodness of a fit was discussed using the correlation coefficient (r in the case of simple linear regression and R in the case of multiple linear regressions) and standard deviation. The percentage contribution ($\mathbf{P}_x$) of a parameter to the total effect on reactivity was computed using the regression coefficient of each parameter as reported earlier [13].

Product Analysis

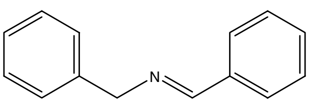
The product analysis was carried out, under kinetic conditions, by employing GC-MS technique. The results revealed that the oxidation products were benzaldehyde and *N*-benzylidene(phenyl)methanamine. The following major fragments with corresponding m/z values were obtained in the GC-MS analysis. In addition to these, as reported earlier [14], two more fractions corresponding to complex intermediates were also obtained.



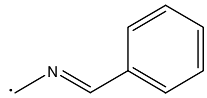
$m/z = 106$



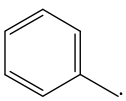
$m/z = 77$



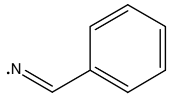
$m/z = 195$



$m/z = 118$



$m/z = 91$



$m/z = 104$

RESULTS AND DISCUSSION

The kinetics of oxidation of benzylamine and *meta*-(Me, OMe, Cl, F)- and *para*-(Me, OMe, Cl, F, Ph, COOH)-substituted benzylamines was carried out under pseudo-first-order conditions with [substrate] > [IFC] in varying mole fractions of benzene (0.13, 0.15, 0.18, 0.32, 0.42, 0.52, 0.67, and 0.86) in 2-methylpropan-2-ol. The mole fraction values selected as the solvatochromic parameters for these mole fractions are available in the literature [1].

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]. The oxidation process is remarkably slow, but found to be catalyzed in the presence of *p*-toluenesulfonic acid and the reaction proceeds at a comfortable rate. A plot of log [acid] versus log k_{obs} was found to be linear ($r = 0.998$) with a slope of unity, indicating that the order with respect to acid

Table I Pseudo-First-Order Rate Constants for the Oxidation of Benzylamine by IFC at 299 K in 0.67 Mole Fraction of Benzene in 2-Methylpropan-2-ol

10^2 [BA] (M)	10^3 [IFC] (M)	10^2 [TsOH] (M)	10^4 k_{obs} (s^{-1})
3.0	2.0	2.0	4.17
4.0	2.0	2.0	4.21
5.0	2.0	2.0	4.19
6.0	2.0	2.0	4.08
4.0	1.0	2.0	4.17
4.0	1.5	2.0	4.22
4.0	2.0	2.0	4.21
4.0	2.5	2.0	4.17
4.0	2.0	1.0	1.82
4.0	2.0	2.0	4.21
4.0	2.0	3.0	6.45
4.0	2.0	4.0	8.24
3.0	2.0	–	1.86
4.0	2.0	–	1.92
5.0	2.0	–	1.88
6.0	2.0	–	1.89

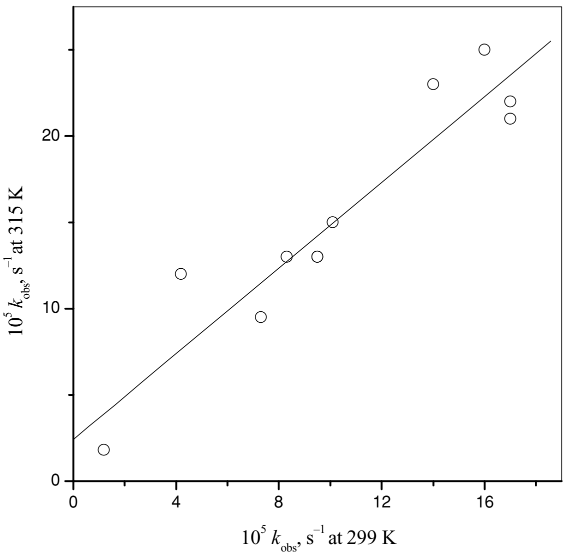


Figure 1 Isokinetic plot for the oxidation of benzylamines by IFC in 0.32 mole fraction of benzene in 2-methylpropan-2-ol.

is also one. Catalysis by *p*-toluenesulfonic acid suggested protonation of IFC species rather than the benzylamine molecule, which would have resulted in rate retardation. Parallel observations were made in the oxidation of substituted anilines by the same oxidant [4]. The participation of protonated chromium species in Cr(VI) oxidations is well known [15]. Furthermore, 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 collected 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 [16].

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

A representative plot is shown in Fig. 1 ($r = 0.938$, isokinetic temperature = 248 K). In the present study, a fairly linear plot implied the validity of the isokinetic relationship, which revealed the operation of the compensation effect in the present system [16].

The thermodynamic parameters were also calculated for the oxidation of *meta*-methyl benzylamine in

Table II Activation Parameters for the Oxidation of Benzylamines by IFC in 0.32 Mole Fraction of Benzene in 2-Methylpropan-2-ol

	$10^4 k_{\text{obs}}$ (s^{-1})						
R	299 K	307 K	315 K	322 K	$\Delta H^{\#}$ (kJ mol^{-1})	$-\Delta S^{\#}$ (J K^{-1} mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})
H	4.2	9	12	17	44	180	97.9
m-Me	1.2	1.4	1.8	2.5	23	242	95.8
m-OMe	9.5	10.4	13	20	22	248	96.6
m-Cl	16	17	25	36	24	238	94.9
m-F	9.5	9.9	13	19	21	238	96.5
p-Me	7.8	10.5	15	24	36	202	97.0
p-OMe	17	18	21	26	10	285	94.9
p-Cl	14	16	23	29	22	245	95.3
p-F	8.3	8.9	13	19	27	235	96.9
p-Ph	17	18	22	33	20	251	95.0
p-COOH	7.3	7.5	9.5	14	21	254	97.1

Table III Activation Parameters for the Oxidation of *m*-Me Benzylamine by IFC in Different Mole Fractions of Benzene in 2-Methylpropan-2-ol

Mole Fraction of Benzene	$10^4\,k_{obs}$ (s^{-1}) 299 K	307 K	315 K	322 K	$\Delta H^{\#}$ (kJ mol^{-1})	$-\Delta S^{\#}$ (J K^{-1} mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})
0.13	0.13	0.15	0.45	0.90	69	110	101
0.15	0.38	0.46	0.71	0.99	32	224	99
0.18	0.63	0.93	1.15	1.39	24	244	97
0.32	1.18	1.35	1.8	2.52	23	242	96
0.42	2.1	2.53	3.5	8	40	182	95
0.52	2.9	3.2	6	10	42	172	94
0.67	6.2	6.4	9.3	22	39	176	92
0.86	9.4	12	20	39	37	179	91

all the mole fractions of benzene in a 2-methylpropan-2-ol solvent mixture (Table III). The observed, negative entropies of activation indicated 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, $r = 0.995$, isokinetic temperature = 292 K) between log k_{obs} at 322 K and log k_{obs} at 299 K indicated that operation of the compensation effect in all the mole fractions of the solvent mixture systems studied.

Structure–Reactivity Correlation

The effect of substituents on the rate of oxidation was studied with 11 para- and meta-substituted benzylamines in benzene/2-methylpropan-2-ol solvent mixtures (Table IV). The results revealed that the rate constants vary with the substrate in a particular mole fraction of the solvent mixture, though the rate of the reaction is independent of [substrate]. This may be due to the fact that because of difference in polarity of

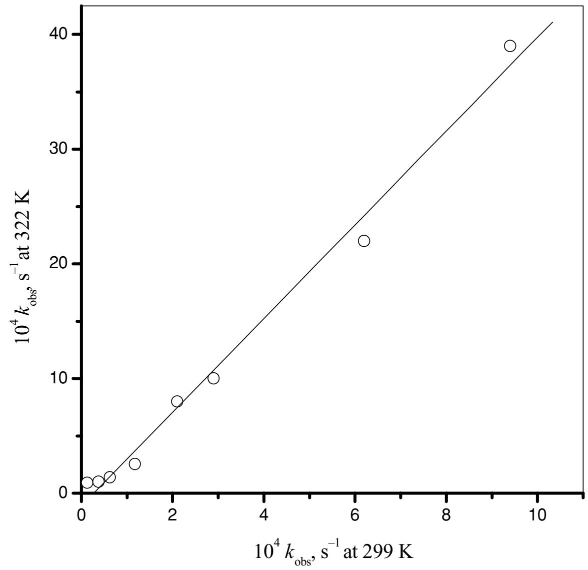


Figure 2 Isokinetic plot for the oxidation of *m*-Me compound by IFC in different mole fractions of benzene in 2-methylpropan-2-ol.

Table IV Pseudo-First-Order Rate Constants ($10^4\,k_{obs}$, s^{-1}) for the Oxidation of meta- and para-Substituted Benzylamines by IFC at 299 K

	Mole Fractions of Benzene							
X	0.13	0.15	0.18	0.32	0.42	0.52	0.67	0.86
H	0.11	0.14	0.16	0.18	1.56	2.39	4.21	4.89
m-Me	0.13	0.38	0.63	1.18	2.11	2.96	6.27	9.39
m-OMe	0.32	0.50	0.71	0.95	1.72	1.89	2.57	3.84
m-Cl	0.46	0.54	0.84	1.71	1.72	2.50	2.97	4.76
m-F	0.40	0.52	0.57	0.96	1.74	2.89	3.99	5.78
p-Me	0.25	0.36	0.41	0.77	0.94	1.41	1.95	2.21
p-OMe	0.67	0.79	0.99	1.80	2.70	3.87	6.02	8.25
p-Cl	0.51	0.67	0.85	1.47	3.31	5.69	8.28	9.70
p-F	0.48	0.57	0.59	0.83	1.50	1.84	2.47	2.83
p-Ph	0.51	0.75	0.98	1.66	2.95	3.44	9.39	11.6
p-COOH	0.48	0.49	0.57	0.73	1.75	2.09	2.78	6.02

X: Substituent in benzylamine moiety.

Table V Specific Rate Constants ($10^4\ k_2$, s^{-1}) for the Oxidation of meta- and para-Substituted Benzylamines by IFC at 299 K

	Mole Fractions of Benzene							
X	0.13	0.15	0.18	0.32	0.42	0.52	0.67	0.86
H	2.7	3.5	4.1	11	39	60	105	122
m-Me	3.2	9.6	16	30	53	74	157	235
m-OMe	7.9	13	18	24	43	47	64	96
m-Cl	11.6	13.6	21	42	43	63	74	119
m-F	9.9	13	14	39	44	72	100	144
p-Me	6.3	9	11	19	24	36	49	55
p-OMe	17	20	25	45	68	97	150	206
p-Cl	13	17	21	37	83	142	207	243
p-F	12	14	15	21	37	46	62	71

X: Substituent in benzylamine moiety.

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 by us in the present study. The rate data failed to conform to either the usual Hammett equation or its modified ones [17]; plots of log k_{obs} versus substituent constants are nonlinear.

Benzylamines in basic and neutral media are present as free bases, but in acid medium they 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 [$XC_6H_4CH_2NH_2$]/[$XC_6H_4CH_2NH_3^+$]) depends on the pK_a of the benzylamines and the acidity of the medium. The reported oxidation of benzylamines, in the present study, was 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 were calculated by dividing k_{obs} values with [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 hence the analysis of rate constants in terms of the Hammett equation is erroneous, i.e., it yields a nonlinear plot.

Hence, the specific reaction rates of molecular benzylamine with IFC have been obtained from the measured pH and the reported pK_a values of corresponding benzylamines [18]. The measured pH varies linearly with the pK_a of benzylammonium ion. This clearly revealed 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 due to the nonavailability of pK_a values. In the reactions of benzylamines 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 collected in Table V. The rate constants (k_2) calculated through the modified method are analyzed using the usual Hammett equation. A representative Hammett plot (in 0.13 mole fraction of benzene in 2-methylpropan-2-ol) is shown in Fig. 3. The Hammett plot has a concave shape with a minimum for the unsubstituted benzylamine, and all other benzylamines either with electron-donating or electron-withdrawing

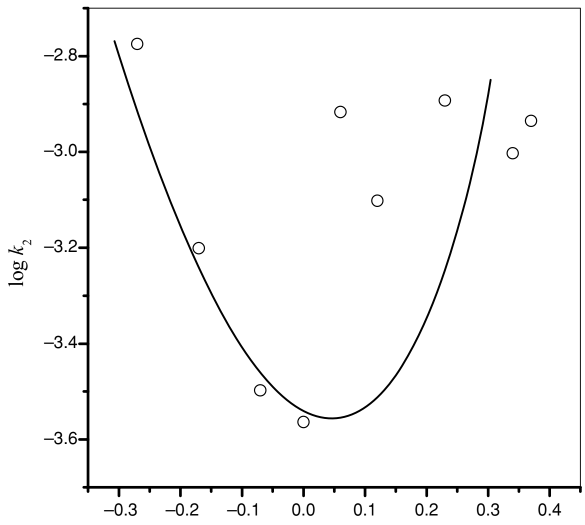


Figure 3 Hammett plot for the Cr(VI) oxidation of benzylamines at 299 K.

substituents react faster than the parent. The observed U-shaped Hammett plot may be due to a change in the relative importance of bond formation and bond breaking in the transition state [19].

Solvent–Reactivity Correlation

The Cr(VI) oxidation of benzylamines has been studied, in varying mole fractions of benzene in 2-methylpropan-2-ol, with a view to understand the effect of preferential solvation on the reaction. Solvent mixtures are very useful for studying solvent effects on reactions since the properties of the medium can be adjusted continuously by changing the composition of the mixture. The rate constants (Table IV) were correlated with solvent macroscopic parameters, viz. relative permittivity [20] and Dimroth–Reichardt's E_{T}^{N} [12]. The plots of log k_{obs} versus the above-mentioned solvent parameters were nonlinear, and a representative plot is shown in Fig. 4. This nonlinear dependence of the rate with solvent macroscopic parameters indicated that no single macroscopic physical parameter could possibly account for the multitude of solute–solvent interactions on the molecular microscopic level. These bulk solvent properties have poorly described the microenvironment around the reacting species, which governs the stability of the transition state and hence the rate of the reaction. Hence, the operation of selective or preferential solvation, which includes both nonspecific 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 electron pair donor/electron pair acceptor interactions), is likely in the present case [12].

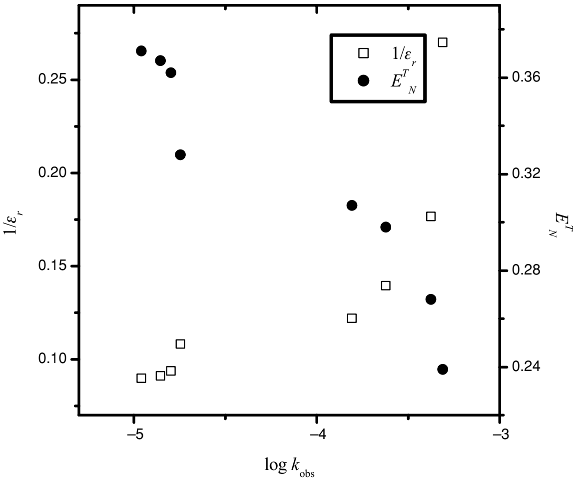


Figure 4 Plot of log k_{obs} versus solvent macroscopic parameters.

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 [21]. 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 linear solvation energy relationship (LSER):

$$\log\ k = A_o + s\pi^* + a\alpha + b\beta \qquad (2)$$

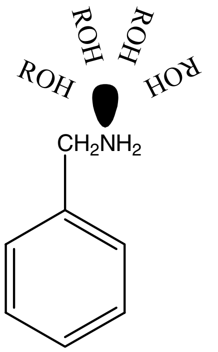
where π^* in an index of solvent dipolarity/polarizability, which measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect, α is the solvent HBD acidity, β is the solvent HBA (hydrogen bond acceptor) basicity, and A_o is the regression value of the solute 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 showed an excellent correlation with solvent via the above-mentioned LSER (Eq. (2)) with an explained variance of ca. 98%. Such an excellent correlation indicated the existence of both specific and nonspecific solute–solvent interactions in the present study.

From the values of the regression coefficients, the contributions of each parameter, on a percentage basis, to reactivity were calculated and are listed in Table VI. The weighted percentage contributions of these solvatochromic parameters indicated that (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 solvent HBD acidity, as indicated by the α term, plays a dominant role in governing the reactivity. It alone explains more than 50% of the observed solvent effect. The negative sign of the coefficients of the α term suggests that the specific interaction between the reactants and the solvent (through the HBD property) is relatively more than that between the transition state and the solvent. Since 2-methylpropan-2-ol is a typical HBD solvent, it forms a sheath of solvent shell around the lone pair of electrons residing on N-atom (as shown below) through H-bond donation or, in other words, acts as a very mild form of a blocking reagent [4,7]. Thus restricting the approach of the oxidant molecule to form the transition state and consequently retarded the rate of the oxidation.

Table VI Statistical Results and Weighted Percentage Contributions for the Correlation of k_{obs} for the Cr(VI) Oxidation of Substituted Benzylamines in Benzene/2-Methylpropan-2-ol with Kamlet–Taft's Solvatochromic Parameters α, β, and π^*

X	R^2	Standard Deviation	a	b	s	$\mathbf{P}_\alpha$	$\mathbf{P}_\beta$	$\mathbf{P}_{\pi^*}$
H	0.993	0.08	−10	0.8	6	60	04	36
m-Me	0.932	0.22	−8.5	−0.3	1.5	83	03	14
m-OMe	0.951	0.10	−4.8	−0.1	1.8	72	01	27
m-Cl	0.957	0.12	−2.7	2.3	−3.7	31	26	43
m-F	0.985	0.07	−4.8	−0.3	2.8	61	04	35
p-Me	0.968	0.08	−5.4	−0.1	0.4	92	01	07
p-OMe	0.988	0.05	−5	−0.4	1.2	76	06	18
p-Cl	0.983	0.09	−6.9	0.4	4.9	57	03	40
p-F	0.995	0.03	−3.7	0.1	3	55	01	44
p-Ph	0.984	0.07	−5.3	−0.6	1.9	68	08	24
p-COOH	0.984	0.07	−2.3	−0.8	3.6	34	12	54

X: Substituent in benzylamine moiety.



R = *t*-Bu

Such a specific solvation of the $-NH_2$ moiety by HBD solvents has already been demonstrated by us using electronic spectral and cyclic voltammetric techniques [22,23]. When the mole fraction of benzene (a typical non-HBD solvent) in the mixture is increased, the mild block has been removed progressively, the formation of transition state has increasingly become easier and consequently increased the rate of oxidation, as observed. Parallel observations were made in the Cr(VI) oxidation of anilines in neat organic solvents [4,7] wherein such retardation in rate in 2-methylpropan-2-ol medium was observed when compared to that in other nonpolar solvents. (iii) The solvent polarizability/dipolarity, as indicated by $\mathbf{P}_{\pi*}$, also plays an appreciable role in governing the reactivity. The positive sign of the coefficients of this term suggests that with an increase in the polarizability/dipolarity of the medium the rate of the oxidation process will increase. Since benzene is a more polarizable solvent ($\delta = 1$) than 2-methylpropan-2-ol ($\delta = 0$) [1], an increase in its mole fraction in the mixture increases the polarizability of the medium and consequently increased the rate of the oxidation. Parallel observations were recorded in the Cr(VI) oxidation of anilines in the binary mixture [5,8].

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 lapse of time the intensity of the peak decreased, which indicated the participation of the amine group in the reaction. The result of the structure–reactivity correlation indicated that molecular benzylamines are the reactive species [24]. A perusal of data in Table II indicated that the enthalpy of activation of the oxidation is susceptible to the substituent present in the ring. This indicated the involvement of substrate in or prior to the rate-limiting step in such a way that

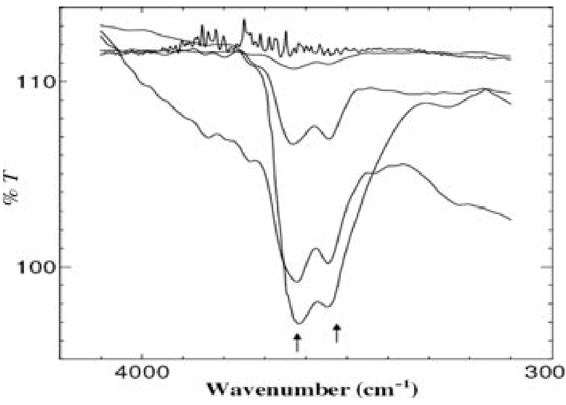
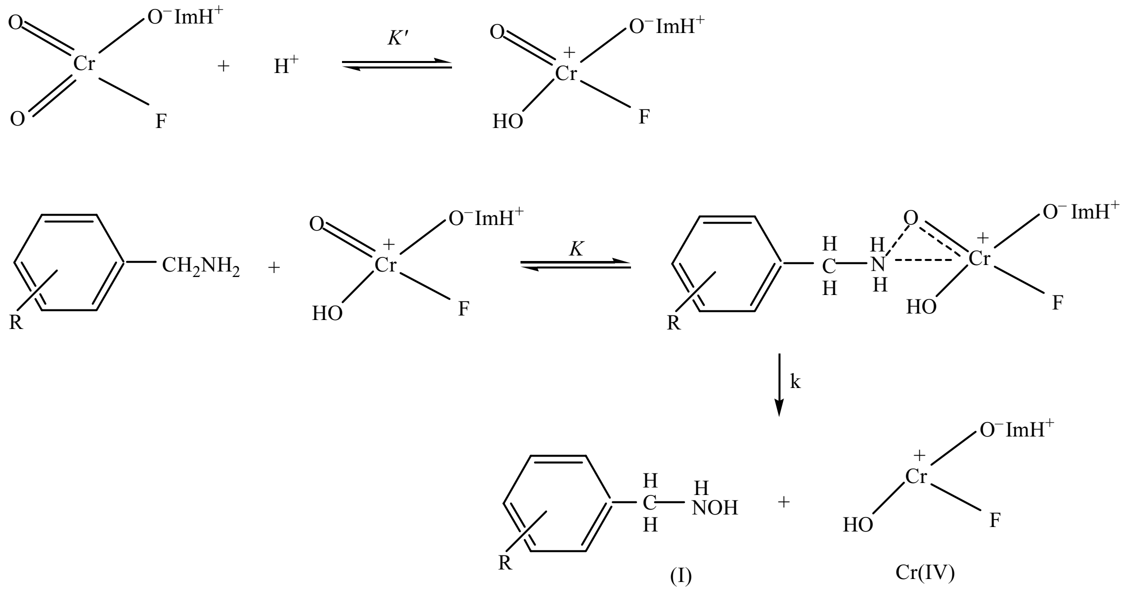


Figure 5 FT-IR spectra of the reaction mixture with lapse of time.



Scheme 1

the rate is independent of [substrate] [15]. In nonaqueous media, Cr(VI) reagents complex 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 a zero-order dependence on [substrate] [5,8,25]. Based on the foregoing results and discussions, a plausible mechanism (see Scheme 1) has been proposed for the IFC oxidation of benzylamines in benzene/2-methylpropan-2-ol mixtures.

The compound (I) undergoes further reactions to give the products [9,14]. The above-mentioned mechanism leads to, under the condition that the formation constant (K) of the oxidant–substrate complex is large, the following rate law:

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

$$[\mathrm{IFCH}^+ - \mathrm{Sub}] = K\,[\mathrm{IFCH}^+]\,[\mathrm{Sub}]/1 + K\,[\mathrm{Sub}]$$

$$\text{If } K\,[\mathrm{Sub}] \gg 1$$

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

$$\text{Therefore, } -\mathrm{d}[\mathrm{IFC}]/\mathrm{d}t = k\,K'\,[\mathrm{IFC}]\,[\mathrm{H}^+]$$

The above scheme accounts for the observed orders.

CONCLUSION

The Cr(VI) oxidation of benzylamines is first order with respect to [IFC] and [acid] and zero order in [substrate]. The rate of the reaction was found to increase with the increase in mole fraction of benzene in the mixture. The validity of the isokinetic relationship and various linear free-energy relationships has been tested and discussed. Both the electron-donating and electron-withdrawing substituents facilitate the rate of oxidation and correlation with Hammett substituents constants yielded a concave upward curve. Solvent variation studies indicated that the rate of oxidation is relatively faster in non-HBD solvent-rich mixtures than in HBD solvent-rich mixtures. The correlation of the experimental data with solvent parameters suggested that solvent H-bonding plays a major role in governing the reactivity.

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