

Kinetics of oxidative hydrolysis of benzaldoximes, acetophenoneoxime and benzophenoneoxime by manganese(III) acetate

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The kinetics of oxidative hydrolysis of benzaldoximes, acetophenone oximes and benzophenone oximes by manganese(III) acetate have been studied at $28 \pm 0.2^\circ\text{C}$ in acetic acid (76%, v/v). Respective aldehydes/ketones are obtained in about 80% yield at ambient temperature. One mole of oxime requires about two moles of $\text{Mn}^{\text{III}}(\text{OAc})_3$ for the reaction. The electronic influence on the rate of $\text{Mn}^{\text{III}}(\text{OAc})_3$ reaction with benzaldoximes is in contrast to polar effect observed on the rate of the reaction with ketoximes as revealed by the change in Hammett reaction constant from -1.0 to $+0.73$ and $+0.33$ respectively. Possibly one electron transfer to $\text{Mn}^{\text{III}}(\text{OAc})_3$ occurs in a slow step in the reactions with aldoximes while the addition of $\text{Mn}^{\text{III}}(\text{OAc})_3$ to $\text{C}=\text{N}$ bond seems to be rate limiting in the reaction with ketoximes.

Metal ion oxidants are the reagents of choice for the regeneration of carbonyl compounds from the respective oximes. Navaneeth Rao and coworkers¹ studied oxidative hydrolysis of benzaldoximes by $\text{Mn}^{\text{III}}(\text{OAc})_3$ in acetic acid medium and reported a free radical mechanism involving the intermediacy of an iminoxy radical. The title investigation has been undertaken not only to arrive at optimum conditions for the regeneration of carbonyl compounds but also to have an insight into the mechanism of oxidative hydrolysis.

Materials and Methods

Oximes were prepared by the literature procedure. Manganese(III) acetate (Aldrich), acetic acid, sodium acetate trihydrate and manganese(II) acetate (BDH) were of reagent grade.

The kinetics of manganese(III) acetate oxidation of benzaldehyde, acetophenone and benzophenone oximes have been studied in aqueous acetic acid (76%, v/v) at $28^\circ \pm 0.2^\circ\text{C}$. The rate of disappearance of $\text{Mn}(\text{III})$ was followed by measuring the decrease in absorbance for $\text{Mn}(\text{III})$ at 360 nm using Systronics 108-UV visible spectrophotometer. The specific rates evaluated using integrated rate equations from duplicate runs agreed within $\pm 5\%$. These values also agreed with those obtained from plots of logarithms of change in absorbance versus time.

Product analysis and stoichiometry

The stoichiometric mixture [1-4 mmol of oxime

and 10-30 mmol of $\text{Mn}^{\text{III}}(\text{OAc})_3$], after 9 half-lives, was diluted with equal volumes of ice and water, extracted with CHCl_3 , the CHCl_3 portion washed with NaHCO_3 till neutral, concentrated, extracted with ether and dried. The product thus obtained was found to be the corresponding aldehyde or ketone. The amount of benzaldehyde, benzophenone or acetophenone formed was determined by measuring the absorbance of the ether extracts at 250 nm ($\epsilon = 11,400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), 257 nm ($\epsilon = 18,500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) or 246 nm ($\epsilon = 12,600 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)^{2,3} respectively.

As manganese(III) acetate, under the reaction conditions, did not oxidise benzaldehyde or acetophenone or benzophenone, the yield of aldehyde or ketone was about 80%. The stoichiometric results obtained [in the concentration range of oxime from 1.0 to $4.0 \times 10^{-3} \text{ mol dm}^{-3}$ and $[\text{Mn}(\text{III})] = 10$ to $30 \times 10^{-3} \text{ mol dm}^{-3}$ in 76% aqueous acetic acid] indicate that one mole of oxime required one mole of $\text{Mn}^{\text{III}}(\text{OAc})_3$ for oxidation, yielding nearly 75% to 80% of respective aldehyde or ketone.

Results and Discussion

From the kinetic data collected in Table 1, the order in each reactant is found to be unity. Hence the rate law is given by Eq. (1).

$$-\frac{d[\text{Mn}(\text{III})]}{dt} = k_2 [\text{Mn}(\text{III})][\text{oxime}] \quad \dots (1)$$

Substituent effects

The introduction of electron-donating group like $p\text{-CH}_3$ enhances the rate while an electron-with-

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Table 1—Kinetic data for $\text{Mn}^{\text{III}}(\text{OAc})_3$ reaction with oximes^{a,d}
 $[\text{R}^2 - \text{C}_6\text{H}_4 - \text{CR}^1 = \text{N.OH}]$

$10^3 [\text{oxime}]$ (mol dm^{-3})	$10^4 [\text{Mn(III)}]$ (mol dm^{-3})	$10^3 k_1^b$ (s^{-1})	k_2^c ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)
Benzaldoxime ($\text{R}^1 = \text{R}^2 = \text{H}$)			
2.0	2.0	2.2	1.1
4.0	2.0	4.5	1.13
6.0	2.0	6.6	1.1
9.7	2.0	9.9	1.02
2.0	1.2	2.3	1.15
2.0	2.8	2.4	1.20
2.0	4.0	2.4	1.20
Acetophenoneoxime ($\text{R}^1 = \text{CH}_3, \text{R}^2 = \text{H}$)			
1.0	2.0	10.1	10.1
2.0	2.0	20	10.0
3.0	2.0	30	10.0
8.0	1.94	86	—
1.0	1.0	10.1	10.1
1.0	1.6	10.1	10.1
Benzophenoneoxime ($\text{R}^1 = \text{Ph}, \text{R}^2 = \text{H}$)			
2.0	2.0	6.9	3.5
4.0	2.0	12.7	3.2
6.0	2.0	18.8	3.1
8.0	1.94	23	2.9
2.0	2.2	6.9	3.5
2.0	2.8	7.1	3.6
2.0	4.0	7.2	3.6

^aReactions were carried out in 76% aqueous acetic acid at $28 \pm 0.2^\circ\text{C}$, unless otherwise mentioned. The ionic strength was maintained at 0.20 mol dm^{-3} using NaOAc.

$$b \quad \frac{-d \ln [\text{Mn(III)}]}{dt} = k_1 (\text{s}^{-1})$$

$$c \quad k_2 = k_1 / [\text{oxime}]$$

^dUnder the reaction conditions, the decomposition of $\text{Mn}^{\text{III}}(\text{OAc})_3$ is less than 2% of initial concentration.

drawing group like $p\text{-NO}_2$ retards the rate markedly (Table 2). The plot of log of specific rates versus Hammett substituent constant, σ , is linear with a slope giving $\rho = -1.01$ ($\gamma = 0.99$). Such a negative ρ -value is indicative of an electron-deficient transition state.

As the reactivity of acetophenoneoxime is comparable to that of benzaldoxime and since benzophenoneoxime (with no $\alpha\text{-C-H}$ bond) gets oxidatively hydrolysed even much faster than benzaldoxime (Table 2), it rules out the possibility of participation of $\alpha\text{-C-H}$ bond in Mn(III) oxidation of oximes. This is further corroborated by the forma-

 Table 2—Substituent effect on the rate of Mn(III) acetate reaction with oximes^{a,c}
 $\text{R}^2 - \text{C}_6\text{H}_4 - \text{CR}^1 = \text{N.OH}$

Benzaldoxime ($\text{R}^1 = \text{H}$)

k_2^b
($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)

R^2	
H	1.1
$p\text{-Cl}$	0.65
$p\text{-CH}_3$	2.6
$p\text{-NO}_2$	0.19
$m\text{-NO}_2$	0.26
$o\text{-Cl}$	1.75

Acetophenoneoxime ($\text{R}^1 = \text{CH}_3$)

H	1.03
$p\text{-Cl}$	0.62
$p\text{-CH}_3$	0.72
$p\text{-NO}_2$	1.84
$m\text{-NO}_2$	3.2

Benzophenoneoxime ($\text{R}^1 = \text{Ph}$)

H	3.5
$p\text{-Cl}$	3.6
$p\text{-CH}_3$	0.77
$p\text{-NO}_2$	6.1
$m\text{-NO}_2$	1.85

^aReactions were carried out in 76% aqueous acetic acid at $28 \pm 0.2^\circ\text{C}$ at constant ionic strength.

^b $k_2 = k_1 / [\text{oxime}]$.

^cUnder identical conditions, $\text{Mn}^{\text{III}}(\text{OAc})_3$ does not oxidise hydroxylamine hydrochloride.

tion of respective aldehyde or ketone as the product in quantitative yield at ambient temperature.

In contrast to the observed electronic effect in the Mn^{III} reaction with benzaldoxime, the rates for the Mn^{III} reaction with acetophenoneoxime or benzophenoneoxime are enhanced by electron-withdrawing groups like $p\text{-NO}_2$ while electron donating groups like $p\text{-CH}_3$ retards the rate (Table 2). When these data are cast into a Hammett correlation of log k_2 (k_2 in $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) versus σ , linear plots with positive slopes $\rho = +0.73$ ($\gamma = 0.999$) and $\rho = +0.33$ ($\gamma = 0.97$) are obtained for these two systems respectively. The positive ρ -value of lower magnitude observed in the case of acetophenone and benzophenone oximes is suggestive of an electron rich transition state or a radical intermediate.

Solvent influence

These reactions are susceptible to change in the polarity of the solvent medium and with increasing

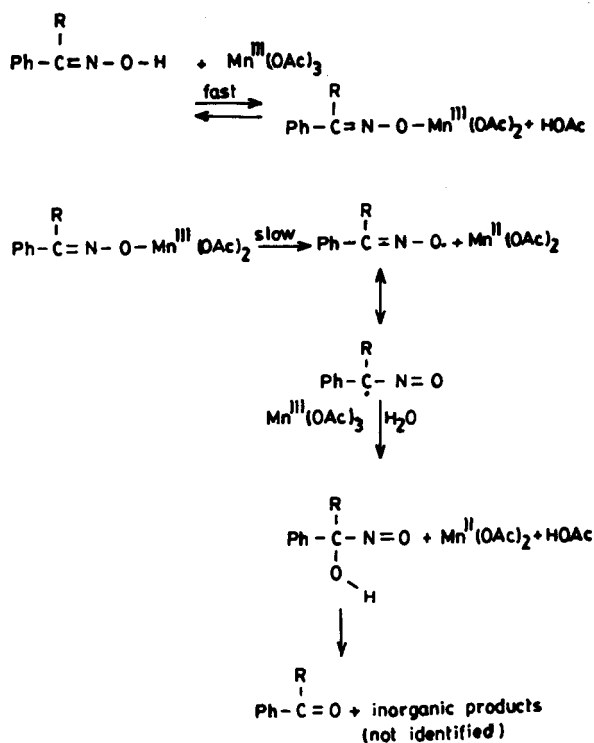
percentage of acetic acid from 76% to 90%, the rate of oxidative hydrolysis of benzaldoxime increases by about 5 times [from $1.1 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ to $5.6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for benzaldoxime] while the rate is reduced by 2 fold [from $10.0 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ to $4.9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for acetophenoneoxime and from $3.5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ to $2.8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for benzophenoneoxime]. As $\text{Mn}^{\text{III}}(\text{OAc})_3$ is less stable in aqueous acetic acid medium, with less than 70% acetic acid, lower compositions have not been tried. The trend in rate observed with change in acetic acid content of the medium may be due to a composite factor.

Mechanism

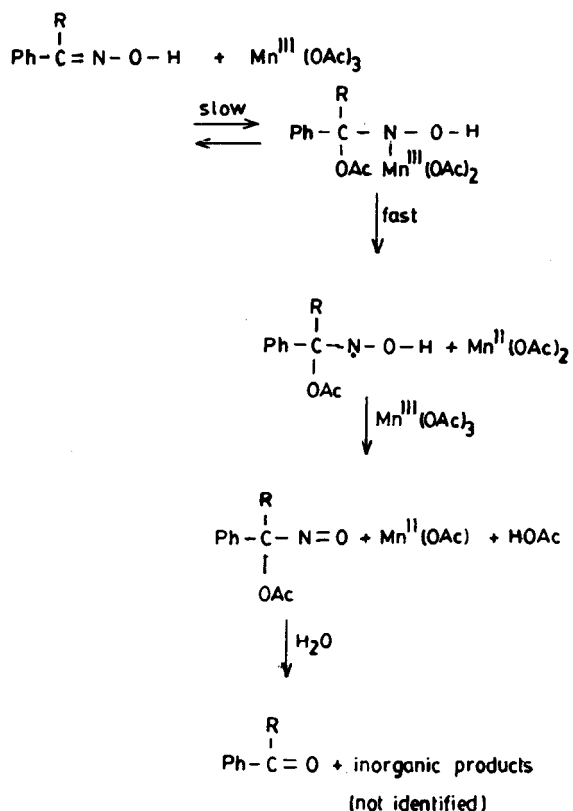
The observed results can be best explained by two mechanisms (see Schemes 1 and 2). The mechanism in Scheme 1 envisages substitution of $\text{Mn}^{\text{III}}(\text{OAc})_3$ at hydroxyl oxygen of oxime followed by transfer of one electron to Mn^{III} in a slow step, ultimately leading to the formation of a carbon radical. With one more equivalent of $\text{Mn}^{\text{III}}(\text{OAc})_3$, the radical undergoes oxidation to yield the carbonyl product ultimately. The formation of benzaldehyde in good yield and the comparable rate of reactivity of benzaldoxime and acetophenoneoxime, rules out the participation of $\alpha\text{-C-H}$ bond of benzaldoxime in the rate-determining step.

In the alternate mechanism shown in Scheme 2 $\text{Mn}^{\text{III}}(\text{OAc})_3$ can add to C=N bond of the oxime in a slow equilibrium step and in the precursor complex, an one-electron transfer to Mn^{III} may lead to the formation of iminoxy radical. Such a radical may undergo oxidation with one more equivalent of $\text{Mn}^{\text{III}}(\text{OAc})_3$ yielding carbonyl product.

The rate of one-electron transfer to Mn^{III} through O-Mn^{III} bond in the slow step (as shown in Scheme 1) will be enhanced by electron-releasing group like *p*-CH₃ and retarded by *p*-NO₂ group which is in keeping with the observed electronic effect in benzaldoximes only. But the addition of $\text{Mn}^{\text{III}}(\text{OAc})_3$ to C=N bond may be aided by electron-withdrawing *p*-NO₂ group and retarded by electron donating *p*-CH₃ group. Such a trend in reactivity has been observed in the Mn^{III} oxidation of ketoximes only and not in aldoximes. Possibly the slow step in $\text{Mn}^{\text{III}}(\text{OAc})_3$ oxidation of benzaldoxime is the one electron transfer to Mn(III) while the addition of $\text{Mn}^{\text{III}}(\text{OAc})_3$ to C=N bond seems to be rate-limiting in the $\text{Mn}^{\text{III}}(\text{OAc})_3$ reaction with acetophenone and benzophenone oximes. The contrasting electronic effect observed in the $\text{Mn}^{\text{III}}(\text{OAc})_3$ reaction with benzaldoximes and ketoximes can be traced to the difference in the rate limiting steps in Schemes 1 and 2.



Scheme 1



Scheme 2

As the rate of these reactions is independent of initially added $\text{Mn}^{\text{II}}(\text{OAc})_2$ possibly an equilibrium involving $\text{Mn}^{\text{II}}(\text{OAc})_2$ and radical intermediate, does not form a part of the overall reaction mechanism. The reaction mixture does not initiate acrylonitrile polymerisation, indicating that probably short lived radical intermediates are formed during the course of reaction.

References

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