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Kinetics and mechanism of the oxidation of substituted benzylamines by cetyltrimethylammonium permanganate

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Abstract. Oxidation of meta- and para-substituted benzylamines by cetyltrimethylammonium permanganate (CTAP) to the corresponding aldimines is first order with respect to both the amine and CTAP. Oxidation of deuteriated benzylamine ($PhCD_2NH_2$) exhibited the presence of a substantial kinetic isotope effect (k_H/k_D = 5·60 at 293 K). This confirmed the cleavage of an *a*-C–H bond in the rate-determining step. Correlation analyses of the rates of oxidation of 19 monosubstituted benzylamines were performed with various single and multiparametric equations. The rates of the oxidation showed excellent correlations in terms of Yukawa–Tsuno and Brown's equations. The polar reaction constants are negative. The oxidation exhibited an extensive cross-conjugation, in the transition state, between the electron-donating substituents and the reaction centre. A mechanism involving a hydride-ion transfer from the amine to CTAP in the rate-determining step has been proposed.

Keywords. Substituted benzylamines; cetyltrimethylammonium permanganate; hydride-ion transfer.

1. Introduction

Cetyltrimethylammonium permanganate (CTAP) has been reported as a synthetic reagent for the oxidation of alcohols to carbonyl compounds[1] and for the regeneration of carbonyl compounds from their oximes and 2,4-dinitrophenylhydrazones.[2] It seems that there are no reports about the oxidation of aromatic amines by CTAP. However, the kinetics of the oxidation of aromatic amines by many reagents have been studied, e.g. by permanganate,[3] N-chlorosuccinimide (NCS),[4] N-bromoacetamide (NBA),[5] N-chloroacetanilide,[6] acid bromate[7] and periodate[8] etc. 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.[9] In addition, benzamide, benzaldehyde and benzoic acid are also formed.[9] In this article, the kinetics of oxidation of nineteen monosubstituted benzylamines by CTAP in dichloromethane as a solvent are being reported. Attempts have been made to correlate rate and structure in this reaction. Suitable mechanism has been proposed.

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2. Experimental

2.1 *Materials*

CTAP was prepared by the reported method[1] and its purity was checked by an iodometric method and melting point determination. [1,1-$^2H_2$]Benzylamine was prepared by the reduction of phenyl cyanide with lithium aluminium deuteride.[10] Its isotopic purity, determined by the ^{1}H NMR spectra, was $93 \pm 2\%$. *m*-Aminobenzylamine was prepared by the reported method.[11] The other amines were commercial products and were purified by distillation.

2.2 *Product analysis*

The oxidation of benzylamines leads to the formation of the corresponding aldimines. The quantitative product analysis was carried out under kinetic conditions. In a typical experiment, benzylamine (0·1 mol) and CTAP (0·01 mol) were made up to 50 ml with CH_2Cl_2 and kept in the dark for $\approx$ 12 h to ensure completion of the reaction. The amount of aldimine formed was then determined by the reported 2,4-dinitrophenylhydrazine method.[12] As per this method, the aldimine is hydrolysed to the aldehyde and then isolated as 2,4-dinitrophenylhydrazone (DNP), vacuum dried, weighed, recrystallized from ethanol and weighed again. The yields of DNP before and after recrystallization were 4·17 g (97%) and 3·53 g (82%) respectively. The DNP was found identical (m.p. and mixed m.p.) with the DNP of benzaldehyde. In similar experiments, with the other substituted benzylamines the yields of DNP, after recrystallization, were in the range of 74–85%.

2.3 *Kinetic measurements*

The reactions were studied under pseudo-first-order conditions by keeping an excess ($\times$ 20 or greater) of the amine over CTAP. The solvent was dichloromethane. The reactions were studied at constant temperature ($\pm$ 0·1 K) and were followed by monitoring the decrease in the [CTAP] spectrophotometrically at 529 nm for up to 80% reaction. Beer's law was found to be valid within the concentration range used in our experiments. Pseudo-first-order rate constants, k_{obs}, were evaluated from linear plots ($c^2 > 0{\cdot}995$) of log [CTAP] against time. CTAP is known to undergo auto-decomposition in solution. The observed rate constants were therefore corrected by taking into account the rate of auto-decomposition. Duplicate kinetic runs showed that the rates were reproducible to within $\pm$ 4%. We have used coefficient of determination (C^2 or c^2), standard deviation (s.d.) and Exner's[13] parameter (y) as the measures of goodness of fit in correlation analysis.

3. Results

Oxidation of benzylamines by CTAP results in the formation of corresponding aldimines. Analyses of products indicate the following overall reaction,

$$3\ ArCH_2NH_2 + 2\ MnO_4^- \rightarrow 3\ ArCH{=}NH + 3\ H_2O + MnO_2 + MnO_3^{-2}. \qquad (1)$$

The reactions were found to be first-order with respect to CTAP. Individual kinetic runs were strictly first order w.r.t. CTAP. Further, the pseudo-first-order rate constants, k_{obs},

do not depend on the initial concentration of CTAP. The reaction rate increases linearly with an increase in the concentration of the amine. Thus the reaction is first order with respect to amines also.

Oxidation of benzylamine, in an atmosphere of nitrogen, failed to induce the polymerization of acrylonitrile. Further, the addition of acrylonitrile had no effect on the rate of oxidation.

3.1 *Effect of substituent*

The rates of the oxidation of benzylamine and eighteen monosubstituted benzylamines were determined at different temperatures and the activation parameters were calculated (table 1).

3.2 *Kinetic isotope effect*

To ascertain the importance of the cleavage of the *a*-C–H bond in the rate-determining step, the oxidation of [1,1-$^2H_2$]benzylamine ($PhCD_2NH_2$) by CTAP was studied. The results (table 2) showed the presence of a substantial primary kinetic isotope effect (k_H/k_D = 5·77 at 293 K).

4. Discussion

The isokinetic correlation between enthalpies and entropies of activation of the oxidation of the nineteen amines is not very good (c^2 = 0·9508, s.d. = 2·94). However, according to

Table 1. Rate constants for the oxidation of substituted benzylamines by CTAP and the activation parameters.

	$10^4\ k_2$ (dm^3 mol^{-1} s^{-1}) at temp. (K)						
Subst.	293	303	313	323	ΔH^* (kJ mol^{-1})	ΔS^* (J mol^{-1} K^{-1})	ΔG^* (kJ mol^{-1})
p-NO_2	0·51	1·13	2·84	6·13	63·4 ± 1·3	–111 ± 4	96·5 ± 1·0
p-CF_3	0·54	1·28	3·50	8·06	69·2 ± 1·1	–91 ± 3	96·2 ± 1·0
p-CO_2Me	0·89	2·11	5·64	12·2	67·0 ± 1·1	–94 ± 2	95·0 ± 1·0
p-Br	4·95	10·0	23·9	49·1	58·4 ± 1·0	–110 ± 3	90·9 ± 1·2
p-Cl	6·08	13·3	29·2	58·0	56·9 ± 0·6	–113 ± 2	90·4 ± 0·5
H	8·52	19·0	44·6	93·2	60·4 ± 0·7	–97 ± 2	89·5 ± 0·6
p-F	14·0	28·7	62·0	109	52·0 ± 1·1	–122 ± 3	88·4 ± 0·9
p-Me	42·1	83·5	172	332	51·9 ± 0·7	–114 ± 2	86·7 ± 0·7
p-OMe	503	848	1360	1990	33·7 ± 0·7	–155 ± 2	79·8 ± 0·6
p-NH_2	13100	18400	22400	27400	16·5 ± 0·6	–187 ± 2	71·9 ± 0·7
m-NO_2	0·43	1·02	2·68	6·10	67·6 ± 1·1	–98 ± 3	95·8 ± 1·0
m-CF_3	0·77	1·83	5·02	11·3	68·6 ± 1·2	–90 ± 4	96·5 ± 0·5
m-CO_2Me	1·68	3·83	9·45	20·2	63·3 ± 1·0	–102 ± 3	93·5 ± 0·9
m-Cl	1·44	3·32	8·51	18·7	65·4 ± 0·8	–96 ± 2	93·8 ± 0·6
m-I	2·05	4·78	11·5	24·5	62·9 ± 0·6	–101 ± 2	93·0 ± 0·5
m-F	1·86	4·07	10·1	23·0	63·9 ± 1·2	–99 ± 2	93·3 ± 1·0
m-OMe	7·54	16·5	38·2	77·8	59·2 ± 0·8	–103 ± 2	89·8 ± 0·6
m-Me	11·6	25·8	59·7	124	60·0 ± 0·6	–97 ± 2	88·7 ± 0·5
m-NH_2	18·5	39·7	88·2	184	58·0 ± 0·7	–100 ± 2	87·6 ± 0·6

Table 2. Kinetic isotope effect in the oxidation of benzylamine by CTAP.

Compound	$10^4 k_2$ (dm^3 mol^{-1} s^{-1}) at temp. (K)				ΔH^* (kJ mol^{-1})	ΔS^* (J mol^{-1} K^{-1})	ΔG^* (kJ mol^{-1})
	293	303	313	323			
$PhCH_2NH_2$	8·52	19·0	44·6	93·2	60·4 ± 0·7	–97 ± 2	89·5 ± 0·6
$PhCD_2NH_2$	1·48	3·38	8·14	17·4	62·5 ± 0·8	–105 ± 2	93·8 ± 0·6
k_H/k_D	5·77	5·62	5·48	5·36			

Exner,[14] an isokinetic relationship between the calculated values of enthalpies and entropies of the reactions is often vitiated due to the errors inherent in their values. He devised an alternative procedure for the verification of isokinetic relationship. An Exner's plot[14] between log k_2 at 293 K and at 323 K is linear (c^2 = 0·9967, slope = 0·818 ± 0·011). The value of the isokinetic temperature is 601 ± 32 K. A linear isokinetic relationship is a necessary condition for the validity of linear free energy relationships. It also implies that all reactions so correlated follow similar mechanism.[14]

4.1 *Correlation analysis of reactivity*

Rate constants for the oxidation of the meta- and para-compounds were correlated in terms of the Hammett[15] equation but no significant correlation was obtained,

$$\log k_2 = -(2{\cdot}73 \pm 0{\cdot}24)\, s - 2{\cdot}15, \quad (3)$$
$$c^2 = 0{\cdot}9145;\ \text{s.d.} = 0{\cdot}42;\ n = 19;\ y = 0{\cdot}46;\ T = 323\ \text{K}.$$

The main points of deviation correspond to *p*-substituents capable of electron-donation by resonance, viz. methoxy and amino. Their rates are higher than those required by their Hammett's s values. This indicates that in the transition state of the reaction, there is an electron-deficient centre, which is stabilised by cross-conjugation with the electron-donating substituents at the *p*-position. Substituent effects in such systems can be described by the Yukawa–Tsuno[16] equation,

$$\log k_2 = r s^0 + rr\,(s^+ - s^0) + \log k_0. \quad (4)$$

Here s^0 is the normal substituent constant, which does not involve any additional *p*-electronic interaction between the substituent and the reaction centre, $(s^+ - s^0)$ is the resonance substituent constant measuring the capability for *p*-delocalization of *p*-electron donor substituent, and the parameter r is characteristic of the given reaction measuring the extent of resonance demand, i.e. the degree of resonance interaction between the aryl group and the reaction centre in the rate-determining transition state.

The correlations of rates of oxidation of *p*- and *m*-substituted benzylamines in terms of (4) are excellent (table 3) with the value of r ranging from –1·76 to –1·94 and the value of r being ≈ 1·1. The value of r indicates that the resonance demand is slightly more than that for the model reaction[17] for s^+ values, i.e. solvolysis of 2-aryl-2-chloropropanes for which the value of r is, by definition, 1·0. In view of this, an attempt was made to correlate the rates of the oxidation of *m*- and *p*-substituted amines with Brown's s^+ values. This correlation is very good and in fact, the significance of the two correlations is almost equal,

$$\log k_2 = -(1{\cdot}71 \pm 0{\cdot}01)\ s^+ - 2{\cdot}05, \quad (5)$$
$c^2 = 0{\cdot}9994$, s.d. = 0·02, $n = 19$, $y = 0{\cdot}02$, $T = 323$ K.

4.2 *Mechanism*

The absence of any effect of the radical scavenger on the reaction rate and the failure to induce polymerization of acrylonitrile, point against a one-electron oxidation, giving rise to free radicals.

The presence of a substantial kinetic isotope effect in the oxidation of [1,1-$^2H_2$]benzylamine confirmed the cleavage of the *a*-C–H bond in the rate-determining step. The large negative values of reaction constants and significant resonance interaction between the aryl group and the reaction centre in the rate-determining transition state suggest that the activated complex has considerable carbocationic character. Therefore, transfer of a hydride ion from the methylene group of the amine to CTAP in the rate-determining step is indicated. Formation of a benzylic carbocationic activated complex generally leads to higher magnitudes of reaction constants, e.g. in the bromination of styrene[18] in acetic acid at 298 K, the value of r and r is –4·61 and 1·25 respectively. The relatively lower magnitudes of the reaction constants in the present reaction may well be due to the presence of an electron-donor group ($-NH_2$) adjacent to the cationic carbon. The non-bonded pair of electron on nitrogen can delocalize the positive charge on the carbon and therefore, reduce the electronic demand of the reaction centre. In the acid-catalysed solvolysis of acetophenone acetals,[19] where electron-donating alkoxy and methyl groups are present adjacent to the cationic carbon, the values of r and r are –1·7 and 0·6 respectively. The mechanism depicted in scheme 1 accounts for the experimental

Table 3. Correlation of rate of oxidation of *m*- and *p*-substituted benzylamines by CTAP in terms of Yukawa–Tsuno equation[a].

Temp. (K)	r	r	c^2	s.d.	y
293	–1·94 ± 0·02	1·16 ± 0·02	0·9998	0·02	0·02
303	–1·90 ± 0·02	1·10 ± 0·02	0·9997	0·02	0·02
313	–1·81 ± 0·01	1·02 ± 0·01	0·9998	0·01	0·01
323	–1·76 ± 0·02	0·93 ± 0·02	0·9996	0·03	0·04

[a]No. of data points = 19

$$Ar{-}CH_2{-}NH_2 + MnO_4^- Q^+ \xrightarrow{\text{slow}}$$

$$[Ar\overset{+}{C}H{-}NH_2 \leftrightarrow Ar{-}CH{=}\overset{+}{N}H_2] + \underset{(Mn\ (V))}{HMnO_4^{-2}} + Q^+ \xrightarrow{\text{fast}} Ar{-}CH{=}NH + H^+$$

$$3\ Mn(V) \xrightarrow{\text{fast}} 2\ Mn(IV) + Mn(VII)$$

$Q = (Me_3C_{16}H_{33}N)^+$

Scheme 1.

results. The values of activation parameters support the proposed mechanism. The large negative entropy of activation indicate a rigid activated complex in the transition state. When two species come together to form a single activated complex, they lose the independence to move singly and there is a loss of entropy. Further, as the charge separation takes place in the transition state, the charged ends become highly solvated. This results in an immobilization of a large number of solvent molecules. This also results in a loss of entropy. The large enthalpies of activation indicates that the formation of activated complex involves a greater degree of the bond cleavage.

It is of interest to compare the results of this investigation with the earlier reports on the oxidation of benzylamine. In the permanganate[3] ion oxidation and Ru(III)-catalysed oxidation by acid bromate,[7] the reaction constants are $-0{\cdot}28$ and $0{\cdot}87$ respectively, indicating the possibility of one-electron oxidation. The oxidations by NCS[4] and NBA[5] exhibited large negative polar reaction constants and substantial primary kinetic isotope effects. The mechanism proposed for the oxidation by NBA, NCS and CTAP is essentially the same i.e. transfer of a hydride-ion from the amine to the oxidant resulting in the formation of a cationic species in the rate-determining step.

5. Conclusion

The oxidation of benzylamines by CTAP to the corresponding aldimines proceeds through the formation of a carbocationic activated complex in the rate-determining step. There is a considerable amount of cross-conjugation between the reaction centre and the electron-donating substituents in the transition state.

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References

1. Bhushan V, Rathore R and Chandrasekaran S 1984 *Synthesis* 431
2. Vanker P, Rathore R and Chandrasekaran S 1986 *J. Org. Chem.* **51** 3063
3. Wei M M and Stewart R 1966 *J. Am. Chem. Soc.* **88** 1974
4. Banerji K K 1988 *J. Chem. Soc. Perkin Trans. 2* 1015
5. Banerji K K 1988 *Bull. Chem. Soc. Jpn.* **61** 3717
6. Kumar A and Bhattacharjee G 1991 *J. Indian Chem. Soc.* **68** 523
7. Radhakrishnamurti P S and Sarangi L D 1982 *Indian J. Chem.* **A21** 132
8. Srivastava S P, Bhattacharjee G and Malik P 1990 *J. Indian Chem. Soc.* **67** 347
9. Shechter H, Rawaley S S and Tubis M 1964 *J. Am. Chem. Soc.* **86** 1701; Shechter H and Rawaley S S 1964 *J. Am. Chem. Soc.* **86** 1706
10. Halevi E A, Nussim M and Ron A 1963 *J. Chem. Soc.* 866
11. Kornblum N and Iffland C 1949 *J. Am. Chem. Soc.* **71** 2137
12. Freeman S 1953 *Anal. Chem.* **25** 1750
13. Exner O 1966 *Collect. Czech. Chem. Commun.* **31** 3222
14. Exner O 1973 *Prog. Phys. Org. Chem.* **10** 411
15. Hammett L P 1973 *Physical organic chemistry* (New York: Academic Press) p 411
16. Tsuno Y and Fujio M 1999 *Adv. Phys. Org. Chem.* **32** 267
17. Brown H C and Okamoto Y 1958 *J. Am. Chem. Soc.* **80** 4979
18. Ruasse M F, Aegile A and Dubois J E 1978 *J. Am. Chem. Soc.* **100** 7645
19. Toullec J and El-Allaoui M 1985 *J. Org. Chem.* **50** 4928