Kinetics and Mechanisms of Redox Reactions in Aqueous Solution. Part 6.[1] Oxidation of Cyclohexanone by Aquamanganese(III) Ions in Aqueous Perchloric Acid

By **Ratan Raj Nagori, Mahendra Mehta,** and **Raj Narain Mehrotra,*** Department of Chemistry, University of Jodhpur, Jodhpur 342001, India

The rate of the title reaction has a first-order dependence both on Mn^{III} and cyclohexanone. The rate is retarded by increasing $[H^+]$ but unaffected by Mn^{II}. Unlike the oxidations by manganese(III) pyrophosphate and manganese(III) acetate, in which the enolic form was oxidised, the oxidation of cyclohexanone by aquamanganese(III) ions is found to be much faster than the rate of enolisation. An outer-sphere mechanism is suggested. The rate constants corresponding to the oxidation effected by $Mn^{3+}(aq)$ and $[Mn(OH)]^{2+}(aq)$ are separated and the associated thermodynamic parameters discussed.

THE oxidation of cyclohexanone by two-electron oxidants is effected by attack of the metal ion on its enolic form.[2] A number of one-electron oxidants, *viz.* Co^{III}, Ce^{IV}, V^{V}, and Mn^{III} were also examined in the presence of sulphuric acid and it was concluded that these oxidants attacked the ketonic rather than the enolic form.[3] Similarly, the tris(1,10-phenanthroline)iron(III) complex, which is a one-electron oxidant, according to Littler and Sayce,[4] was reduced by an electron transferred from the ketone. However, this contention has been questioned lately.[5] Ng and Henry[5] have shown that the kinetics were more consistent with electron transfer from the enol. The enol form is also believed to be oxidised in the oxidation of cyclohexanone by hexachloroiridate.[6]

Cerium(IV) sulphate, which oxidised cyclohexanone by attacking the ketonic form,[3] behaved differently in the oxidation of aliphatic ketones where enolisation was considered to be a prerequisite for oxidation.[7] This suggestion was further substantiated in the oxidation of acetone by ammonium cerium(IV) nitrate $Ce[NH_4]_2[NO_3]_6$, in aqueous nitrate solution.[8] Venkatkrishnan and Santappa[9] have shown that cerium(IV) perchlorate and acetone form a complex prior to the rate-limiting oxidation.

Although manganese(III) sulphate attacked the ketonic form of cyclohexanone,[3] manganese(III) pyrophosphate is reported to attack the enolic form of the substrate.[10] Similar kinetics are reported for the oxidation of ketones by manganese(III) acetate.[11]

Hence, it was considered worthwhile to examine yet another manganese(III) species in an attempt to discover whether it attacked the ketonic or the enolic form of cyclohexanone. The choice was the aquamanganese(III) ion since its solution chemistry is much better known.[12,13]

EXPERIMENTAL

Reagents.—Cyclohexanone (B.D.H.) was purified by distillation, b.p. 156—158 °C (lit.,[14a] 156.7 °C), in which the middle portion was collected. A stock solution was prepared by direct weighing of the distilled sample.

The preparation and standardisation of aquamanganese(III) ions in perchloric acid solution has been described.[15] Anhydrous sodium perchlorate (G. F. Smith) was used to maintain the ionic strength at 4 mol dm^{-3}. The stock solution was standardised gravimetrically.

Rate Measurements.—The kinetics were followed under pseudo-first-order conditions, with cyclohexanone present in excess. Before adopting the titrimetric method for rate measurements[15] it was ensured that the concentration of cyclohexanone present in the reaction mixtures would not alter the titrimetric readings of iron(II) solution against the vanadium(V) solution.

The correlation coefficient for the linearity of the plots between log $(a - x)$ and time was >0.998. The linearity itself extended well beyond two half-lives of the reaction indicating that none of the products produced during the reaction affected the rate. The observed first-order rate constant, $k_{obs.}$, with respect to Mn^{III} was obtained from the gradients of the linear plots mentioned earlier. The reproducibility of $k_{obs.}$ values in repeated runs was within 2—3% and the mean values are reported in the Tables.

Stoicheiometry and Product Study.—Reaction mixtures having different concentration ratios of cyclohexanone and Mn^{III} at different acidities were prepared and placed in a

TABLE 1

Details of the stoicheiometric investigations carried out to determine $[Mn^{III}]/[\text{cyclohexanone}]$ at $I = 4$ mol dm^{-3} ($Na[ClO_4]$) and 25 °C

$10^3[Mn^{III}]$/ mol dm^{-3}	10^4[Cyclohexanone]/ mol dm^{-3}	$[H^+]$/ mol dm^{-3}	Experimental conditions	$10^4[Mn^{III}]$/ mol dm^{-3} (left unreacted)	$\frac{\Delta[Mn^{III}]}{\Delta[\text{Cyclohexanone}]}$
1.2	0.8	1.0	Aerobic	7.1	6.1
2.0	1.6	2.0	Aerobic	10.6	5.9
2.0	2.1	3.0	Nitrogen	7.5	6.0
3.0	4.0	1.2	Aerobic	5.5	6.1
3.6	5.0	3.0	Aerobic	5.1	6.2
3.6	5.5	3.5	Nitrogen	3.9	5.8
					Average 6.0 ± 0.2

thermostatted water-bath maintained at 25 ± 0.1 °C. The unreacted [$\mathrm{Mn^{III}}$] was estimated periodically till it had attained a constant value. At this point, the unreacted $\mathrm{Mn^{III}}$ was destroyed by heating the reaction solution slightly and on cooling the reaction product(s) was(were) repeatedly extracted with diethyl ether. The ethereal solution deposited white crystals on slow evaporation. These crystals were washed repeatedly with chloroform.[3] The m.p. of the purified crystals was found to be 151—153 °C and the mixed m.p. with an authentic sample of adipic acid was found to be 152—154 °C. The m.p. of adipic acid reported in the literature [14b] is 151—153 °C.

The details and results of stoicheiometric investigations are summarised in Table 1. It can be seen that the average value of $\Delta[\mathrm{Mn^{III}}]/\Delta[\text{cyclohexanone}]$ is 6.0 ± 0.2. Hence, the stoicheiometric equation for the oxidation reaction could be expressed by (1). Thus, the correlation between the initial rates measured in terms of [$\mathrm{Mn^{III}}$] or [cyclohexanone] is given by equation (2).

$$\mathrm{C_6H_{10}O + 6Mn^{III} + 3H_2O \longrightarrow HOOC(CH_2)_4COOH + 6Mn^{II} + 6H^+} \quad (1)$$

$$-\mathrm{d}[\mathrm{Mn^{III}}]/\mathrm{d}t = 6(-\mathrm{d}[\text{Cyclohexanone}]/\mathrm{d}t) \quad (2)$$

RESULTS

The kinetics were studied under aerobic conditions. However, some of the runs were also repeated under an inert atmosphere; all the reactant solutions were degassed with nitrogen before mixing and the gas was bubbled through the reaction mixture throughout the period of study. The rate constant $k_{\text{obs.}}$ was found to be unaffected by the change of atmosphere.

Dependence on [$\mathrm{Mn^{III}}$].—A three-fold variation in the initial $10^3[\mathrm{Mn^{III}}]$(1.2—3.6 mol dm^{-3}) indicated that $k_{\text{obs.}}$, the pseudo-first-order rate constant with respect to $\mathrm{Mn^{III}}$, was independent of the initial [$\mathrm{Mn^{III}}$]. This confirmed the first-order dependence of the reaction in [$\mathrm{Mn^{III}}$]. A wide variation in the initial [$\mathrm{Mn^{III}}$] was not possible because of the difficulty experienced in the preparation of more concentrated manganese(III) solutions.

Dependence on [$\mathrm{Mn^{II}}$].—The aquamanganese(III) solutions are unstable with respect to the disproportionation reaction given in equation (3).[12,15] The use of high [$\mathrm{Mn^{II}}$], particularly at lower [$\mathrm{HClO_4}$], is useful in preventing the precipitation of hydrated manganese dioxide.[15] Since $\mathrm{Mn^{II}}$ happened to be one of the oxidation products, its effect on the rate was investigated.

$$\mathrm{2Mn^{III} \rightleftharpoons Mn^{IV} + Mn^{II}} \quad (3)$$

Manganese(II) was gradually replaced with sodium perchlorate in a manner that kept the ionic strength constant (4 mol dm^{-3}) and without precipitating $\mathrm{MnO_2}$. The concentrations of all other reactants were kept constant. It was found that for a variation in the initial $10^2[\mathrm{Mn^{II}}]$ in the range 5.0—14 mol dm^{-3}, $k_{\text{obs.}}$ was not affected. It was thus concluded that neither $\mathrm{Mn^{IV}}$ nor $\mathrm{Mn^{II}}$ intervened in the process of oxidation.

Dependence on [Cyclohexanone].—The effect of [cyclohexanone] on $k_{\text{obs.}}$ was investigated at three temperatures and these results are reported in Table 2. An analysis of these results indicated that $k_{\text{obs.}}$/[cyclohexanone] was reasonably constant at all three temperatures and the plots of $k_{\text{obs.}}$ against [cyclohexanone], Figure 1, were linear and passed through the origin. This indicated a strict first-order dependence on the concentration of ketone.

TABLE 2

Dependence of the first-order rate constant $k_{\text{obs.}}$ on [cyclohexanone] at different temperatures ($10^3[\mathrm{Mn^{III}}] = 2.0$, [$\mathrm{HClO_4}$] = 3.0, and I = 4 mol dm^{-3})

10^2[Ketone]/mol dm^{-3}	1.6	3.2	4.0	4.8	6.4	8.0	12.0
$10^4k_{\text{obs.}}$/s^{-1} (19.2 °C)	0.28	0.55	0.63	0.83	1.1	1.4	2.1
$10^4k_{\text{obs.}}$/s^{-1} (27 °C)	0.94	1.9	2.4	2.9	3.8	4.8	7.2
$10^4k_{\text{obs.}}$/s^{-1} (34.8 °C)	3.3	6.5	8.2	10.0	13.3	16.6	25.5

Dependence on [$\mathrm{H^+}$].—The rate measurements were made over 0.9—3.75 mol dm^{-3} perchloric acid at constant ionic strength (4 mol dm^{-3}, Na[$\mathrm{ClO_4}$]). Later these rate measurements were repeated at other temperatures. These results, given in Table 3, indicated that $k_{\text{obs.}}$ decreased with increasing [$\mathrm{H^+}$]. It is interesting, here, to note the effect of [$\mathrm{H^+}$] on the oxidation of cyclohexanone by other manganese(III) species.

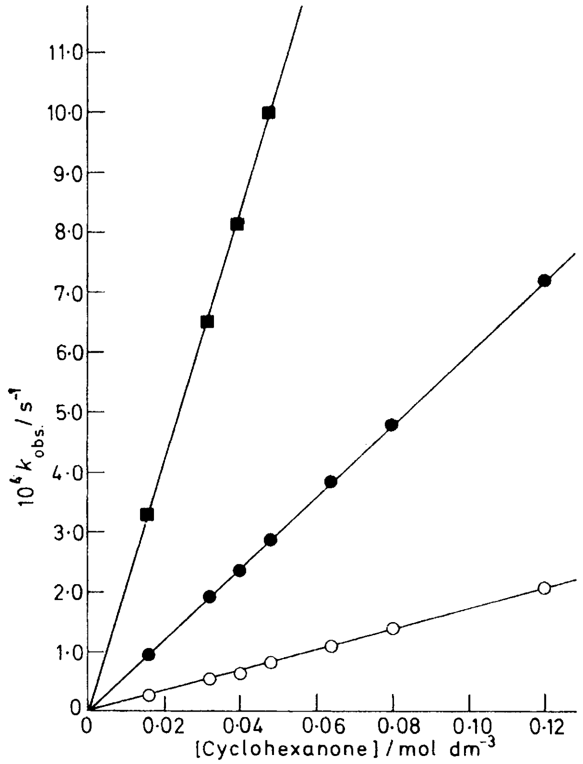

FIGURE 1 Plots of $k_{\text{obs.}}$ against [cyclohexanone] at different temperatures. $10^3[\mathrm{Mn^{III}}] = 2.0$, [$\mathrm{HClO_4}$] = 3.0, and I = 4 mol dm^{-3}; 19.2 (○), 27 (●), and 34.8 °C (■)

In the manganese(III) sulphate oxidation,[3] the dependence of the rate on [$\mathrm{H_2SO_4}$] is complex but at constant [$\mathrm{HSO_4^-}$] the reaction is largely independent of acidity. In the manganese(III) pyrophosphate oxidation, the initial rate was found to increase with decreasing pH.[10] The complex relation between the initial rate and pH is attributed to the dependence of the redox potential of the manganese(III) pyrophosphate complex on pH.[10] The precise nature of the pyrophosphate complex is uncertain.[3]

The exact correlation between $k_{\text{obs.}}$ and [$\mathrm{H^+}$] in the present oxidation is discussed later [see equation (14)].

TABLE 3

Dependence of the first-order rate constant $k_{obs.}$ on $[HClO_4]$ at different temperatures ($10^3[Mn^{III}] = 2.0$, 10^2[cyclohexanone] = 4.0, and $I = 4$ mol dm^{-3})

θ_c/°C $[HClO_4]$/ mol dm^{-3}	20	25	30	35	40
	$10^4k_{obs.}$/s^{-1}				
0.9	2.64	5.7	13.2	26.4	
1.2	1.92	4.3	9.7	21.2	
1.5	1.43	3.3	7.9	17.1	
2.0	1.24	2.7	6.2	13.2	27.4
2.5	0.95	2.1	4.7	10.4	21.2
3.0	0.83	1.8	4.0	8.5	17.5
3.5	0.65	1.5	3.4	7.4	15.4
3.75	0.60	1.4	3.2	6.8	14.3

Thermodynamic Parameters.—The two rate-limiting constants for reaction (7) and (8), k_a, which is independent of $[H^+]$, and k_b, which is dependent on the acidity, were separated from the intercept and slope of the plots drawn in accordance with equation (14) and illustrated in Figure 2 (further details are given later). The values of the rate constants k_a and k_b are reported in Table 4 together with the corresponding values of the enthalpy and entropy of activation. It is interesting to note that the thermodynamic parameters are almost identical for the two rate-limiting constants.

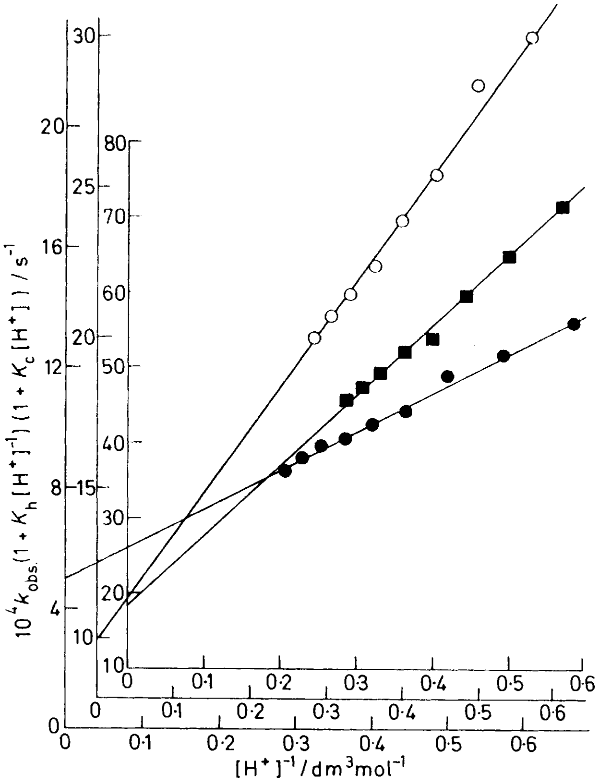

FIGURE 2 Plots of $k_{obs.}(1 + K_h[H^+]^{-1})(1 + K_c[H^+])$ against $[H^+]^{-1}$ at different temperatures. $10^3[Mn^{III}] = 2.0$, 10^2[cyclohexanone] = 4.0, and $I = 4$ mol dm^{-3}; 25 (●), 30 (○), and 35 °C (■)

The value of the rate-limiting constant in the oxidation of cyclohexanone by manganese(III) sulphate is not known.[3] However, the initial rate constant at different temperatures is known.[16] Since adipic acid was reported as the end product,[3] the initial rate constant was converted to the second-order rate constant k_2 (= initial rate/6$[Mn^{III}]$[cyclohexanone]) and the values of ΔH (16 kcal mol^{-1}) and ΔS (17 cal K^{-1} mol^{-1}) * were calculated. The corresponding values of ΔH and ΔS, calculated from the second-order rate constant k_2 (= $k_{obs.}$/6[cyclohexanone]), obtained in the present study at the same acidity (3.5 mol dm^{-3}) were 28.4 kcal mol^{-1} and 22 cal K^{-1} mol^{-1} respectively. It is thus evident that the rate of oxidation in the two cases is controlled by the entropy of activation and not by the enthalpy of activation; the faster rate of oxidation by aquamanganese(III) ion is therefore due to the high positive ΔS value.

TABLE 4

Values of the rate-limiting constants k_a and k_b at different temperatures and the corresponding values of $\Delta H^‡$ and $\Delta S^‡$

θ_c/°C	20	25	30	35	40	$\Delta H^‡$ (kcal mol^{-1})	$\Delta S^‡$ (cal K^{-1} mol^{-1})
10^4k_a/dm^3 mol^{-1} s^{-1}	7.0	16.2	30.8	75.0	146	27.1 ± 0.7	20 ± 2
10^4k_b/dm^3 mol^{-1} s^{-1}	35.0	70.0	158	301	600	25.4 ± 0.8	17 ± 3

DISCUSSION

Whether, in the oxidation of a ketone, the electron is transferred by the keto- or the enol group cannot be determined by a direct comparison of the rate of oxidation with that of enolisation. The difficulty in such a comparison is that the measured rate of oxidation has a first-order dependence on the [oxidant] whereas the rate of enolisation has a zero-order dependence[17] on [oxidant] under similar conditions.

A suitable criterion evolved[3] for the purpose is to compare the second-order rate constant k_2 (= $k_{obs.}$/[cyclohexanone]) for oxidation with the second-order rate constant k_{2e} (=$k_{1e}/[H^+]$) for enolisation. The first-order rate constant k_{1e} is related to $k_{obs.}$ by the relation in equation (4) where $n = 2$. This assumption is based

$$k_{1e} = \frac{k_{obs.}[\text{Oxidant}]}{n[\text{Cyclohexanone}]} \tag{4}$$

on the fact that mercury(II) perchlorate oxidation of cyclohexanone is considered[17] to be a true measure of the initial rate of enolisation and that two equivalents of Hg^{2+} ions were used by each mole of the ketone.

Comparison of k_2 *with* k_{2e}.—The respective values of k_2 and k_{2e} at 25 °C were calculated for three values of $[H^+]$.† The required $k_{obs.}$ values were taken from Table 3 and $[Mn^{III}] = 3.6 \times 10^{-3}$ mol dm^{-3}, the maximum concentration of the oxidant used. These values are given in Table 5. A perusal of the k_2/k_{2e} ratio would indicate that it decreased with decreasing $[H^+]$ and that $k_2 \gg k_{2e}$. Hence it is concluded that the electron is transferred to aquamanganese(III) ions by the keto-group and not by the enol group, as reported in the

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* Throughout this paper: 1 cal = 4.184 J.

† However, if k_{1e} is calculated by taking $n = 6$, according to the stoicheiometry, in equation (4), the required k_2/k_{2e} ratio would be three times the reported ratio in Table 5. This would in no way affect the conclusions drawn; rather it would further strengthen them.

TABLE 5

Comparison of the rate constants k_2 and k_{2e}, both calculated at different $[H^+]$, at 25 °C (see text) ($10^3[Mn^{III}] = 3.6$, 10^2[cyclohexanone] = 4, and I = 4 mol dm^{-3})

$[HClO_4]$/ mol dm^{-3}	$10^4k_{obs.}$/ s^{-1}	10^5k_{1e}/ s^{-1}	10^5k_{2e}/ dm^3 mol^{-1} s^{-1}	10^3k_2/ dm^3 mol^{-1} s^{-1}	k_2/k_{2e}
0.9	5.7	2.6	2.86	14.3	500
2.0	2.7	1.2	0.61	6.7	1 100
3.0	1.8	0.8	0.27	4.5	1 670

oxidations by manganese(III) pyrophosphate[10] and manganese(III) acetate.[11]

Mechanism.—Having ascertained that cyclohexanone is oxidised in the keto-form, a simple mechanism, in view of the observed second-order kinetics and the retarding effect of $[H^+]$, could be written in terms of reactions (5)—(10). 2-Hydroxycyclohexanone which was isolated as the oxidation product from $[Fe(phen)_3]^{3+}$,[4] manganese(III) pyrophosphate,[10] and chromic acid[18] oxidations perhaps escaped detection in the present instance because of its faster oxidation. It should be noted that with vanadium(V), the hydroxy-ketone was oxidised almost 200 times faster than cyclohexanone itself.[19]

$$\text{Ketone} + H^+ \rightleftharpoons \text{Enol} + H^+ \quad (K_e) \qquad (5)$$

$$Mn^{3+}(aq) \rightleftharpoons [Mn(OH)]^{2+}(aq) + H^+ \quad (K_h) \qquad (6)$$

$$\text{Ketone} + Mn^{3+}(aq) \longrightarrow \text{Radical} + Mn^{2+}(aq) + H^+ \quad (k_a) \qquad (7)$$

$$\text{Ketone} + [Mn(OH)]^{2+}(aq) \longrightarrow \text{Radical} + Mn^{2+}(aq) + H_2O \quad (k_b) \qquad (8)$$

$$H_2O + \text{Radical} + Mn^{III} \longrightarrow \text{2-Hydroxycyclohexanone} + Mn^{II} + H^+ \text{ (fast)} \qquad (9)$$

$$2H_2O + \text{2-Hydroxycyclohexanone} + 4Mn^{III} \longrightarrow HOOC(CH_2)_4COOH + 4Mn^{II} + 4H^+ \text{ (fast)} \qquad (10)$$

At the suggestion of one of the referees, the oxidation products formed under kinetic conditions, *i.e.* when [cyclohexanone] ≫ $[Mn^{III}]$, were also characterised. Besides the adipic acid, described earlier, the other product detected was an α-diketone. This α-diketone was found in the chloroform washings obtained during the purification of adipic acid. The chloroform solution was treated with a solution of hydroxylamine hydrochloride and sodium acetate and warmed. A pink-red colour was obtained when this solution was treated with a 5% solution of nickel acetate, confirming the presence of an α-diketone.[20]

Hence the sequence of oxidation of cyclohexanone could be represented as cyclohexanone ⟶ 2-hydroxycyclohexanone ⟶ cyclohexane-1,2-dione ⟶ adipic acid.

The postulated presence of a radical in the reaction mixture was confirmed by the observed polymerisation of acrylonitrile when added to a partially oxidised reaction mixture. The reactant solutions and reaction mixtures were degassed with nitrogen before initiating the reaction and during the addition of the monomer. No polymerisation of the monomer was noted when it was added separately to the solutions of aquamanganese(III) ion and cyclohexanone.

The rate of disappearance of Mn^{III}, based on reactions (5)—(10), is given by (11). Since the value of K_e is[21] 4.1×10^{-6}, equation (11) could be written as (12). Equation (12) indicated that a plot of $k_{obs.}(1 + K_h[H^+]^{-1})$ against $[H^+]^{-1}$ should be linear with an intercept on the rate axis. The plot in Figure 3, although linear, has a negative intercept on extrapolation. Hence, reaction (5) was modified to reaction (13); the protonated ketone is considered to be an intermediate in the enolisation of the ketone. The protonation constant K_c has been determined by Wells[22] and has a value equal to one ($K_c = 1$ dm^3 mol^{-1}).

$$\frac{-d[Mn^{III}]}{dt} = \frac{6(k_a + k_bK_h[H^+]^{-1})[\text{Cyclohexanone}]_0[Mn^{III}]_0}{(1 + K_h[H^+]^{-1})(1 + K_e)} \qquad (11)$$

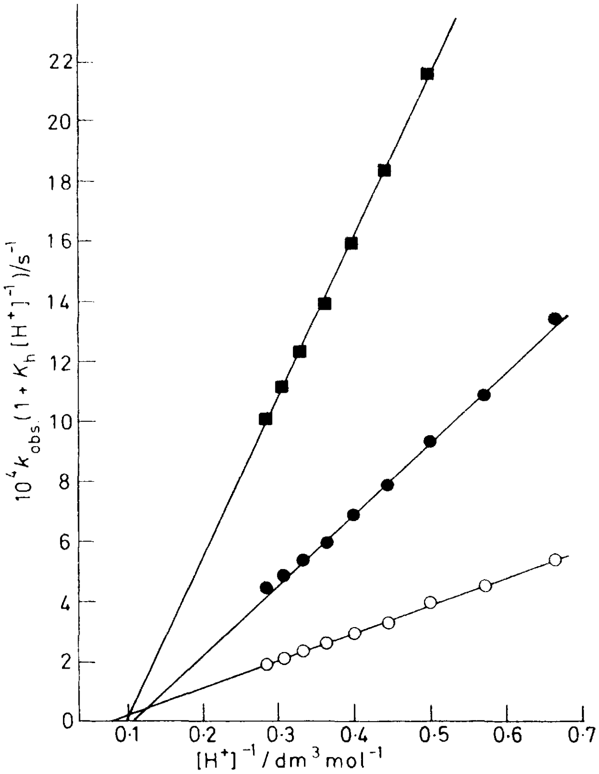
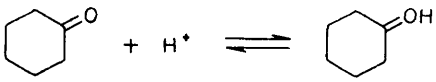


FIGURE 3 Plots of $k_{obs.}(1 + K_h[H^+]^{-1})$ against $[H^+]^{-1}$ at different temperatures. $10^3[Mn^{III}] = 2.0$, 10^2[cyclohexanone] = 4.0, and I = 4 mol dm^{-3}; 25 (○), 30 (●), and 35 °C (■)

$$k_{obs.} = \frac{6(k_a + k_bK_h[H^+]^{-1})[\text{Cyclohexanone}]_0}{(1 + K_h[H^+]^{-1})} \qquad (12)$$



(K_c) (13)

With the inclusion of reaction (13) in place of reaction (5), the rate law (12) is modified to (14) which indicated that a plot of the left-hand-side against $[H^+]^{-1}$ should be linear with an intercept. Such plots were linear at all temperatures and some of these are shown in Figure 2.

$$k_{\text{obs.}}(1 + K_h[H^+]^{-1})(1 + K_c[H^+]) = 6(k_a + k_b K_h[H^+]^{-1})[\text{Cyclohexanone}]_0 \qquad (14)$$

The value of K_h at different temperatures was obtained from the literature.[13] However, the K_c value was considered to remain constant. This assumption is based on the fact that the ρ value in the plots of log K_c against $\Sigma\sigma^*$, the sum of the Taft function,[23] is the same for primary alcohols, ketones, and carboxylic acids;[22] it can be assumed that for cyclohexanone the variation of K_c with temperature might also exhibit a similar broad maximum as observed in the case of alcohols.[24]

The values of the rate constants k_a (= intercept/6[cyclohexanone]) and k_b (= slope/$6K_h$[cyclohexanone]) were thus calculated and are given in Table 4. A perusal of these values indicated that $[Mn(OH)]^{2+}$(aq) is a stronger oxidant than Mn^{3+}(aq), although the enthalpy and entropy of activation values corresponding to these two ions are almost the same. The reason for the higher reactivity of penta-aquamanganese(III) ion, $[Mn(OH)]^{2+}$(aq), might be due to some kind of favourable positioning of –OH in the formation of a suitable ' bridge ' with the substrate on approaching the minimum distance.

As final support for the proposed outer-sphere mechanism, the spectrum of a manganese(III) solution, cyclohexanone solution, and a mixture of these was recorded in the visible region (330—800 nm). The aquamanganese(III) solution (0.002 6 mol dm^{-3}, $[HClO_4]$ = 3.0, $[Mn^{II}]$ = 0.07 mol dm^{-3}) exhibited a maximum near 470 nm; cyclohexanone had no absorbance in this region (a 0.04 mol dm^{-3} solution was used). The addition of cyclohexanone to the manganese(III) solution (concentrations as stated above) did not alter the spectrum. This is consistent with the outer-sphere oxidation of Pr^{i}OH,[25] Bu^{s}OH,[26] and cyclohexanol[26] by aquamanganese(III) ions. It is also reported that these alcohols, together with acetone, do not affect the spectrum of aquamanganese(III) ions.[27]

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REFERENCES

[1] Part 5, R. Nagori, M. Mehta, and R. N. Mehrotra, *J. Chem. Soc., Dalton Trans.*, 1979, 216.

[2] J. S. Littler, *J. Chem. Soc.*, 1962, 827.

[3] J. S. Littler, *J. Chem. Soc.*, 1962, 832.

[4] J. S. Littler and I. G. Sayce, *J. Chem. Soc.*, 1964, 2545.

[5] F. T. T. Ng and P. M. Henry, *J. Am. Chem. Soc.*, 1976, **98**, 3606.

[6] R. Cecil, J. S. Littler, and G. Easton, *J. Chem. Soc. B*, 1970, 626.

[7] J. Shorter and C. N. Hinshelwood, *J. Chem. Soc.*, 1950, 3276 and 3425.

[8] J. Shorter, *J. Chem. Soc.*, 1962, 1868.

[9] R. Venkatkrishnan and M. Santappa, *Z. Phys. Chem. (Frankfurt am Main)*, 1958, **16**, 73.

[10] A. Y. Drummond and W. A. Waters, *J. Chem. Soc.*, 1955, 497.

[11] R. van Halden and E. C. Kooyman, *Recl. Trav. Chim. Pays-Bas*, 1961, **80**, 57; R. van Halden, A. F. Bickel, and E. C. Kooyman, *ibid.*, pp. 1237 and 1257.

[12] H. Diebler and N. Sutin, *J. Phys. Chem.*, 1964, **68**, 174.

[13] C. F. Wells and G. Davies, *J. Chem. Soc. A*, 1967, 1858.

[14] ' Hand-book of Physics and Chemistry,' 43rd edn., The Chemical Rubber Publishing Co., Cleveland, Ohio, 1961, (*a*) 944—945; (*b*) 786.

[15] M. Mehta, R. R. Nagori, and R. N. Mehrotra, *J. Chem. Soc., Dalton Trans.*, 1979, 211.

[16] T. J. Kemp and W. A. Waters, *J. Chem. Soc.*, 1964, 339.

[17] A. J. Green, T. J. Kemp, J. S. Littler, and W. A. Waters, *J. Chem. Soc.*, 1964, 2722.

[18] J. Rocek and Sr. A. Riehl, *J. Org. Chem.*, 1967, **32**, 3569.

[19] J. S. Littler and W. A. Waters, *J. Chem. Soc.*, 1959, 3014.

[20] F. Feigl, ' Spot Tests in Organic Analysis,' Elsevier, Amsterdam, 1960, 216.

[21] R. P. Bell and P. W. Smith, *J. Chem. Soc. B*, 1966, 241.

[22] C. F. Wells, *Trans. Faraday Soc.*, 1967, **63**, 147.

[23] R. W. Taft, in ' Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956, ch. 13.

[24] C. F. Wells, *Trans. Faraday Soc.*, 1965, **61**, 2194.

[25] C. F. Wells and C. Barnes, *Trans. Faraday Soc.*, 1967, **63**, 2737.

[26] C. F. Wells, C. Barnes, and G. Davies, *Trans. Faraday Soc.*, 1968, **64**, 3069.

[27] C. F. Wells, D. Mays, and C. Barnes, *J. Inorg. Nucl. Chem.*, 1968, **30**, 1341.