

Kinetics and Mechanism of the Oxidation of Substituted Benzaldehydes by Oxo(salen)manganese(v) Complexes[†]

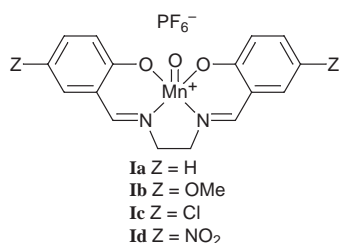
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The oxidation of benzaldehyde by oxo(salen)manganese(v) complexes proceeds *via* either a hydride-ion transfer or a hydrogen-atom transfer from the aldehyde to the manganese(v) complex.

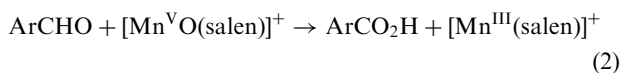
Schiff-base complexes of transition metal ions have been receiving much attention as oxygen atom donors to organic compounds. Recently the mechanisms of the oxidation of sulfides by oxo(salen)manganese(v) complexes were reported by Chellamani *et al.*^{7,8} We report now the kinetics of the oxidation of some monosubstituted benzaldehydes by oxo(salen)manganese(v) complexes **1a–1d** 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 of the aldehydes over the oxidant. The reactions were followed by monitoring the decrease in the concentration of the manganese(v) complex at 680 nm for up to 80% of the reaction. The pseudo-first order rate constant, k_{obs} , was evaluated from the linear ($r^2 > 0.995$) plots of $\log[\text{Mn}^{\text{V}}]$ vs. time. The second order rate constant, k_2 , was obtained from the relation: $k_2 = k_{\text{obs}}[\text{aldehyde}]$.

The oxidation of aldehydes results in the formation of the corresponding benzoic acids. The overall reaction may be represented by eqn. (2).



The reaction is first order with respect to Mn^{V} and the aldehyde. The rates of oxidation of 22 *meta*- and *para*-monosubstituted benzaldehydes by **1a–1d** were determined at different temperatures and the activation parameters were calculated.

The oxidation of benzaldehyde by **1a**, in an atmosphere of nitrogen, failed to induce polymerization of acrylonitrile. Further, the addition of acrylonitrile had no effect on the rate of oxidation.

The rates of *meta*- and *para*-substituted benzaldehydes were subjected to correlation analysis in terms of dual substituent-parameter (DSP) equations of Taft¹³ and Swain *et al.*¹⁴ The rates of oxidation of the *para*-substituted benzaldehydes show an excellent correlation with Taft's

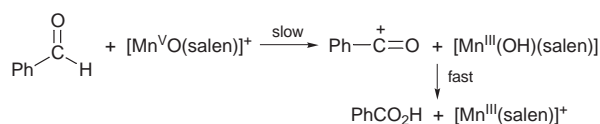
σ_1 and σ_{R}^+ values. The rates of *meta*-substituted benzaldehydes correlated best with σ_1 and σ_{R}^0 . The reaction constants have negative values.

The rates of reduction of 5,5'-disubstituted oxomanganese(v) complexes **1a–1d**, by different aldehydes were correlated in terms of Hammett's σ_{p} values. Since the molecules are disubstituted, the correlation was performed using $2\sigma_{\text{p}}$. Excellent correlations were obtained; the reaction constants being positive (Table 8).

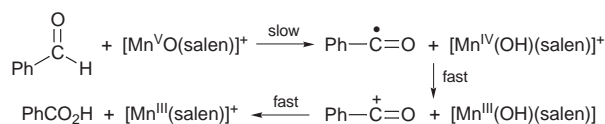
In Table 8, the reaction constants (ρ_{I} and ρ_{R} and correlation coefficients for the effect of substituent in the aldehyde molecules are recorded in the final three rows. The reaction constants (ρ) and correlation coefficients for substituent variation in the oxo(salen)manganese(v) complexes for each aldehyde are recorded in the final two columns.

For the oxidation of aldehydes, the reaction constants are negative which points to an electron-deficient carbon centre in the rate-determining step. On the other hand, the reaction constants for the reduction of the substituted manganese(v) complexes have positive values. Therefore, in the transition state, the manganese(v) complex is more electron-rich than in the reactant state.

The presence of a substantial kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} = 5.30$ at 298 K) in the oxidation of deuteriated benzaldehyde (PhCDO) confirms the cleavage of the aldehydic C–H bond in the rate-determining step. The large negative polar reaction constants, observed in the oxidation of aldehydes, together with the substantial deuterium isotope effect suggest that in the transition state, the aldehydic carbon approaches a carbocation in character. Thus transfer of a hydride ion from the aldehyde to the manganese(v) complex, in the rate-determining step, is indicated (Scheme 1). However, it is not possible to completely discard a hydrogen-atom transfer reaction (Scheme 2) since the propensity of oxomanganese(v) complexes to be involved in one-electron reactions is well documented.⁶ Failure to induce polymerisation of acrylonitrile is not conclusive evidence against the involvement of free radicals; such free radicals might form and react before they can escape from the solvent cage.



Scheme 1



Scheme 2

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[†] H₂salen = *N,N'*-Bis(salicylidene)ethylenediamine.

Table 8 Rate constants and reaction constants for the oxidation of substituted benzaldehydes by **Ia-d** at 298 K

Subst.	$10^4 k_2 / \text{mol dm}^{-3} \text{ s}^{-1}$				ρ	r^2
	Ib	Ia	Ic	Id		
(a) <i>meta</i> -substituted						
NO ₂	0.28	2.85	18.0	1550	1.76 ± 0.02	0.9997
CN	0.45	4.00	25.3	1940	1.72 ± 0.01	0.9997
CF ₃	0.77	6.84	39.4	2740	1.67 ± 0.03	0.9987
Br	1.81	14.6	78.9	4560	1.60 ± 0.01	0.9994
Cl	2.07	15.8	85.7	4790	1.59 ± 0.01	0.9997
F	2.50	18.5	98.8	5240	1.58 ± 0.02	0.9990
SMe	4.45	31.4	153	7200	1.51 ± 0.02	0.9994
NHCOMe	4.73	33.1	166	7300	1.50 ± 0.02	0.9988
H	6.00	40.2	192	8180	1.48 ± 0.01	0.9989
OMe	8.48	55.1	251	10000	1.45 ± 0.03	0.9985
Me	9.86	62.9	292	11200	1.44 ± 0.02	0.9990
ρ_1	-1.72	-1.50	-1.32	-0.92		
	±0.01	±0.01	±0.01	±0.01		
ρ_R	-1.37	-1.21	-1.08	-0.78		
	±0.02	±0.01	±0.02	±0.02		
R^2	0.9994	0.9998	0.9995	0.9991		
(b) <i>para</i> -substituted						
NO ₂	0.42	4.02	25.7	2160	1.75 ± 0.03	0.9997
CN	0.61	5.21	32.2	2500	1.71 ± 0.01	0.9999
CF ₃	0.95	8.09	47.0	3250	1.66 ± 0.02	0.9997
CO ₂ Me	1.18	10.3	57.3	3810	1.65 ± 0.01	0.9995
Br	4.98	35.2	170	7910	1.50 ± 0.01	0.9993
H	6.00	40.2	192	8180	1.48 ± 0.01	0.9989
Cl	6.60	43.2	205	8200	1.46 ± 0.02	0.9992
F	13.8	84.8	377	13400	1.41 ± 0.02	0.9987
Me	20.1	118	511	16800	1.38 ± 0.01	0.9999
SMe	47.2	248	976	25800	1.29 ± 0.03	0.9984
NHCOMe	107	510	1870	40900	1.22 ± 0.03	0.9982
OMe	220	895	2760	60400	1.15 ± 0.02	0.9988
ρ_1	-1.39	-1.21	-1.05	-0.70		
	±0.02	±0.01	±0.02	±0.02		
ρ_R	-1.88	-1.64	-1.44	-1.05		
	±0.02	±0.01	±0.02	±0.01		
R^2	0.9993	0.9998	0.9992	0.9979		

Reactivity-selectivity Principle (RSP).—We have attempted to apply RSP to the present reaction. Data recorded in Table 8 showed that the polar reaction constants have opposite signs. It is apparent that as the reactivity of either the manganese(v) complex or the aldehyde 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 to be genuine by applying the mathematical criteria postulated by Exner.²⁰

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Techniques used: Spectrophotometry, correlation analysis

References: 20

Fig. 1: $\log k_F$ versus $\log k_S$ plots for the oxidation of aldehydes by (A) **Ib** and **Id**, (B) **Ia** and **Id**, (C) **Ic** and **Id**, (D) **Ib** and **Ic**, (E) **Ib** and **Ia** and (F) **Ia** and **Ic**

Table 1: Rate constants for the oxidation of benzaldehyde by **Ia** at 308 K

Table 2: Rate constants and activation parameters for the oxidation of substituted benzaldehydes by **Ia**

Table 3: Rate constants and activation parameters for the oxidation of substituted benzaldehydes by **Ib**

Table 4: Rate constants and activation parameters for the oxidation of substituted benzaldehydes by **Ic**

Table 5: Rate constants and activation parameters for the oxidation of substituted benzaldehydes by **Id**

Table 6: Correlation of the rates of the oxidation of *meta*- and *para*-substituted benzaldehydes by **Ia** with DSP at 288 K^a

Table 7: Temperature dependence of the reaction constants

Table 9: Correlation of $\log k_F$ and $\log k_S$ according to eqn. (5)

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