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Mechanistic Study of the Oxidation of Substituted Benzylamines by *N*-Bromoacetamide

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The oxidation of ortho-, meta-, and para-substituted benzylamines by *N*-bromoacetamide (NBA), to the corresponding benzaldehydes, is first order with respect to NBA and the amine. The pH dependence of the reaction rate suggests that the unprotonated benzylamine is the reductant. There is no effect of added acetamide. NBA itself has been postulated as the reactive oxidizing species. The oxidation of benzylamine-α,α-d_2 exhibited a substantial primary kinetic isotope effect (k_H/k_D=5.81). The rates of the oxidation of the meta- and para-substituted benzylamines were separately correlated in Taft's and Swain's dual substituent parameter equations. For the para-substituted compounds, the best correlation is obtained with σ_I and σ_R^+ values, while meta-substituted compounds correlated best with σ_I and σ_R° values. The reaction constants have negative values. The oxidation rates of the ortho-substituted compounds yield excellent correlation in a triparametric equation involving Taft's σ_I and σ_R^+ values and Charton's steric parameter, *V*. A mechanism involving transfer of a hydride ion from the amine to NBA, in the rate-determining step has been proposed.

We have been interested in the mechanisms of the oxidation of organic compounds by *N*-haloamides.[1-3] The oxidation of benzylamine also presents interesting possibilities. It is known to yield a large number of products including those resulting from condensation of intermediate products of the oxidation with the parent amine.[4] In addition benzamide, benzaldehyde, and benzoic acid are also formed.[4] Wei and Stewart have studied the oxidation of some substituted benzylamines with permanganate ion.[5] We now report the oxidation of a series of ortho-, meta-, and para-substituted benzylamines by *N*-bromoacetamide (NBA) in buffered alkaline solutions. Attempts have been made to correlate structure and reactivity in this reaction.

Experimental

General. Benzylamine-α,α-d_2 ($PhCD_2NH_2$) was prepared by the reduction of benzonitrile by lithium aluminium deuteride.[6] *m*-Amino- and *o*-nitrobenzylamines were prepared by the reported methods.[7,8] The other amines were commercially available. Borate buffers were used to keep the pH constant. NBA and its aqueous solutions were stored in dark brown bottles. The aqueous solutions of the amines were prepared from the freshly distilled amines and doubly distilled water. The concentrations of the amines were determined by titration with standard hydrochloric acid, using Methyl Red as an indicator.

Product Analysis. Ammonia was obtained in 93% yield by the oxidation of benzylamine at pH 10.6 as shown by partial distillation of the aqueous reaction mixture and titration of the distillate with standard acid. Benzaldehyde was isolated as the 2,4-dinitrophenylhydrazone (DNP).

Freshly distilled benzylamine (5.35 g, 0.05 mol) and NBA (1.4 g, 0.01 mol) were made up to 100 ml in water at pH 10.6. The reaction mixture was allowed to stand for ca. 8 h to ensure completion of the reaction. It was treated with an excess (250 ml) of a saturated solution of 2,4-dinitrophenylhydrazine in 2 M HCl (1 M=1 mol dm^{-3}) and kept overnight in a refrigerator. The precipitated DNP was filtered off, dried, weighed, recrystallized, and weighed again. The DNP was identical (mp and mixture mp) with an authentic sample of DNP of benzaldehyde. The yield of the DNP before and after recrystallization were 2.70 g (94%) and 2.52% (88%) respectively. In similar experiments with the other amines, the yields of DNP, after recrystallization, were 84—95%.

Kinetic Measurements. The reactions were studied under pseudo-first-order conditions by keeping a large excess of the amine over NBA. The reaction were carried out in flasks blackened from the outside to prevent any photochemical reaction. Preliminary experiments showed that the reaction is not sensitive to ionic strength (0.05—1.0 M) and hence no attempt was made to keep the ionic strength constant. The reactions were followed at pH 10.6, were the amines are almost completely unprotonated. Corrections were applied to the rate constants for the partial ionization of the amines. The reactions were followed iodometrically for up to 70% of the extent of the reactions. The pseudo-first-order rate constant, k_1, was determined from the linear plots of log[NBA] vs. time. The second order rate constant, k_2, was obtained from the relation $k_2=k_1/[\text{benzylamine}]$. Duplicate kinetic runs showed that the rates were reproducible to within ±3%.

Results

The rate laws and other data were obtained for all the compounds investigated. Since results are similar only representative data are reproduced here.

The oxidation of the amines by NBA results in the formation of corresponding benzaldehydes and ammonia (Eq. 1).

$$PhCH_2NH_2 + MeCONHBr + H_2O \rightarrow PhCHO + NH_3 + HBr + MeCONH_2 \qquad (1)$$

Rate Laws. The reactions are found to be of first order with respect to NBA and the amine (Table 1). The rate of oxidation of benzylamine increases with increasing pH but the dependence is not linear and the rate reaches a limiting value of $k_2=3.40\times10^{-2}\ M^{-1}\ s^{-1}$ at pH 11.3. The limiting rate is represented by k'. A plot of the rate constant vs. pH produces a typical ionization curve (Fig. 1).

Table 1. Rate Constants of the Oxidation of Benzylamine by NBA at 298 K, pH 10.6

$[PhCH_2NH_2]$	$10^3[NBA]$	10^4k_1
M	M	s^{-1}
0.05	5.0	2.00
0.10	5.0	4.21
0.20	5.0	8.52
0.30	5.0	13.0
0.40	5.0	16.4
0.50	5.0	21.0
0.20	2.0	8.72
0.20	3.5	8.63
0.20	7.5	8.25
0.20	10.0	8.60
0.20	15.0	8.52

Table 2. Kinetic Isotope Effect in the Oxidation of Benzylamine by NBA([NBA] 0.005 M, pH 10.6, Temp 298 K)

[amine]	Type	10^5k_1
M		s^{-1}
0.05	$^1H_2$	20.0
0.10	$^1H_2$	42.1
0.20	$^1H_2$	85.2
0.05	$^2H_2$	3.65
0.10	$^2H_2$	7.22
0.20	$^2H_2$	14.1

$10^4k_H=41.6\pm0.1\ M^{-1}\ s^{-1}$
$10^4k_D=7.14\pm0.09\ M^{-1}\ s^{-1}$
$k_H/k_D=5.81\pm0.06$
k_H and $k_D=k_1/[\text{amine}]$

Table 3. Effect of Acetamide on the Oxidation of Benzylamine by NBA, ([NBA]=0.005 M, [amine]=0.10 M, pH=10.6, Temp 298 K)

$10^2[\text{acetamide}]/M$	0	2.5	4.0	5.0	7.5	10.0
$10^4k_1/s^{-1}$	4.21	4.12	4.30	4.40	4.30	4.12

The curve in Fig. 1 indicates that neutral benzylamine is the reactive reducing species. In that case, it has been shown[5] that a plot of $\log[k_2/(k'-k_2)]$ vs. pH, where k' is the rate maxima, should be linear with a unit slope, whose intercept is the pK_{BH^+} of the benzylammonium ion. Figure 2 presents the plot (r=0.9981, slope=1.02±0.02), the pK_{BH^+} of benzylamine is 9.45±0.02, close to the literature value of 9.34.[9]

Kinetic Isotope Effect. To ascertain the importance of the cleavage of α-C-H bond in the rate-determining step, the oxidation of $PhCD_2NH_2$, was studied. The results showed the presence of a substantial primary kinetic isotope effect (Table 2).

Effect of Acetamide. The rate of the reaction is not affected by the addition of acetamide (Table 3).

Effect of Substituents. The rates of the oxidation of benzylamine, nine para-substituted, ten meta-substituted, and ten ortho-substituted benzylamines were determined at different temperatures and the activation parameters were evaluated (Table 4).

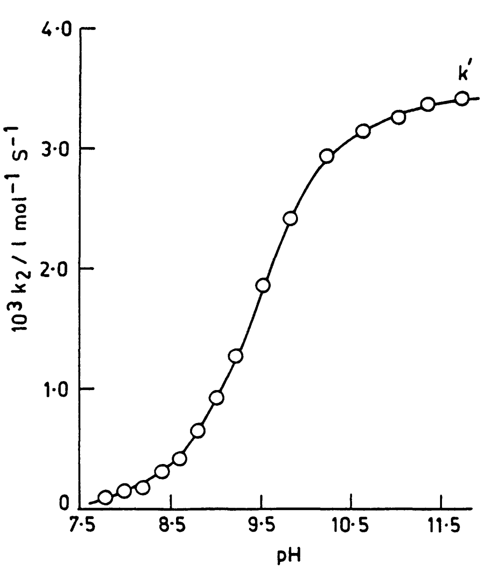


Fig. 1. Dependence of the rate of the oxidation of benzylamine on pH; temp 293 K.

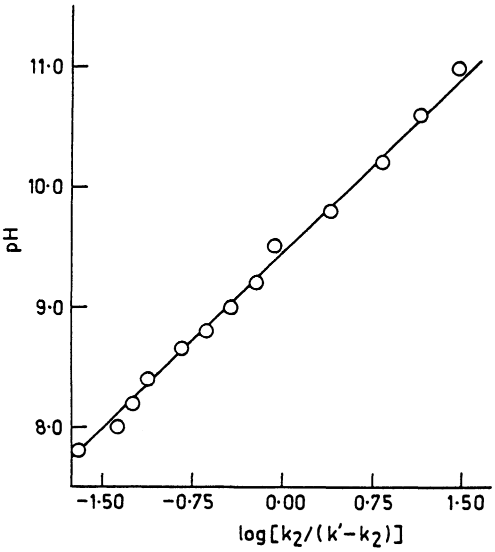


Fig. 2. Plot of pH against the function $\log[k_2/(k'-k_2)]$ for the oxidation of benzylamine by NBA.

Discussion

The linear correlation between $\log k_2$ at 288 K and 308 K (r=0.9977, slope=0.8574) for the oxidation of the 30 amines shows that all the amines are oxidized by the same mechanism.[10] The value of isokinetic temperature is 529 K.

N-Haloamides are known to hydrolyzed and/or disproportionate in aqueous solutions to give hypohalous acids,[1-3] and hypohalous acids have been proposed as the reactive species in many reactions [1-3,11] of *N*-haloamides. However, no effect of the parent amide on the reaction rate rules out the involvement of such preequilibria in the oxidation process and NBA itself seems to be the oxidizing species in the oxidation of benzylamines.

Correlation Analysis of the Reactivity. (i) Para- and Meta-Substituted Benzylamines: Since the rates of oxidation of the mono-substituted benzylamines failed to show satisfactory correlation with any single substituent parameter equation, the rates were subjected to analysis by Taft's[12)] and Swain's[13)] dual substituent parameter (DSP) equations. The rates of oxidation of the meta- and para-substituted benzylamines were separately correlated with σ_I and the four different σ_R substituent constants in Taft's equation[12)] and with the field and resonance substituent constants of Swain et al.[13)] The results are summarized in Table 5. Both the meta- and para-series of substituted benzylamines meet the minimal basic requirements of substituents for the analysis by DSP equations.[14)]

The results show that the rates of para-substituted amines show excellent correlation with σ_I and σ_R^+ values. The correlations with the other three σ_R values and in Swain's equation are relative poor. We have used the standard deviation (SD), coefficient of multiple correlation (R), and f as the measure of the goodness of fit. f has been defined by Dayal et al.[12)] as

Table 4. Rate Constants and the Activation Parameters of the Oxidation of Substituted Benzylamines by NBA

Subs.	$10^5\,k_2/\mathrm{M^{-1}\,s^{-1}}$					$\Delta H^{\neq}$	$\Delta S^{\neq}$
	288 K	293 K	298 K	303 K	308 K	$\mathrm{kJ\,mol^{-1}}$	$\mathrm{J\,mol^{-1}}\,k^{-1}$
H	200	316	421	688	950	54.9±1.6	−105±5.4
p-Me	660	976	1370	2200	2830	52.4±1.5	−104±5.2
p-OMe	5630	8330	11000	17100	21800	48.2±1.5	−101±5.0
p-F	350	548	712	1150	1670	54.5±1.8	−102±6.0
p-Cl	170	271	365	621	875	58.0±1.8	−96±6.1
p-Br	146	230	311	527	744	57.7±1.8	−98±5.9
p-NO_2	13.2	22.5	33.3	58.0	85.4	66.5±1.4	−87±4.6
p-CF_3	35.5	59.0	77.6	133	192	59.2±2.1	−105±7.0
p-COOMe	40.1	66.2	95.7	155	220	60.3±1.1	−100±3.8
p-NHCOMe	3540	5270	6690	10900	14600	50.1±1.9	−98±6.5
m-Me	304	480	635	1070	1490	56.2±1.9	−97±6.3
m-OMe	194	300	392	663	936	55.6±2.0	−103±6.8
m-F	55.0	83.4	105	171	233	50.6±2.0	−131±6.7
m-Cl	56.7	85.5	110	179	242	51.2±1.8	−129±6.1
m-I	69.3	107	139	222	305	52.0±1.5	−124±5.1
m-NO_2	11.5	16.8	21.6	32.0	42.8	45.8±1.1	−161±3.8
m-CF_3	26.5	41.3	60.6	81.2	113	50.3±1.3	−138±4.3
m-COOMe	41.2	61.0	80.3	132	183	52.8±1.8	−126±6.1
m-NH_2	319	496	683	1100	1580	56.4±1.3	−96±4.2
m-NHCOMe	142	222	298	474	664	54.2±1.4	−111±4.5
o-Me	1610	2430	3050	4900	6340	48.3±1.9	−111±6.5
o-OMe	2610	3850	4950	7610	9840	46.7±1.5	−112±4.9
o-F	231	351	462	782	1070	54.5±2.0	−106±6.7
o-Cl	262	413	555	920	1240	55.2±1.7	−102±5.8
o-Br	329	520	668	1080	1450	52.1±1.2	−111±4.1
o-I	534	786	1010	1650	2300	51.5±0.8	−109±2.8
o-NO_2	281	432	582	940	1260	53.2±1.5	−108±5.0
o-CF_3	240	368	495	798	1100	53.8±1.4	−108±4.8
o-COOMe	1600	2270	2910	4530	5950	46.4±1.6	−118±5.3
o-NHCOMe	4240	6100	7470	11500	15300	44.7±1.7	−116±5.9

Table 5. Correlation of the Rates of Oxidation of Substituted Benzylamines by NBA with Dual Substituent Parameters[a)]

Substituent constant	Para-substituted						Meta-substituted					
	ρ_I	ρ_R	R	SD	f	n	ρ_I	ρ_R	R	SD	f	n
σ_I, σ_R°	−1.57	−3.16	0.9364	0.323	0.42	10	−1.76	−1.02	0.9951	0.053	0.09	11
σ_I, σ_R^{BA}	−1.62	−2.62	0.9617	0.252	0.33	10	−1.76	−0.70	0.9849	0.093	0.15	11
σ_I, σ_R^-	−1.17	−1.81	0.9136	0.351	0.72	9[b)]	−1.67	−0.70	0.9890	0.084	0.13	10[b)]
σ_I, σ_R^+	−1.43	−1.73	0.9984	0.053	0.07	10	−1.71	−0.38	0.9746	0.121	0.20	11
Swain et al.[c)]	−0.36	−0.89	0.9914	0.120	0.16	10	−0.93	−0.30	0.9784	0.112	0.18	11

a) Temp 298 K, R=coefficient of multiple correlation; SD=standard deviation; f=SD/root mean squares of log k/k_0; n=No. of data points; σ_I and σ_R values are from Ref. 12. b) Data of NHCOMe substituted compounds not considered, no σ_R^- value is available. c) Field and resonance constants are from Ref. 13.

f=SD/RMS, where RMS is the root mean square of the data points (here log k/k_0). The comparison of f values shows that f is smaller for $\sigma_R{}^+$ scale than those for other scales by factors of ca. 3 to ca. 10. Therefore, it is apparent that the rates of the oxidation para-substituted benzylamines by NBA correlate best with σ_I and $\sigma_R{}^+$.

The rates of meta-substituted benzylamines show excellent correlation with σ_I and $\sigma_R{}^\circ$, though the discriminating factor for the precision of fit with the other σ_R scales or with Swain's equation is not as sharp as in the case of para-substituted compounds. The comparison of f values shows that f is smaller for $\sigma_R{}^\circ$ scale than those for other scales by factors of ca. 1.5 to ca. 2.5. This agrees with the observation of Ehrenson, et al.[15] that the correlation of meta-substituted compounds is generally best with $s_R{}^\circ$ scale and meta-substituted compounds are less discriminating.

The reaction constants and the statistical data at different temperature are given in Table 6. The values of λ^p (ca. 1.24) showed that the oxidation of para-substituted benzylamines is more susceptible to the resonance effect than to the field effect. The selectivity of the reaction is decreased at higher temperature, but this decreases is of similar order for both the field and resonance effects resulting in the almost constant value of λ^p at different temperature.

In the oxidation of the meta-substituted compounds, the value of λ^m is ca. 0.56 indicating greater importance of the field effect. In the case meta-substituted compounds there is a small increase in the magnitude of the reaction constants with an increase in the temperature but this increase is of similar order for both the effects, reflected in the almost constant value of λ^m at different temperatures, the ratio of λ^m/λ^p is ca. 0.45.

(ii) Ortho-Substituted Benzylamines. It was found that the rates of oxidation of ortho-substituted benzylamines failed to yield any significant correlation with either Taft's polar or steric substituent constants.[16] The rates were, therefore, analyzed using Charton's method.[17] The rates were correlated using Eqs. 2 and 3, where σ_I, σ_R, and V are field, resonance and steric substituent constants and the values used were those compiled by Aslam et al.[18] h is the intercept term. α, β, and ϕ represent the susceptibility of the reaction to field, resonance, and steric effects respectively.

Table 6. Temperature Dependence of the Reaction Constants

Temp / K	ρ_I	ρ_R[a)]	λ[b)]	R	SD	f
			Para-substituted			
288	−1.49	−1.80	1.21	0.9987	0.050	0.06
293	−1.43	−1.76	1.23	0.9984	0.052	0.07
298	−1.43	−1.73	1.21	0.9984	0.053	0.07
303	−1.39	−1.71	1.23	0.9983	0.053	0.07
308	−1.32	−1.68	1.27	0.9985	0.048	0.06
			Meta-substituted			
288	−1.69	−1.97	0.57	0.9968	0.041	0.07
293	−1.74	−0.99	0.57	0.9965	0.044	0.07
298	−1.76	−1.02	0.58	0.9951	0.058	0.09
303	−1.82	−1.01	0.55	0.9970	0.043	0.07
308	−1.84	−1.03	0.56	0.9975	0.040	0.06

a) ρ_R is $\rho_R{}^+$ and $\rho_R{}^\circ$ for the para- and meta-substituted compounds respectively. b) $\lambda=\rho_R/\rho_I$.

The results of correlation analysis in the terms of Eq. 2 are given in Eq. 4.

$$\log k_{\text{ortho}} = \alpha\,\sigma_I + \beta\,\sigma_R + h \qquad (2)$$

$$\log k_{\text{ortho}} = \alpha\,\sigma_I + \beta\,\sigma_R + \phi V + h \qquad (3)$$

$$\log k_2 = -0.85\,\sigma_I - 0.66\,\sigma_R - 1.74 \qquad (4)$$

$$R = 0.5001;\ \text{SD} = 0.48;\ n = 11.$$

where n is number of data points.

In the multiple linear regression using Eq. 2, the coefficient of correlation is poor and the standard deviation is high. The lack of a significant correlation with Eq. 2 leads to the conclusion that electric effects alone are not sufficient to account for the ortho-substituent effect in this reaction.

The correlation in the terms of Eq. 3 was performed assuming both orthogonal and planar conformations for NO_2 and COOMe groups. It was observed that the correlation was better with planar conformation of both the groups. The results Eq. 5 showed that the correlation with Eq. 3 is also not good.

$$\log k_2 = -2.19\sigma_I - 2.15\sigma_R + 1.29\,V - 2.43 \qquad (5)$$

$$R = 0.9599;\ \text{SD} = 0.17;\ n = 11.$$

It may be recalled that the rates of oxidation of para- and meta-substituted benzylamines showed excellent correlation in Taft's[12] DSP equation with $\sigma_R{}^+$ and $\sigma_R{}^\circ$ constants respectively. Therefore, the rates of the oxidation of ortho-substituted benzylamines were correlated in triparametric equations using Taft's σ_I, $\sigma_R{}^+/\sigma_R{}^\circ$ and Charton's steric parameters. The results showed that excellent correlations were obtained with Taft's σ_I, $\sigma_R{}^+$, and Charton's V values. The reaction constants and the statistical data are recorded in Table 7. The series of ortho-substituted benzylamines also meet the basic minimal requirements for the analysis by Taft's equation.[12]

The behavior of o-NO_2 and o-COOMe is consistent

Table 7. Temperature Dependence of the Reaction Constants of the Oxidation of Ortho-Substituted Benzylamines by NBA

Temp / K	ρ_I	$\rho_R{}^+$	ϕ	R	SD	p_S	p_R
288	−1.81	−1.18	1.08	0.9988	0.028	39.5	26.5
293	−1.77	−1.15	1.04	0.9990	0.025	39.4	26.3
298	−1.72	−1.12	1.02	0.9987	0.030	39.4	26.4
303	−1.69	−1.09	0.99	0.9989	0.025	39.2	26.3
308	−1.64	−1.07	0.96	0.9988	0.026	39.5	26.2

with their planar conformation.

The significance of the correlation, tested by the F-test,[19] is >99.9%. Similarly the confidence level for the significance of σ_I, σ_R^+, and V terms, obtained by the Student's t-test,[19] is > 99.9%. This indicates the operation of significant field, resonance, and steric effects in the reaction.

To test the significance of the three substituent constants, multiple linear regression analyses were carried out with Taft's σ_I and σ_R^+, Taft's σ_I and V, and with σ_R^+ and V. The absence of significant correlations (Eqs. 6—8) showed that all the three σ_I, σ_R^+, and V substituent constants are significant.

$$\log k_2 = -0.79\sigma_I - 0.60\sigma_R^+ - 1.84 \quad (6)$$

$$R = 0.6518;\ SD = 0.42;\ n = 11$$

$$\log k_2 = -1.39\sigma_I + 0.46V - 1.78 \quad (7)$$

$$R = 0.5731;\ SD = 0.45;\ n = 11$$

$$\log k_2 = -0.97\sigma_R^+ + 0.58V - 2.61 \quad (8)$$

$$R = 0.7366;\ SD = 0.37;\ n = 11$$

There is no significant colinearity between Taft's σ_I and V, σ_R^+ and V, and between Taft's σ_I and σ_R^+ (r= 0.4694, 0.3029, and 0.1076) for the eleven substituents.

The regression coefficients of σ_I and σ_R^+ terms are negative indicating that electron-releasing groups accelerate the reaction. The positive regression coefficient for the steric term indicates that the reaction is subject to steric acceleration by the ortho-substituents. The contribution of the resonance effect[17] to the total polar effect of the ortho-substituents was calculated using Eq. 9.

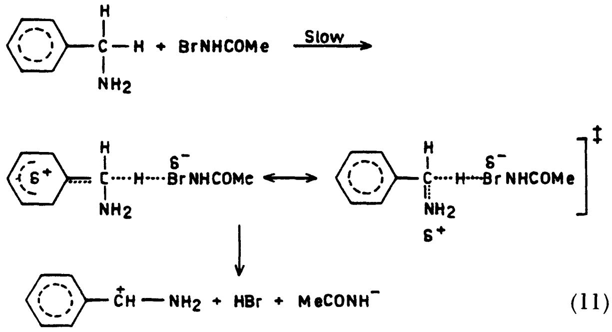
$$p_R = \frac{100 \times |\rho_R^+|}{|\rho_I| + |\rho_R^+|} \quad (9)$$

The contribution of steric parameter[17] to the total effect of the substituents, p_S, was determined using Eq. 10.

$$p_S = \frac{|\phi| \times 100}{|\rho_I| + |\rho_R^+| + |\phi|} \quad (10)$$

The values of p_R and p_S are also listed in Table 7. The values of p_R is ca. 39%. The value of p_R for the para-substituted compounds in ca. 55%. This shows that the balance of field and resonance effect is different for ortho- and para-positions, resonance effects being less pronounced in the former case. This may be due to the twisting away of the aminomethyl group from the plane of the benzene ring. The value of p_S shows that there is considerable steric effect in this reaction.

Mechanism. The kinetics are consistent with a mechanism in which as molecule each of the amine and NBA participate in the rate-determining step. The observed kinetic isotope effect confirms the rupture of the α-C-H bond in the rate-determining step. The large negative polar reaction constants and the correlation of the rates of para- and ortho-substituted benzylamines with σ_R^+ point to a transition state in which there is a strong resonance interaction between the substituent and a developing positive charge. This suggests the transfer of a hydride ion from the methylene group to the oxidant. There is no doubt that the amino group strongly activates the adjacent methylene and this supports the idea of hydride transfer. Thus the following mechanism may be proposed Eqs. 11—13.



(11)

$$Ph\overset{+}{C}HNH_2 + H_2O \xrightarrow{Fast} PhCHO + NH_4^+ \quad (12)$$

$$MeCONH^- + H^+ \xrightarrow{Fast} MeCONH_2 \quad (13)$$

The steric acceleration of the reaction may be explained on the basis of high ground state energy of the sterically crowded amines. Since the crowding is relieved in the product aldehyde as well as the transition state leading to it, the transition state energy of the crowded and uncrowded amines do not differ much and steric acceleration, therefore, result.

It is of interest the compare the oxidations of benzylamine by permanganate ion[5] and NBA. The rates of oxidation of 8 (out of 11 studied) meta- and para-substituted benzylamines by permanganate[5] correlate with σ^+ values, the reaction constant, ρ, being −0.28. The small value of ρ suggested the possibility of a one-electron oxidation. In the oxidation by NBA, the rates of 30 substituted benzylamine exhibited large negative polar reaction constants. A strong resonance interaction between the substituent and a developing positive charge, in the transition state, is also indicated. Hence a one-electron oxidation can be excluded.

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