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Kinetics and mechanism of the oxidation of substituted benzylamines by oxo(salen)manganese (V) complexes

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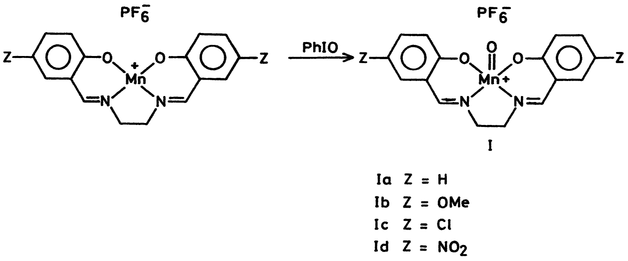
The oxidation of substituted benzylamines by oxo(salen) Mn(V) complexes, to the corresponding aldimine, proceeds through a hydride ion transfer from the amine to the oxidant.

Keywords: oxidation, benzylamine, oxo(salen)manganese (V), kinetics, mechanism, H_2salen (N,N'- bissalicylideneethylenediamine)

Schiff base complexes of transition metal ions have been receiving much attention as oxygen atom donors to organic compounds. Recently the mechanisms of the oxidation of sulfides,[7,8] benzaldehydes,[9] and alcohols[10,11] by oxo(salen)manganese (V) complexes were reported. There seems to be no report on the oxidation of amines. We report here the kinetics of the oxidation of some substituted benzylamines by oxo(salen)manganese(V) complexes(**Ia–Id**) in acetonitrile as the solvent. Mechanistic aspects are discussed.

Oxo (salen)manganese(V) complexes(Eqn (1)), were prepared by the reported methods.[7] Pseudo-first order conditions were attained by keeping a large excess (× 20 or greater) of the amines over the oxidant. The solvent was acetonitrile. The reactions were followed by monitoring the decrease in the concentration of the Mn(V) complex at 680 nm for up to 80% of the reaction. Duplicate kinetic runs showed that the rate constants were reproducible to within ±5%. The second order rate constant, k_2, was obtained from the relation: $k_2 = k_{obs}/[\text{amine}]$.

The oxidation of amines results in the formation of the corresponding aldimine. The overall reaction may be represented as Eqn (2).



$$ArCH_2NH_2 + (\text{salen})OMn(V) \rightarrow ArCH = NH + H_2O + (\text{salen})Mn(III) \quad (2)$$

The reaction is of first order with respect to Mn(V). Further, the pseudo-first-order rate constants do not depend on the initial concentration of Mn(V). The reaction rate increases linearly with an increase in the concentration of amine. The oxidation of deuteriated benzylamine by **Ia** exhibited a substantial kinetic isotope effect ($k_H/k_D = 5.21$ at 303 K).

An addition of pyridine N-oxide has no effect on the rate of the oxidation. The rates of oxidation the 19 amines by **Ia – Id** were determined at different temperatures and the activation parameters were calculated.

The rate constants for the oxidation of the meta- and para-substituted benzylamines were correlated in terms of the Hammett[27] equation but no significant correlation was obtained. The main deviating points correspond to *para*-substituents capable of electron-donation by resonance *viz.* methoxy, and amino. Their rates are higher than those required by their Hammett's σ 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 *para*-position. The substituent effects in such systems can be described by the Yukawa–Tsuno[28] Eqn (4).

$$\log k_2 = \rho\sigma^0 + \rho r\,(\sigma^+ - \sigma^0) + \log k_0 \quad (4)$$

Here σ^0 is the normal substituent constant, which does not involve any additional π-electronic interaction between the substituent and the reaction centre, ρ is the corresponding reaction constant, $(\sigma^+ - \sigma^0)$ is the resonance substituent constant measuring the capability for π-delocalisation of a π-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 correlation of the rate of oxidation of the *para*- and *meta*-substituted benzylamines in terms of Eqn (4) is excellent. The value of reaction constant, ρ, ranges from – 1.76 to –1.94 and the value of *r* is *ca.*1.1. Therefore, an attempt was made to correlate the rates of the oxidation of *meta*- and *para*-substituted benzylamines with Brown's σ^+ values. The correlation is very good. In fact, the significance of the two correlations is almost equal.

$$\log k_2 = -(1.80 \pm 0.02)\,\sigma^+ - 2.06 \quad (5)$$
$$c^2 = 0.9975,\ \text{Sd} = 0.05,\ n = 19,\ \psi = 0.05,\ T = 323\ \text{K}$$

The rates of reduction of **Ia – Id** by different amines were correlated in terms of Hammett's σ values. Since the molecules are disubstituted, the correlation was done with 2σ. Excellent correlations were obtained with the reaction constant being positive (Table 6).

For the oxidation of amines, the polar reaction constant is negative. This points to an electron-deficient carbon centre in the rate-determining step. On the other hand, the reaction constant for the reduction of the substituted Mn(V) complexes has positive values, indicating an electron-rich reaction centre in the transition state. The presence of a substantial kinetic isotope effect in the oxidation of benzylamine confirms the cleavage of the α – C – H bond in the rate-determining step. The hydrogen may leave as a cation, an anion or an atom. The sign of the reaction constants militates against a proton trans-

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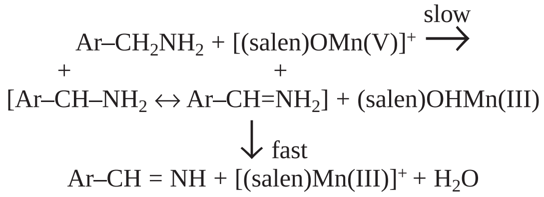
Table 6 Rate constants and reaction constants for the oxidation of substituted benzylamines by **Ia – Id** at 293 K

Substance	$10^5\ k_2$ (mol^{-1} dm^{-3} s^{-1})				ρ	c^2
	Ib	**Ia**	**Ic**	**Id**		
p-CF$_3$	0.010	0.37	6.71	6540	2.74	0.9998
m-NO$_2$	0.011	0.38	6.83	6870	2.73	0.9999
p-No$_2$	0.014	0.45	7.93	6900	2.69	0.9997
m-CF$_3$	0.021	0.62	10.3	8000	2.63	0.9989
p-CO$_2$Me	0.028	0.76	11.9	8580	2.59	0.9994
m-Cl	0.045	1.15	17.4	10200	2.53	0.9996
m-CO$_2$Me	0.052	1.28	18.8	10800	2.51	0.9998
m-F	0.057	1.39	19.9	11200	2.50	0.9997
m-I	0.068	1.61	20.6	11500	2.47	0.9986
p-Br	0.19	3.87	47.2	17000	2.34	0.9996
p-Cl	0.27	5.04	56.8	19100	2.29	0.9988
m-OMe	0.31	5.68	61.6	19700	2.27	0.9997
H	0.35	6.37	69.0	20600	2.35	0.9999
m-Me	0.49	8.34	85.6	23100	2.20	0.9991
p-F	0.74	11.8	113	26700	2.15	0.9993
m-NH$_2$	0.85	13.0	125	27100	2.13	0.9990
p-Me	2.37	30.9	251	41600	2.00	0.9995
p-OMe	63.1	487	2630	128000	1.56	0.9987
p-NH$_2$	3680	14100	42000	547000	1.02	0.9988
ρ	–2.27	–1.86	–1.52	–0.76		
ρr	–2.91	–2.43	–2.03	–1.04		
r	1.28	1.31	1.34	1.37		
C^2	0.9995	0.9998	0.9998	0.9996		

fer from the amine to the oxidant. However, with the present data, it is not possible to differentiate categorically between a hydrogen atom transfer and a hydride-ion transfer. The propensity of oxomanganese (V) complexes to be involved in hydrogen atoms transfer reactions is well documented.[6] The oxidation of organic sulphides by oxo(salen)–manganese(V) complexes is proposed[7,8] to involve a single-electron transfer (SET) mechanism. The oxidation of benzylamine by **Ia** failed to induce polymerization of acrylonitrile. Further, the addition of acrylonitrile had no effect on the rate of oxidation. This points against a one-electron oxidation, generating free radicals. However, these evidences are not conclusive. The free radical might form and react before escaping from the cage. Thus the possibility of a one-electron reaction cannot be ruled out. The large negative polar reaction constants, observed in the oxidation of amines, indicate a hydride-ion transfer in the rate-determining step. A SET mechanism is unlikely on the basis of high oxidation potential of amines also.

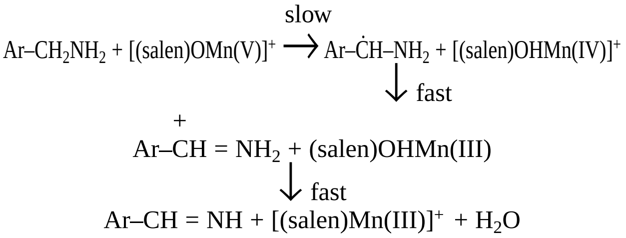
To conclude, though it seems that either of the mechanisms (Schemes 1 and 2) is possible, the balance of evidence is in favour of a hydride-ion transfer (Scheme 1).



$$\mathrm{Ar{-}CH_2NH_2 + [(salen)OMn(V)]^+} \xrightarrow{\text{slow}}$$
$$\mathrm{[Ar{-}\overset{+}{C}H{-}NH_2 \leftrightarrow Ar{-}CH{=}\overset{+}{N}H_2] + (salen)OHMn(III)}$$
$$\downarrow \text{fast}$$
$$\mathrm{Ar{-}CH = NH + [(salen)Mn(III)]^+ + H_2O}$$

Scheme 1

Reactivity–selectivity principled: The reactivity-selectivity principle (RSP) states that there is an inverse relationship between the reactivity of a reagent and its selectivity among a set of similar substrates. We have attempted to apply RSP to the present reaction. Data recorded in Table 6 showed that the polar reaction constants have opposite signs. It is further observed that introduction of substituents have opposite effects. The introduction of an electron-withdrawing group in the amine molecule retards the reaction, whereas the same process in the Mn(V) complex facilitates the reaction. The data in Table 6 are arranged in the order of increase in reactivity. The values of the reaction constants show that there is a significant variation in the magnitudes of the reaction constants (selectivity) when the nature of the substituent in either the amine or the Mn(V) complex is varied. It is also apparent that as the reactivity of either the Mn(V) complex or the amine increases the magnitude of the reaction constants decrease i.e. there is an inverse relationship between the reactivity and selectivity in both cases. It may be mentioned here that while the magnitudes of ρ and ρr decrease with an increase in the reactivity of the Mn(V) complex, the magnitude of r increases, though slightly. The applicability of RSP in this reaction was verified by Exner's[35] mathematical criterion.



$$\mathrm{Ar{-}CH_2NH_2 + [(salen)OMn(V)]^+} \xrightarrow{\text{slow}} \mathrm{Ar{-}\dot{C}H{-}NH_2 + [(salen)OHMn(IV)]^+}$$
$$\downarrow \text{fast}$$
$$\mathrm{Ar{-}\overset{+}{C}H = NH_2 + (salen)OHMn(III)}$$
$$\downarrow \text{fast}$$
$$\mathrm{Ar{-}CH = NH + [(salen)Mn(III)]^+ + H_2O}$$

Scheme 2

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Table 1. Rate constants for the oxidation of benzylamine by **Ia** at 313 K
Table 2. Effect of pyridine oxide on the oxidation of benzylamine by **Ia** at 313 K
Table 3. Kinetic isotope effect in the oxidation of benzylamine by **Ia**
Table 4. Rate constants for the oxidation of substituted benzylamines by **Ia** and the activation parameters.
Table 5. Correlation of rate of oxidation of *meta*- and *para*-substituted benzylamines by **Ia** in terms of Yukawa-Tsuno equation
Table 7. Correlation of log $\mathbf{k_{Fi}}$ and log $\mathbf{k_{Si}}$ according to Eqn. (5)

Techniques: Spectrophotometry, Correlation analysis

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