# Kinetics and Mechanism of the Oxidation of Formaldehyde by Permanganate Ion In Aqueous Perchloric Acid

**Y.N. Lohdip & A.K. Davies**
**Department of Chemistry & Applied Chemistry, University of Salford, M5 4WT, England.**


*And*


**J.F. Iyun**
**Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria.**

## ABSTRACT

The kinetics of the oxidation of formaldehyde by permanganate ion has been investigated in aqueous perchloric acid medium. The rate of the reaction was found to be acid dependent and the empirical rate law given as follows;

$$-\frac{d[HCHO]}{dt} = \{a + b[H^+]\}[HCHO][MnO_4^-]$$

$a = 1.17 \times 10^4 s^{-1}$, $b = 6.71 \times 10^{-2} mol^{-1}dm^3s^{-1}$; at $[H^+] = 0.05 mol\ dm^{-3}$; $I = 0.5 mol\ dm^{-3}$, $\lambda = 635nm$, $T = 25 \pm 0.1^{\circ}C$

The activation parameters were evaluated as, $E_a = 45.18 KJmol^{-1}$; $\Delta H^{\#} = 42.76\ KJmol^{-1}$ and $\Delta S^{\#} = -168.55 Jmol^{-1}K^{-1}$. The outer--sphere pathway was proposed for the title reaction.

## INTRODUCTION

The permanganate ion has several advantages as an analytical reagent (Insauti, et. al., 1995). Thus it is a strong vividly coloured oxidant, serving as its own indicator. It reacts very rapidly with U(VI), $PtCl_4^{2-}$ Ti (III) and V(IV) (Iyun & Ajibade, 1992) and the inner sphere mechanism has been suggested for such reactions. It has also been suggested that aliphatic ketones are oxidized by acid permanganate via the enol form (Banerji, 1973). There is also the possibility that the oxidation of aliphatic aldehydes by $MnO_4$ and other oxyanions may involve similar enol intermediates.

In a quest for more understanding of the reactions of aldehydes, the authors have investigated and reported the results of the redox reactions between HCHO and $BrO_3$ (Lohdip *et al.*, 1995), $CH_3CHO$ and $MnO_4$ and $Cr_2O_7^{2-}$ (Iyun & Ajibade, 1992) and $CH_3CHO$ and $BrO_3$ (Lohdip *et al.*, 1996). In this paper, the results of the $HCHO/MnO_4^-$ system are presented.

## EXPERIMENTAL WORK

### Materials

Standard solutions of formaldehyde (Analar) were prepared before use. Potassium permanganate (Analar) solution was prepared and standardized using the conventional method (Bassett *et al.*, 1982). Perchloric acid was used as the acid medium and for investigating the effect of hydrogen ion on the rate, while sodium perchlorate was used to maintain the ionic strength constant at 0.5 mol $dm^{-3}$. All other chemicals were used as supplied.

### Stoichiometry

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method. Reaction mixtures containing varying ratios of HCHO and $MnO_4$ at $(H^+) = 0.05$ mol $dm^{-3}$, $I = 0.5$ mol $dm^{-3}$ ($NaClO_4$) were allowed to stand until the reaction had gone to completion. The absorbances of the solutions were then measured at 635 mm and the stoichiometry was evaluated from the plot of the absorbance versus mole ratio.

### Kinetics

All kinetic measurements were conducted under pseudo-first-order conditions with the concentration of formaldehyde maintained in large excess over the permanganate-ion concentration. The reaction was followed by monitoring the rate of change of absorbance of the reaction mixture at 635 nm using the solid state photometer (Trojanowicz *et al.*, 1988; Lohdip *et al.*, 1997). Pseudo-first-order rate constants were obtained from the plots of log $(A_0 - A_t)$ versus time (where Ao and At are the absorbances at time zero and time t respectively). The temperature was maintained constant at $25.0 \pm 0.1^{\circ}C$ for all runs, $(H^+) = 0.05$ mol $dm^{-3}$, and $I = 0.5$ mol $dm^{-3}$ ($NaClO_4$), unless otherwise stated.

## RESULTS AND DISCUSSION

### Stoichiometry

The stoichiometry of the reaction between HCHO and $MnO_4^-$ was found to be in the ratio 5:2 and represented by equation(1).

$$5HCHO + 2MnO_4^- + 6H^+ \rightarrow 5HCOOH + Mn^{2+} + 3H_2O \qquad (1)$$
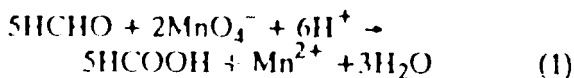
This stoichiometric equation is in agreement with earlier reports involving similar systems (Iyun & Ajibade, 1992; Lohdip et al., 1995; Lohdip *et al.*, 1996; Hassan, 1991). The products of the reaction were qualitatively identified, i.e. $Mn^{2+}$ by indole (Ayoko et al. 1992) and HCOOH by reacting with $NaHCO_3$ and testing with lime water (Iyun & Ajibade, 1992; Lohdip et al., 1995; Lohdip *et al.*, 1996).

### Order of reaction

Pseudo-first-order plots of log $(A_0 - A_t)$ versus time were linear to more than 70% of the extent of reaction indicating first order in $[MnO_4^-]$. Least squares plot of the pseudo-first-order rate constants $k_0$ versus $[MnO_4]$ was linear (r = 0.96) and a slope of about

unity was obtained, confirming first order in $(MnO_4^-)$. The second-order-rate constants $k_2$, obtained as $k_2 = k_0 / [MnO_4^-]$ were fairly constant (Table 1), indicating that the reaction is also first order in [HCHO]. Therefore, the rate equation for the reaction can be written as in equation (2):

$$-\frac{d[HCHO]}{dt} = k_2 [HCHO][MnO_4^-] \quad (2)$$

$$k_2 = (2.29 \pm 0.30) \times 10^2 mol^{-1}dm^3s^{-1}.$$

### Acid dependence

The influence of $H^+$ on the rate of the reaction was determined by varying $HClO_4$ in the range 0.01 - 0.15 mol $dm^{-3}$ with ionic strength kept constant at 0.5 mol $dm^{-3}$. The values of the acid dependent rate constants are given in Table 1. A least squares plot of $k_2$ versus $[H^+]$ was linear (r=0.94) with a positive intercept and the relationship fitted into equation (3).

$$k_2 = a + b[H^+] \quad (3)$$

$$a = 1.17 \times 10^4 s^{-1}.$$

$b = 6.71 \times 10^{-2} mol^{-1}dm^3s^{-1}$, so that the rate equation becomes;

$$-\frac{d[HCHO]}{dt} =$$

$$\{a + b[H^+]\}[HCHO][MnO_4^-] \quad (4)$$

### $Mn^{2+}$ dependence

The effect of $Mn^{2+}$ on the reaction rate was studied and results presented in Table 1. Least squares plot of $k_0$ versus $[Mn^{2+}]$ was linear (r = 0.99) and the relationship is given in equation (5).

$$k_0 = c + d[Mn^{2+}] \quad (5)$$

It has been reported (Hassa, 1991), that acidified $MnO_4^-$ is reduced by $Mn^{2+}$ to give intermediate forms as exemplified by equation (6), so that if the intermediate manganese species are the active oxidizing species, the addition of $Mn^{2+}$ should cause an acceleration of the reaction rate (Radhakrishnamurti & Sabu, 1977).

$$MnO_4^- + 3Mn^{2+} + 8H^+$$
$$\rightarrow 3Mn^{3+} + Mn^{4+} 4H_2O \quad (6)$$
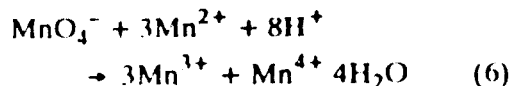
In our reaction system, the rate increased with increase in the concentration of added $Mn^{2+}$ which suggests that $Mn^{7+}$ may be converted to the products via the intermediate manganese ions. This was confirmed by the observed disappearance of the induction period. Metal catalysis has also been observed for some Oxyanion reaction systems (Ayoko et al., 1992; Iyun et al., 1992a, b)

### Ionic strength dependence

The rate was found to increase with increase in the ionic strength of the medium in the range 0.15 -1.95 mol $dm^{-3}$ (Table 1). The positive salt effect is an indication that the rate determining steps or one such steps involve(s) charged ions or an ion and a neutral molecule (Hassan 1991) which is in agreement with our experiential results.

### Added anion dependence

The effect of added formate and acetate ions on the rate was investigated and found to retard the rate. A plot of the added anion dependent rate constants versus the anion concentration is give in Figure 1. This dependence is similar to an earlier report (Hassan, 1991) and is suggestive of the outer sphere pathway.

*Y. N. Lohdip, A. K. Davies and J. F. Iyun*

## Table I

### Rate Constants for the Oxidation of Formaldehyde by Permanganate Ion In Aqueous perchloric Acid

$[HCHO] = 6.7 \times 10^{-2} mol\ dm^{-3}$, $\quad \lambda = 635\ nm$, $\quad$ Temperature $= 25.0 \pm 0.1^{\circ}C$

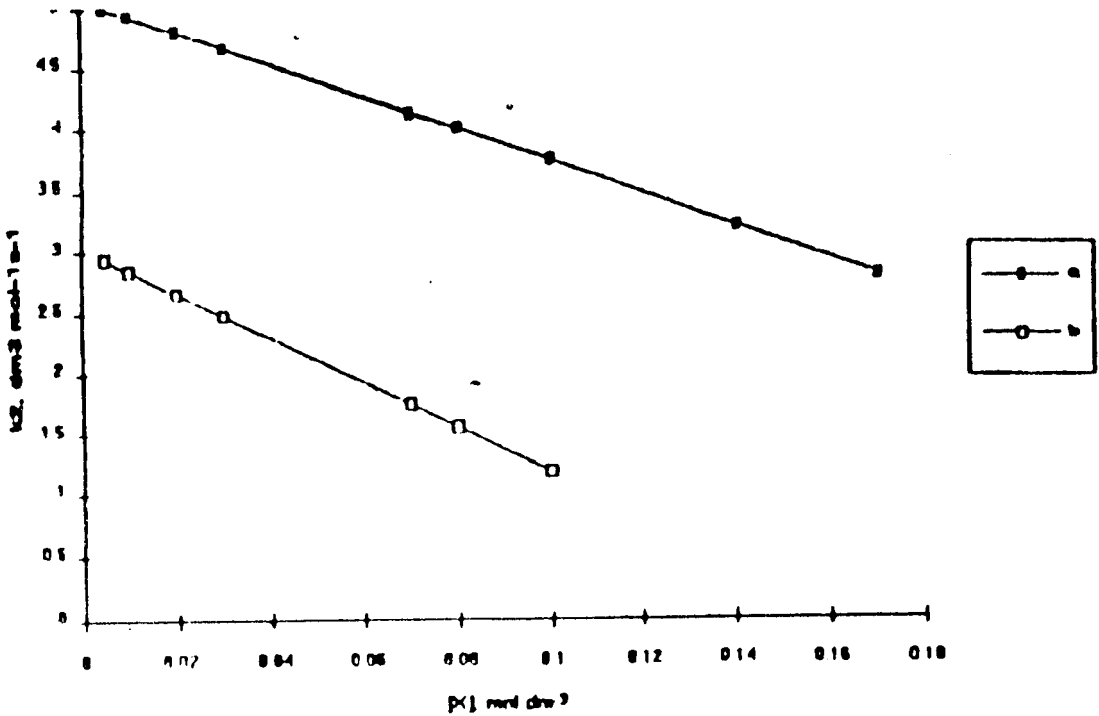| $10^4[MnO_4^-]$, mol dm$^{-3}$ | $10^2[H^+]$, mol dm$^{-3}$ | I, mol dm$^{-3}$ | $10^4[Mn^{2+}]$, mol dm$^{-3}$ | $k_2$, dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|
| 8.0 | 5.0 | 0.5 | - | 2.78 |
| 12.0 | 5.0 | 0.5 | - | 2.47 |
| 16.0 | 5.0 | 0.5 | - | 1.97 |
| 20.0 | 5.0 | 0.5 | - | 2.10 |
| 24.0 | 5.0 | 0.5 | - | 2.13 |
| 8.0 | 1.0 | 0.5 | - | 2.05 |
| 8.0 | 3.0 | 0.5 | - | 2.96 |
| 8.0 | 8.0 | 0.5 | - | 3.83 |
| 8.0 | 10.0 | 0.5 | - | 7.31 |
| 8.0 | 12.0 | 0.5 | - | 11.05 |
| 8.0 | 15.0 | 0.5 | - | 13.60 |
| 8.0 | 5.0 | 0.15 | - | 2.06 |
| 8.0 | 5.0 | 0.25 | - | 2.24 |
| 8.0 | 5.0 | 0.35 | - | 2.28 |
| 8.0 | 5.0 | 0.45 | - | 2.36 |
| 8.0 | 5.0 | 0.55 | - | 2.39 |
| 8.0 | 5.0 | 0.65 | - | 2.51 |
| 8.0 | 5.0 | 0.75 | - | 2.70 |
| 8.0 | 5.0 | 0.95 | - | 2.95 |
| 8.0 | 5.0 | 1.95 | - | 3.86 |
| 8.0 | 5.0 | 0.5 | 1.0 | 2.83 |
| 8.0 | 5.0 | 0.5 | 2.0 | 2.93 |
| 8.0 | 5.0 | 0.5 | 5.0 | 4.11 |
| 8.0 | 5.0 | 0.5 | 8.0 | 5.26 |
| 8.0 | 5.0 | 0.5 | 10.0 | 7.75 |

**Fig. 1**

Plot of $k_2$ versus $(X^-)$ for the Oxidation of Formaldehyde by Permanganate Ion in Aqueous Perchloric Acid: (a) $X = HCOO$; (b) $X = CH_3COO$; $[H^+] = 0.05$ mol dm$^{-3}$; $(MnO_4^{-3}) = 8.0 \times 10^{-4}$ mol dm$^{-3}$; $(HCHO) = 6.7$ mol dm$^{-3}$; $1 = 0.5$ mol dm$^{-3}$, $\lambda = 635$ nm, $T = 25 \pm 0.1°C$.

**Temperature dependence**

The effect of temperature on the rate of the reaction was studied over a temperature range of $11°C - 23°C$ and the rate was found to be dependent on change in temperature. Least squares analysis of the plots of ln $k_0$ versus $T^{-1}$ and ln($K_v/T$) versus $T^{-1}$ gave the following values of the activation parameters: $E_a = 45.18$ KJmol$^{-1}$; $\Delta H^{\#} = 42.76$ KJmol$^{-1}$ and $\Delta S^{\#} = -168.55$ Jmol$^{-1}$K$^{-1}$.

**Reaction mechanism**

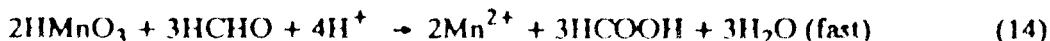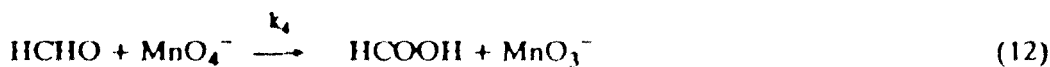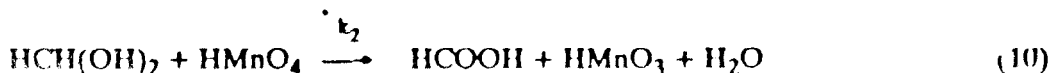The redox reactions of many oxyanions have been observed to have strong depend-

ence on acid concentration (Iyun *et al.*, 1992a, b). Under the experimental conditions, therefore, it is reasonable to postulate that $MnO_4^-$ is protonated in a fast step to give $HMnO4$ which then reacts with HCHO in a slow step to give the products (Hassan, 1991; Sen et al., 1995).

$$MnO_4^- + H^+ \xrightarrow{K_1} HMnO_4 \qquad (7)$$
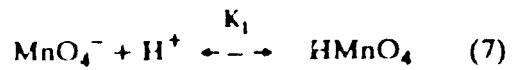
$K_1 = 2.29 \times 10^3$ dm$^3$ mol$^{-1}$ at $25°C$

The intercept obtained for the plot of $k_2$ versus $[H^+]$ indicates that the unprotonated $MnO_4^-$ also reacts with HCHO to from the

products. In similar reaction systems, (Lohdip et al., 1995; 1996), [$H^+$] dependence has also been ascribed to the substantial and rapid hydrolysis of aliphatic aldehydes. From the statement above, the following scheme is proposed for the reaction;

$$MnO_4^- + H^+ \xleftarrow{K_1}\rightarrow HMnO_4 \tag{7}$$

$$HCHO + H_2O \xleftarrow{K_2}\rightarrow HCH(OH)_2 \tag{8}$$

$$HCH(OH)_2 + MnO_4^- \xrightarrow{k_1} HCOOH + MnO_3^- + H_2O \tag{9}$$

$$HCH(OH)_2 + HMnO_4 \xrightarrow{k_2} HCOOH + HMnO_3 + H_2O \tag{10}$$

$$HCHO + HMnO_4 \xrightarrow{k_3} HCOOH + HMnO_3 \tag{11}$$

$$HCHO + MnO_4^- \xrightarrow{k_4} HCOOH + MnO_3^- \tag{12}$$

$$MnO_3^- + H^+ \longrightarrow HMnO_3 \text{ (fast)} \tag{13}$$

$$2HMnO_3 + 3HCHO + 4H^+ \rightarrow 2Mn^{2+} + 3HCOOH + 3H_2O \text{ (fast)} \tag{14}$$
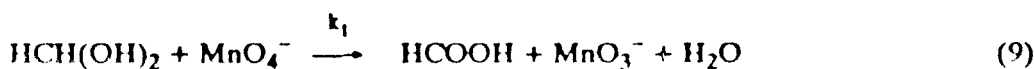
From the above scheme (7) - (14), the rate of loss of HCHO is expressed by equation (15)

$$\frac{d[HCHO]}{dt} = \left\{ \left(k_1K_2 + k_4\right) + \left(k_2K_1K_2 + k_3K_1\right)\left[H^+\right] \right\}\left[HCHO\right]\left[MnO_4^-\right] \tag{15}$$

Equation (15) is similar to equation (4) with $(k_1K_2 + k_4) = a$ and $(k_2K_1K_2 + k_3K_1) = b$, $K_1 = 2.29 \times 10^{-3}$ dm$^3$ mol$^{-1}$ at 20°C.

In trying to assign mechanistic pathway for this reaction the following points are considered:

i.  The inhibition of the rate of this reaction by the presence of added formate and acetate ions tends to suggest that the reaction occurs via the other sphere pathway. The $Mn^{2+}$ Catalysis is also in support of this mechanism.

ii. The absence of gel formations after addition of a solution of acrylamide to a partially oxidized reaction mixture suggests the absence of a free radical intermediate in the reaction. Alternatively if such a radical is formed it may have a very small formation constant so that it cannot be a major species in the

determining step. This evidence is also in support of the outer sphere mechanism.

iii. There was no change in $\lambda_{max}$ from 635 nm when the absorbance of the reaction mixtures were recorded one minute after mixing at different wave lengths. This evidence is against the inner sphere pathway, where a pre-electron transfer association exists between the reactants.

iv. Michealis-Menten Plot of $1/k_0$ versus $1/[MnO_4^-]$ was liner with an insignificant intercept which suggests that inner-sphere intermediate or ion-pair intermediate is unimportant in this reaction.

The evidence provided in (i) - (iv) above, is in support of the outer sphere mechanism and so this pathway is hereby proposed for the reaction

## CONCLUSION

The rate of oxidation of formaldehyde by permanganate ion was found to be dependent acid, added cation and anion concentrations. Other evidence was in support of the outer sphere mechanism and so this pathway was proposed for the process.

## ACKNOWLEDGMENT

## REFERENCES

Arabel, J.M., Ayoko, G.A. and Singh, K. (1997). Unpublished material

Ayoko, G. A., Iyun, J.F. and El-Idris, I.F. (1992). "Electron transfer at tetrahedral cobalt(II) Part III Kinetics of copper (II) ion catalysed reduction of periodate". *Transition. Met. Chem.* 17, p. 423 - 425.

Banarji, K.K. (1973). "kinetics and mechanism of oxidation of aliphatic aldehydes by acid permanganate'. *Indian. J. Chem.*, 11, p. 242.

Bassett, J., Denney, R. C.; Jeffery, G. C., Jeffert, G.H. and Mandham, J. (1982). *Vogels textbook of quantitative inorganic analysis: including elementary instrumental analysis* The E.L. B.S and Longman, London. p. 352 -354.

Insausti, F.; Mata-Perez, and Alvare-Macho, M.P. (1995). "Kinetic studies of the oxidation of L-Phenylalanine by potassium permanganate in acid medium", Int. *J Chem. Kinet.* 27, p. 507.

Hassan, R. M. (1991). "Kinetics and mechanism of oxidation of DL-α-alanine by permanganate ion in acid perchlorate media". *Can J. Chem.* 69, p. 2018.

Iyun, J.F. and Ajibade, F. (1992). "The kinetics and the mechanism of the oxidation of acetaldehyde by dichromate and permanganate ions in aqueous acidic medium", *J. Chem. Soc Nigeria,* 17, p. 35.

Iyun, J.F., Ayoko, G. A.; Lawal, H.M. (1992a) "Kinetics and mechanism of the oxidation of iodide by diaquotetrakis (2,2'-Bipyridine)-μ-oxodiruthenium (III) ion in acid medium." *Transition. Met. Chem.* 17, p. 63 -65.

Iyun, J.F., Ayoko, G.A. and Lohdip, Y.N. (1992b). "The kinetics and mechanism of the oxidation of diaquotetrakis (2,2'-bipyridne) -U-oxodiruthenium (III) ion by bromate in

aqueous perchloric acid". *Polyhedron.*, 11 (18), p. 2389-2394.

Lohdip, Y.N., Iyun J. F and Mutihir, J.I. (1995). "Kinetics of the oxidation of formaldehyde by bromate ion in aqueous perchloric acid". *Ghana. J. Chem.*, Vol. 1. No 11.

Lohdip, Y.N., Davies A.K. and J.F. Iyun (1996). "Kinetics and mechanism of the oxidation of acetaldehyde by bromate ion in aqueous perchloric acid". *Nigerian. J. Chem. Research.* 1, p. 49.

Lohdip, Y.N., Davies, A.K. and Iyun, J. F. (1997). "Construction and evaluation of a solid state Photometer as an alternative to conventional spectrophotometer". *Nigerian. J. Chem. Res.* In Press.

Radhakrisnam·irti, P.S. and Sahu, B. (1977). "Kinetics of Os (VIII)-catalysed oxidation of benzaldehyde and substituted benzaldehydes by chloramine-T". *Indian. J. Chem* 15A, p. 700.

Sen, P.K., Sanyal, A and Gupta, K.K.S. (1995). "Evidence of protonation during the Oxidation of some aryl alcohols by permanganate in perchloric acid medium and mechanism of the oxidation". *Int. J. Chem. Kinet*, 27, p. 389.

Trojanowicz, M.; Worsfold, P.J. and J.R. Clinch (1988). "Solid-state photometric detectors for flow injection analysis". *Trends. Anal. Chem.* 7 (8), p. 302-305.