Indian Journal of Chemistry
Vol. 22A, March 1983, pp 244-245

Interaction of Alkaline Permanganate with Chloramine-T—A Kinetic Study[a]

S. VIVEKANANDAN[b], K. VENKATARAO &
M SANTAPPA[c]

Department of Physical Chemistry, University of Madras,
Guindy Campus, Madras 600 025

and

Sp. SHANMUGANATHAN*[d]

Department of Chemistry, Pachaiyappa's College,
Madras 600 030

Received 16 *June* 1982; *revised* 25 *september* 1982;
accepted 3 *November* 1982

The kinetics of oxidation of chloramine-T (CAT) by alkaline permanganate, studied spectrophotometrically, shows first order in [CAT] and fractional order in $[MnO_4^-]$. Michaelis-Menten kinetics has been observed with varying $[OH^-]$. Added complexing agents like pyrophosphate and fluoride have no effect on the kinetics. The rate increases in presence of added Cl^-. The reaction has an activation energy of 27.6 kJ mol^{-1} and a positive salt effect. A suitable mechanism has been proposed.

Chloramine-T (CAT) is known to function as (i) an oxidant and a chlorinating agent[1,2], (ii) a free radical generator in chlorinative oligomerisation[3], and (iii) a decarboxylative chlorinating agent[4,5] in aqueous sulphuric acid. Its function as a reductant in its reaction with transition metal oxyanions like permanganate in sulphuric acid solutions has been recently reported by us[6]. The title investigation is an extension of our earlier work on the reaction of CAT with permanganate in acid medium[6].

The reaction was initiated in a pyrex boiling tube kept in a thermostat (±0.1°C), the reaction mixture quickly transferred to the thermostated quartz cell of 1 cm path length and the absorbance of the solution measured at 416 nm on a Carl Zeiss SPECORD UV/VIS spectrophotometer for every minute upto about 15 min when the rate started levelling off. Basic kinetics was established from the initial slopes of the absorbance versus time plots.

In alkaline medium, permanganate oxidations involve the loss of three electrons from the oxidant[7]. However, other species like Mn(VI), Mn(V), O^-, HO_2^- and HO^- have also been proposed as oxidising species in this system[8]. Absence of sigmoid-shaped reaction-time curves (Fig. 1) and the rate being completely unaffected by the addition of complexing agents like fluoride (0 to 14.4×10^{-3} mol dm^{-3}) and pyrophosphate (1.35 to 10.8×10^{-3} mol dm^{-3}) are characteristics of permanganate oxidations suggesting the non-involvement of ions of intermediate oxidation states but only direct attack by MnO_4^- (ref 9,10). Like in some earlier investigations on alkaline permanganate oxidations[11,12], difficulties were also encountered in the present study during the determination of stoichiometry and analysis of products.

In the presence of dilute sodium hydroxide (0.009 mol dm^{-3}) and excess [CAT] (1:10), the order in [CAT] was unity while that in $[KMnO_4]$ was 0.66. Michaelis-Menten kinetics was noticed when $[OH^-]$ was varied suggesting the formation of an alkali-permanganate complex. A plot of log $(\text{rate})_i$ versus $\sqrt{\mu}$ gave a slope of 0.45 (Fig. 2). Between 30° and 50°C, a low overall activation energy (27.6 kJ mol^{-1}) was obtained supporting the fastness of the process. Another distinct feature was the absence of induction period. Hence an entirely new course of reaction under alkaline conditions is suggested as shown in Scheme 1, taking into account the failure to detect in this system the products *p*-toluenesulphonyl chloride and chlorine obtained in the acid medium experiments[6].

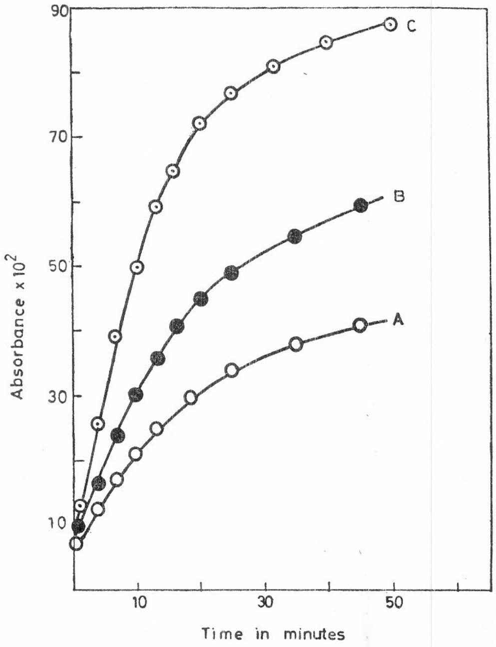

Fig. 1—Typical absorbance versus time plots $\{[KMnO_4]=5.561 \times 10^{-4}$ mol dm^{-3}; $[OH^-]=8.55 \times 10^{-3}$ mol dm^{-3}; $\mu=0.5$ mol dm^{-3}; $\lambda=416.7$ nm; temp.=35°C; [CAT]=(A) 4.86×10^{-3} mol dm^{-3}; (B) 7.28×10^{-3} mol dm^{-3}; (C) 11.1×10^{-3} mol dm^{-3}.$\}$

---

[a] Presented at the Sixth Annual Symposium in Chemistry, 1981, Madras.

[b] Department of Chemistry, Pachaiyappa's College, Madras 600 030.

[c] Vice-Chancellor, University of Madras, Madras 600 005.

[d] Dean, College Development Council, University of Madras, Centenary Buildings, Chepauk, Madras 600 005.

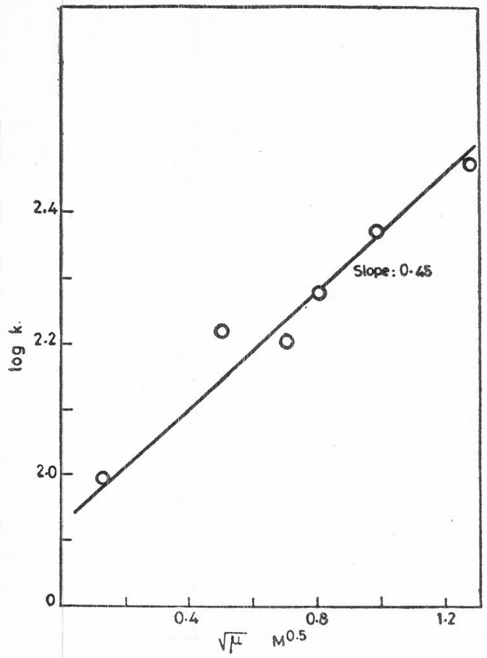

Fig. 2—Effect of varying ionic strength on reaction rate {[KMnO$_4$]=5.56 × 10^{-4} mol dm^{-3}; [CAT]=4.86 × 10^{-3} mol dm^{-3}; [OH$^-$]=8.55 × 10^{-5} mol dm^{-3}; temp=35°C.}

$$MnO_4^- + OH^- \overset{K}{\rightleftharpoons} APM^* \qquad \ldots(1)$$

$$APM \xrightarrow{k_1} HMnO_4^- + O^- \qquad \ldots(2)$$

$$\qquad\qquad \downarrow\uparrow H^+$$

$$\qquad\qquad OH^{\cdot}$$

$$R\bar{N}Cl + OH^{\cdot} \xrightarrow{k_2} R\dot{N}H + Cl^- + O \qquad \ldots(3)$$

$$R\dot{N}H + H_2O \xrightarrow{k_3} RNH_2 + OH^{\cdot} \qquad \ldots(4)$$

$$MnO_4^- + Cl^- \xrightarrow{k_4} MnO_4Cl^{2-} \qquad \ldots(5)$$

$$MnO_4Cl^{2-} + OH^- \xrightarrow{k_5} HMnO_4^{2-} + OCl^- \qquad \ldots(6)$$

$$2OH^{\cdot} \xrightarrow{k_6} H_2O + O \qquad \ldots(7)$$

$$2HMnO_4^- \xrightarrow{k_7} MnO_4^- + H_2MnO_4^- \qquad \ldots(8)$$

*APM refers to the alkali-permanganate complex

Scheme 1

Assuming Mn(V) as the reacting species, the rate of the reaction is given by Eq. (9).

$$\frac{d\,[Mn(V)]}{dt} = k_4[MnO_4^-][Cl^-] + k_7[HMnO_4^-]^2 \qquad \ldots(9)$$

Under steady-state conditions Eq. (9) takes the form

$$\frac{d\,[Mn(V)]}{dt} = k_2\,[R\bar{N}Cl][OH^{\cdot}] + k_1\,[APM] \qquad \ldots(10)$$

Substituting [APM] in terms of K, we get Eq. (11)

$$\frac{d\,[Mn(V)]}{dt} = k_2\,[R\bar{N}Cl]\left\{\frac{k_1}{k_6}\cdot\frac{k\,[MnO_4^-][OH^-]}{1+K\,[OH^-]}\right\}^{\frac{1}{2}} + \frac{k_1K\,[MnO_4^-]\,[OH^-]}{1+K[OH^-]} \qquad \ldots(11)$$

Equation (11) explains the observed orders. On rearranging we get

$$\frac{d\,[Mn(V)]/dt}{[MnO_4^-]^{1/2}} = k_2\,[R\bar{N}Cl]\left\{\frac{k_1}{k_6}\cdot\frac{K[OH^-]}{1+K[OH^-]}\right\}^{\frac{1}{2}} + \frac{k_1K\,[MnO_4^-]^{1/2}[OH^-]}{1+K[OH^-]} \qquad \ldots(12)$$

A plot of rate/$[MnO_4^-]^{1/2}$ against $[MnO_4^-]^{1/2}$ is linear with an intercept showing the first term to be predominant on the right hand side of Eq. (12) Hence, omitting the second term, Eq. (12) could further be rearranged to Eq. (13)

$$\frac{1}{\left\{\frac{d\,[Mn(V)]}{dt}\right\}^2} = \frac{k_6}{k_1k_2^2\,K[R\bar{N}Cl]^2[MnO_4^-][OH^-]} + \frac{k_6}{k_1k_2^2\,[R\bar{N}Cl]^2\,[MnO_4^-]} \qquad \ldots(13)$$

As expected from Eq. (13) a plot of 1/(rate)^2 versus 1/[OH$^-$] is linear. The suggested scheme is justified by the increase in rate observed (from 1.56 × 10^{-2} a.u. to 2.54 × 10^{-2} a.u.) in presence of Cl$^-$ (8.00 × 10^{-3} mol dm^{-3}).

SV thanks the UGC, New Delhi, for the award of a teacher fellowship.

References

1 Jennings V J, *CRC Crit Rev Anal Chem*, **3** (1974) 407.
2 Campbell M M, & Johnson G, *Chem Rev*, **78** (1978) 65.
3 Vivekanandan S, Venkatarao K, Santappa M & Shanmuganathan Sp, *Indian J Chem*, **16A** (1978) 519.
4 Vivekanandan S, Venkatarao K, Santappa M, & Shanmuganathan Sp, *Indian J Chem*, **18A** (1979) 503.
5 Vivekanandan S, Venkatarao K, Santappa M, & Shanmuganathan Sp, *Indian J Chem*, **19A** (1980) 364.
6 Vivekanandan S, Venkatarao K, Santappa M, & Shanmuganathan Sp, *Indian J Chem*, **20A** (1981) 86.
7 Waters W A, *Quart Rev*, **12** (1958) 277.
8 Wiberg K B, Stewart R, *J Am chem Soc*, **78** (1956) 1214.
9 Cullis C F, Ladbury J W, *J chem Soc*, (1955) 555, 1407, 2850, 4116.
10 Hinshelwood C N, *Trans chem Soc*, **115** (1919) 1180.
11 Drummond A Y & Waters W A, *J chem Soc*, (1953) 435, 2836, 3119.
12 Browne A W, *J Am chem Soc*, **31** (1909) 221.