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

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The oxidation of benzyl alcohol by oxo(salen)manganese (V) complexes proceeds *via* either a hydride-ion or a hydrogen-atom transfer from the alcohol to the manganese (V) complexes.

Keywords: benzyl alcohols, oxo(salen)manganese(v) complexes

Schiff base complexes of transition metal ions have been receiving much attention as oxygen atom donors to organic compounds. The kinetics of the oxidation of sulfides by oxo(salen)manganese(V) (H_2salen = N,N′-Bis(salicylidene) ethylenediamine) complexes were reported by Chellamani *et al*.[7,8] Recently we have reported the kinetics of the oxidation of substituted benzaldehydes by these complexes.[9] We report here the kinetics of the oxidation of some monosubstituted benzyl alcohols by oxo(salen)manganese(V) complexes (**Ia–Id**) in acetonitrile. Mechanistic aspects are discussed.

Oxo (salen)manganese(V) complexes [eqn (1), see full text] were prepared by the reported methods.[7]

Pseudo-first order conditions were attained by keeping a large excess (× 20 or greater) of the alcohols over the oxidant. 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: $k_2 = k_{obs}/[\text{alcohol}]$.

The oxidation of benzyl alcohols resulted in the formation of the corresponding benzaldehydes. The overall reaction may be represented as follows:

$$\mathrm{PhCH_2OH + (salen)OMn(V) \rightarrow PhCHO + H_2O + (salen)Mn(III)} \quad (2)$$

It was observed that during the course of the reaction Mn(V) is reduced to Mn(III). This is confirmed by the appearance of the characteristic peak of the Mn(III) complexes at 350 nm. No noticeable oxidation of the alcohols by Mn(III) was observed.

The reaction is first order with respect to Mn^V and the alcohol. The rates of oxidation the alcohols by **Ia–Id** were determined at different temperatures and the activation parameters were calculated.

The oxidation of benzyl alcohol by **Ia**, in an atmosphere of dinitrogen, failed to induce polymerisation of acrylonitrile. Further, the addition of acrylonitrile had no effect on the rate of oxidation. The oxidation [1,1-$^2H_2$]benzyl alcohol ($PhCD_2OH$) by **Ia** exhibited a substantial kinetic isotope effect.

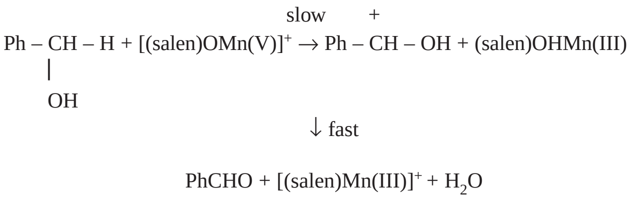
The rates of oxidation failed to exhibit a significant correlation in terms of any single substituent-parameter equation. Therefore, the rates of *para*- and *meta*-substituted benzyl alcohols were subjected to analyses in terms of dual-substituent parameter (DSP) equations of Taft[18] and Swain *et al.*[19]

The rates of the oxidation of *ortho*-substituted benzyl alcohols showed excellent correlation in terms of Charton's[24] triparametric equation.

The rates of reduction of 5,5′-disubstituted oxomanganese(V) complexes, **Ia–Id**, by different alcohols were correlated in terms of Hammett's σ_p values. Since the molecules are disubstituted, the correlation was done with $2\sigma_p$. Excellent correlations were obtained; the reaction constants being positive (Table 7). In Table 7, the reaction constants and coefficient of determination for the effect of substituent in the alcohol molecules are recorded in the last rows of the table. The reaction constants for the substituent variation in the oxo(salen)manganese(V) complexes for the each alcohol are recorded in the last columns.

For the oxidation of alcohols, the polar reaction constants, ρ_I and ρ_R, are 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 benzyl alcohol confirms the cleavage of an $\alpha - C - H$ bond in the rate-determining step. The failure to induce polymerisation of acrylonitrile and no effect of the radical scavenger on the reaction rate point against a hydrogen atom transfer reaction 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 (Scheme 2) cannot be ruled out. The large negative polar reaction constants, observed in the oxidation of alcohols, indicate a hydride-ion transfer in the rate-determining step. The excellent correlation of rates of the *para*-substituted compounds with σ_R^+ values show that there is an extensive resonance interaction between a developing positive charge at the reaction centre and the *para*-substituents. This also supports a hydride-ion transfer in the rate-determining step (Scheme 1).

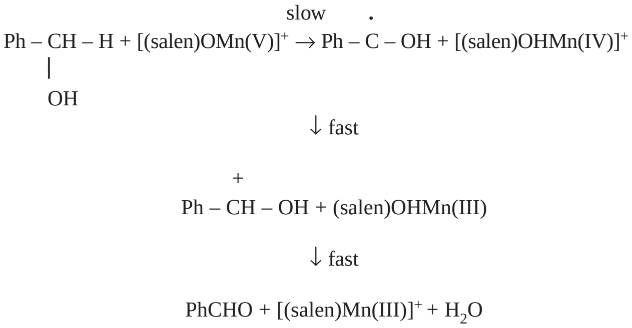


$$\mathrm{Ph-\underset{\displaystyle OH}{\underset{|}{CH}}-H + [(salen)OMn(V)]^+ \xrightarrow{slow} Ph-\overset{+}{C}H-OH + (salen)OHMn(III)}$$

$$\downarrow \mathrm{fast}$$

$$\mathrm{PhCHO + [(salen)Mn(III)]^+ + H_2O}$$

Scheme 1



$$\mathrm{Ph-\underset{\displaystyle OH}{\underset{|}{CH}}-H + [(salen)OMn(V)]^+ \xrightarrow{slow} Ph-\overset{\bullet}{C}-OH + [(salen)OHMn(IV)]^+}$$

$$\downarrow \mathrm{fast}$$

$$\mathrm{Ph-\overset{+}{C}H-OH + (salen)OHMn(III)}$$

$$\downarrow \mathrm{fast}$$

$$\mathrm{PhCHO + [(salen)Mn(III)]^+ + H_2O}$$

Scheme 2

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Table 7 Rate constants and reaction constants for the oxidation of benzyl alcohols by **Ia–Id** at 298 K

Subst.	$10^4 k_2$ (mol/dm^3/s^1)				ρ	r^2
	Ib	**Ia**	**Ic**	**Id**		
(a) *meta*-substituted						
NO_2	0.50	4.45	27.0	1840	1.68 ± 0.02	0.9997
CN	0.76	6.42	37.8	2360	1.65 ± 0.01	0.9996
CF_3	1.30	10.2	57.0	2900	1.58 ± 0.02	0.9995
Br	2.86	21.0	111	4800	1.52 ± 0.02	0.9989
Cl	3.34	22.7	122	5020	1.50 ± 0.01	0.9998
F	3.62	24.1	128	5090	1.49 ± 0.01	0.9998
OPh	6.24	39.5	188	6870	1.44 ± 0.01	0.9999
SMe	7.39	47.4	220	7700	1.42 ± 0.01	0.9994
NHCOMe	7.92	49.4	230	7830	1.40 ± 0.02	0.9989
H	12.0	70.6	304	8850	1.35 ± 0.01	0.9997
OMe	12.9	74.8	310	8900	1.33 ± 0.02	0.9988
Me	20.4	110	409	10300	1.27 ± 0.02	0.9988
NH_2	27.4	141	501	11200	1.23 ± 0.01	0.9996
ρ_I	−1.87 ± 0.03	−1.63 ± 0.01	−1.35 ± 0.02	−0.84 ± 0.02		
ρ_R	−1.20 ± 0.03	−1.04 ± 0.01	−0.92 ± 0.03	−0.60 ± 0.03		
R^2	0.9988	0.9993	0.9971	0.9985		
(b) *para*-substituted						
NO_2	0.63	5.46	33.4	1970	1.65 ± 0.02	0.9997
CF_3	1.57	12.8	70.4	3880	1.60 ± 0.01	0.9999
CO_2Me	2.45	17.0	87.2	4230	1.53 ± 0.02	0.9997
Br	10.8	64.8	282	8450	1.36 ± 0.02	0.9986
H	12.0	70.6	304	8850	1.35 ± 0.01	0.9997
Cl	14.2	83.0	351	9560	1.33 ± 0.02	0.9993
F	32.5	175	683	16800	1.28 ± 0.02	0.9985
Me	42.8	226	865	19300	1.25 ± 0.03	0.9969
SMe	118	558	2040	37900	1.18 ± 0.02	0.9984
NHCOMe	265	1160	3830	62800	1.12 ± 0.01	0.9999
OMe	553	2180	6750	97100	1.06 ± 0.03	0.9980
ρ_I	−1.48 ± 0.04	−1.29 ± 0.02	−1.14 ± 0.02	−0.78 ± 0.03		
ρ_R	−2.04 ± 0.02	−1.81 ± 0.02	−1.61 ± 0.01	−1.17 ± 0.03		
R^2	0.9993	0.9998	0.9997	0.9943		
(c) *ortho*-substituted						
OMe	553	2180	6750	97100	1.06 ± 0.03	0.9980
NO_2	1.42	12.1	70.2	4020	1.63 ± 0.02	0.9992
CO_2Me	7.89	49.7	234	7780	1.41 ± 0.02	0.9986
H	12.0	70.6	304	8850	1.35 ± 0.01	0.9997
CF_3	16.4	93.0	387	10100	1.31 ± 0.02	0.9989
Cl	22.1	123	404	11500	1.28 ± 0.03	0.9983
F	30.3	144	564	12500	1.24 ± 0.01	0.9999
Br	32.8	161	579	12900	1.22 ± 0.02	0.9990
I	41.8	201	710	13900	1.19 ± 0.03	0.9985
SMe	98.6	408	1310	18900	1.07 ± 0.01	0.9999
Me	111	421	1330	19100	1.06 ± 0.03	0.9982
NHAc	131	468	1400	19400	1.03 ± 0.01	0.9998
OMe	142	554	1610	19700	1.01 ± 0.03	0.9979
ρ_I	−1.72 ± 0.06	−1.40 ± 0.03	−1.18 ± 0.06	−0.60 ± 0.02		
ρ_R	−2.01 ± 0.05	−1.65 ± 0.02	−1.34 ± 0.05	−0.69 ± 0.02		
ϕ	1.15 ± 0.05	0.95 ± 0.02	0.78 ± 0.04	0.41 ± 0.02		
R^2	0.9971	0.9991	0.9954	0.9953		

Reactivity-selectivity principle (RSP): We have attempted to apply RSP to the present reaction. Data recorded in Table 7 showed that the polar reaction constants have opposite signs. It is apparent that as the reactivity of either the Mn(V) complex or the alcohol increases the magnitude of the reaction constant decreases *i.e.* there is an inverse relationship between the reactivity and selectivity in both cases. The validity of the RSP was checked and found genuine by applying the mathematical criteria postulated by Exner.[30]

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Techniques used: Spectrophotometry, correlation analysis

References: 30 Figures:2

Table 1. Rate constants for the oxidation of benzyl alcohol **Ia** at 298 K

Table 2. Effect of pyridine N-oxide on the oxidation of benzyl alcohol at 298 K

Table 3. Rate constants and the activation parameters for the oxidation of substituted benzyl alcohols by **Ia**.

Table 4. Correlation of rate constants of the oxidation of *para*- and *meta*- substituted benzyl alcohols with dual substituent-parameters

Table 5. Temperature dependence of the reaction constants for the oxidation of *para*- and meta-substituted benzyl alcohols by **Ia**

Table 6. Temperature dependence of the reaction constants of the oxidation of *ortho*-substituted benzyl alcohols by **Ia**

Table 8. Correlation of log k_F and log k_S according to equation (15)

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References cited in this synopsis

7 A. Chellamani, N.M.I. Alhaji, S. Rajagopal, R. Sevvel and C. Srinivasan, *Tetrahedron*, 1995, **51**, 12677.
8 A. Chellamani, N.M.I. Alhaji and S. Rajagopal *J. Chem. Soc., Perkin Trans. 2*, 1997, 299.
9 V. Bansal, P.K. Sharma and K.K. Banerji, *J. Chem Res(S)* 1999, 480; *(M)* 2052.
18 S. Dayal, S. Ehrenson and R.W. Taft, *J. Am. Chem. Soc.*, 1972, **94**, 9113.
19 C.G. Swain, S.H. Unger, R.S. Rosenquest and M.S. Swain, *J. Am. Chem. Soc.*, 1983, **105**, 492.
24 M. Charton, *J. Org. Chem.*, 1975, **40**, 407.
30 O. Exner, *J. Chem. Soc., Perkin Trans.*, *2*, 1993, 973.