

Kinetics of chromic acid-oxalic acid reaction catalysed by manganese(II)— Kinetic analysis of the consecutive pathway

P V Subba Rao*, G S R Krishna Rao, K Ramakrishna & P S N Murthy
School of Chemistry, Andhra University, Visakhapatnam 530 003

Received 21 February 1990; revised 7 August 1990; accepted 18 September 1990

Manganese(II) catalyses the chromic acid-oxalic acid reaction. The absorbance of the mixture of Cr(VI), oxalate and Mn(II) (at 480 nm) increases with time, reaches a maximum and thereafter decreases with time and this has been shown to be due to the consecutive path-way, $A \xrightarrow{k_a} I \xrightarrow{k_b} C$. $D_{\max}$ is directly proportional to $[Cr(VI)]_0$. k_a varies with variation in $[Mn(II)]_0$ and $[OX]_0$ whereas k_b is unaffected by variation in $[Mn(II)]_0$. Mechanism of the consecutive pathway has been proposed.

Unlike in many chromium(VI) oxidations, manganese(II) catalyses the chromic acid-oxalic acid reaction¹⁻⁵. Ayyar⁴ and Chakravarty and Ghosh⁵ obtained evidence for Mn(III)-oxalate complex as an intermediate which undergoes intramolecular electron-transfer. It has also been shown⁶ that Mn(II) is oxidised to Mn(III)-oxalate quantitatively by chromium(VI) in the presence of excess of oxalate. However, no kinetic analysis of this consecutive pathway has been so far made and we present that in this paper.

Materials and Methods

All the solutions were prepared in doubly distilled water. Stock solutions (10^{-1} mol dm⁻³) of chromium(VI), oxalic acid and manganese(II) were standardised using standard methods. Ionic strength was maintained using sodium perchlorate solution (2 mol dm⁻³).

The intermediate Mn(III)-oxalate complex has been found to have strong absorbance at 480 nm and hence the consecutive pathway was monitored by measuring the absorbance at this wavelength at different time intervals using a Hilger-UVispek spectrophotometer with thermostatic attachment. The absorption spectra were scanned using Milton-Roy spectronic-1201 spectrophotometer with microprocessor arrangement. The kinetic runs were carried out in the presence of sodium oxalate/oxalic acid buffer (pH 2.2-2.5).

Results and Discussion

The absorbance of the reaction mixture increases with increase in reaction time, reaches a maximum value and thereafter decreases (Fig. 1). Further, $D_{\max}$ is directly proportional to $[Cr(VI)]_0$. These results

point to the consecutive pathway $A \xrightarrow{k_a} I \xrightarrow{k_b} C$,

where A represents Cr(VI), I, the Mn(III)-oxalate complex and C the product(s). The [I] is given by Eq. (1)

$$[I] = \frac{k_a [Cr(VI)]_0}{(k_b - k_a)} (e^{-k_a t} - e^{-k_b t}) \quad \dots (1)$$

Two rigorous methods are available^{7,8} in support of the consecutive pathway. In the first method the plot of $\log P$ (where $P = D_t - D_{\infty}$) versus time is generally curved at early t but becomes linear at later t (Fig. 1). Thus the plot can be described by Eq. (2),

$$\log P = -k_{\text{slow}} t + \text{constant} \quad \dots (2)$$

from which k_{slow} can be determined. Now the linear plot is extended to early t and the value of P' is cal-

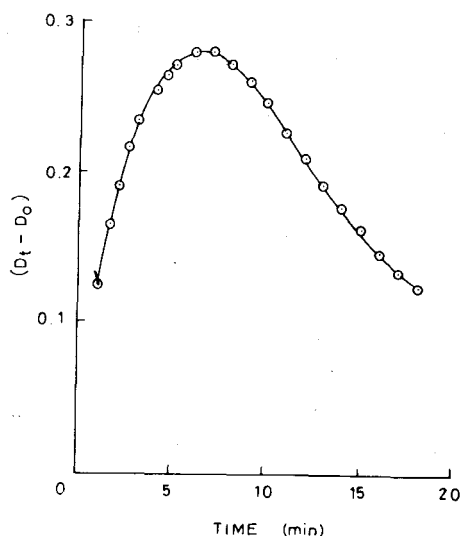


Fig. 1—Plot of absorbance versus time ($[Cr(VI)]_0 = 5.00 \times 10^{-4}$ mol dm⁻³, $[Mn(II)]_0 = 2.50 \times 10^{-3}$ mol dm⁻³, [oxalic acid]₀ = 2.5×10^{-2} mol dm⁻³, $\mu = 0.50$ mol dm⁻³; pH = 2.45, temp. = $30.0 \pm 0.1^\circ\text{C}$)

culated at various times. P and P' differ due to contribution from the faster of the consecutive steps (k_{fast}). The value of k_{fast} is given by the slope of the $\log(P' - P)$ versus time plot which should be linear if the above consecutive mechanism holds. Such linear plots were obtained with the experimental data. A typical plot is presented in Fig. 2. The values of k_{slow} and k_{fast} were also determined using the alternative procedure⁸ and the rate constants calculated by both the methods agree within $\pm 5\%$. The rate constant of the decomposition of I, k_b , can be considered to be k_{slow} whose value $(1.2-1.4) \times 10^{-3} \text{ s}^{-1}$ at 30°C is in agreement with the rate of decomposition of manganese(III)-oxalate complex reported in the literature^{9,10}. Thus k_a corresponds to k_{fast} .

The values of k_a and k_b have been determined at different initial $[\text{Mn(II)}]_0$, $[\text{oxalate}]_0$ and $[\text{H}^+]$ and are presented in Table 1. In all the cases, k_a increases with increase in $[\text{Mn(II)}]_0$, $[\text{Ox}]_0$ and $[\text{H}^+]$ where Ox represents total oxalate; k_b is independent of $[\text{Mn(II)}]_0$ under the experimental conditions employed. These kinetic features can be explained by assuming that fast equilibria are associated with the consecutive pathway. Mn^{2+} and Mn^{3+} are capable of forming 1:1, 1:2 and 1:3 complexes with oxalate ion(Ox) and the fraction of these complexes present in the system can be represented by Eq. (3).

$$[\text{MOx}] = \frac{K_1[\text{C}_2\text{O}_4^{2-}]}{N}, [\text{MOx}_2] = \frac{K_1 K_2 [\text{C}_2\text{O}_4^{2-}]^2}{N} \text{ and}$$

$$[\text{MOx}_3] = \frac{K_1 K_2 K_3 [\text{C}_2\text{O}_4^{2-}]^3}{N} \quad \dots (3)$$

Under the conditions $[\text{M}]_0 \ll [\text{Ox}]_0$, (where M represents Mn^{2+} or Mn^{3+}) and $N = 1 + K_1[\text{C}_2\text{O}_4^{2-}] + K_1 K_2 [\text{C}_2\text{O}_4^{2-}]^2 + K_1 K_2 K_3 [\text{C}_2\text{O}_4^{2-}]^3$.

$$[\text{C}_2\text{O}_4^{2-}] = \frac{K'_a K''_a [\text{Ox}]_0}{[\text{H}^+]^2 + K'_a [\text{H}^+] + K'_a K''_a} \quad \dots (4)$$

$$\approx \frac{K''_a [\text{Ox}]_0}{[\text{H}^+]} \quad \dots (5)$$

in the pH range employed.

In Eqs (3-5) $K_1 K_2$ and K_3 are the stepwise stabil-

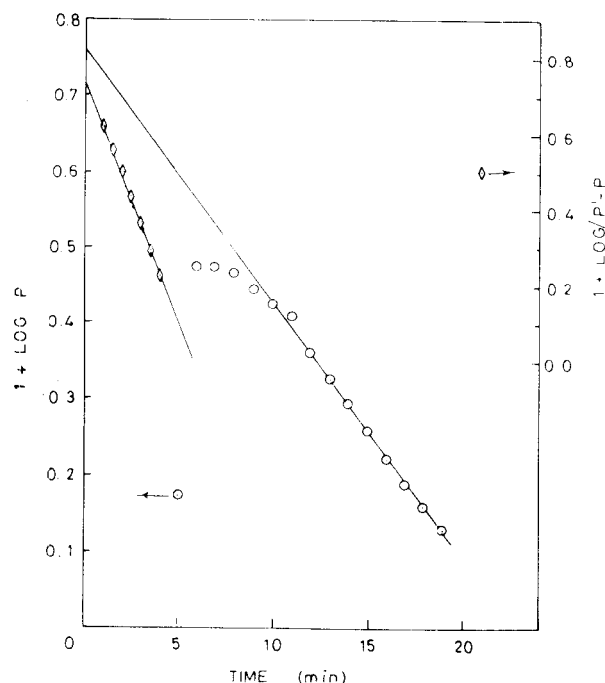


Fig. 2—Plot of $\log P$ versus time and plot of $\log |P - P'|$ versus time ($[\text{Cr(VI)}]_0 = 5.00 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{Mn(II)}]_0 = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{oxalic acid}]_0 = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$, $\mu = 0.50 \text{ mol dm}^{-3}$; pH = 2.45, temp. = $30.0 \pm 0.1^\circ\text{C}$)

Table 1—Consecutive rate constants under the conditions, $[\text{Ox}]_0 \gg [\text{Mn(II)}]_0$, $[\text{Cr(VI)}]_0 = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$, $\mu = 0.5 \text{ mol dm}^{-3}$, temp. = $30.0 \pm 0.1^\circ\text{C}$

$10^3 [\text{Mn(II)}]$ (mol dm^{-3})	$10^2 [\text{Ox}]_0$ (mol dm^{-3})	$10^3 [\text{H}^+]$ (mol dm^{-3})	$10^3 k_a$ (s^{-1})	$10^3 k_b$ (s^{-1})	$10^3 k_b$ (s^{-1}) Calculated from Eq. 11b)
2.50	3.50	3.16	3.40	1.25	1.27
2.50	5.00	3.53	5.10	1.33	1.29
2.50	7.00	4.56	7.00	1.30	—
2.50	10.00	5.50	8.35	1.32	—
2.50	13.00	6.58	10.50	1.22	1.32
2.50	5.00	4.56	5.08	1.33	1.27
3.50	5.00	4.56	6.91	1.40	1.27
4.25	5.00	4.56	7.90	1.40	1.27
5.00	5.00	4.56	10.00	1.40	1.27
6.00	5.00	4.56	11.23	1.33	1.27

ity constants and K'_a and K''_a are the first and second ionisation constants of oxalic acid ($K'_a = 5.6 \times 10^{-2}$, $K''_a = 5.4 \times 10^{-5}$)⁶. In the case of Mn(II) ($\log K_1 = 3.9$, $\log K_2 = 1.43$ and $\log K_3 < 0.1$)⁶ only 1:1 complex, $Mn C_2O_4$, is predominant at pH 2.0-2.5. Considering the stability constants of manganese(III)-oxalate complexes, it can be shown that in the pH range employed, only 1:2 and 1:3 complexes predominate ($\log K_1 = 9.88$, $\log K_2 = 6.59$ and $\log K_3 = 2.85$)⁶ and hence contribution to the rate by the pathway involving 1:1 complex, $Mn(C_2O_4)^+$, can be neglected.

To study the nature of the coloured intermediate formed in the reaction, the absorption spectra of the reaction mixture after 1 min and 10 min were scanned setting the scanning time at 6 sec during which time the change in absorbance due to reaction has been found to be negligibly small. The spectra at both the times show broad peak at 465 and shoulder at 510 nm (Fig. 2a). Dingle¹¹ has reported that bis-oxalato-diaquomanganese(III) has absorption maximum at 460 nm ($\epsilon = 130$) while the tris-oxalato manganese(III) exhibits peaks at 487 and 515 nm ($\epsilon = 230$). Chromium(III) obtained as a reaction product as well as Cr(VI) under these conditions have been found to have negligible absorbances at these wavelengths. The peak at 465 nm indicates the presence of bis-oxalato manganese(III) and the shoulder due to the tris complex whose concentration is less than that of the bis complex under the experimental conditions employed. The peak due to the tris complex at 487 nm appears to be submerged in the peak at 465 nm.

The kinetic analysis can be carried out by analysing the k_a and k_b -paths separately¹². These paths

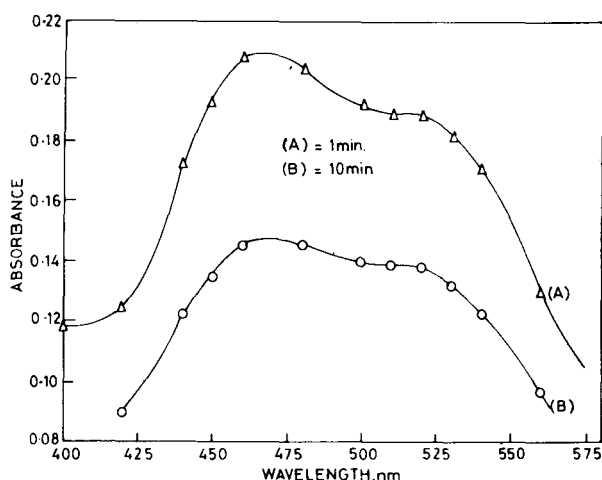
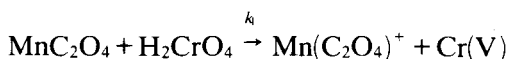
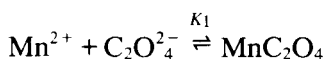
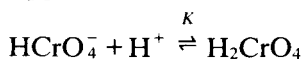


Fig. 2a—Visual absorption spectra of intermediate Mn(III)-oxalate complexes ($[Cr(VI)]_0 = 5.0 \times 10^{-4}$ mol dm⁻³, $[Ox]_0 = 2.5 \times 10^{-2}$ mol dm⁻³, $[Mn(II)]_0 = 5.0 \times 10^{-3}$ mol dm⁻³, pH = 2.1; $\mu = 0.5$ mol dm⁻³; temp. = $25.0 \pm 0.1^\circ C$)

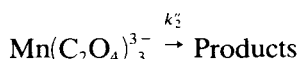
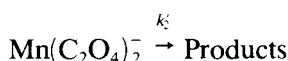
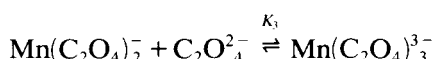
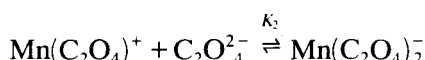
can be represented by Schemes (1) and (2) which explain all the results.

k_a -path



Scheme 1

k_b -path



Scheme 2

If $[Mn(III)]_t$ is the total Mn(III) concentration and I_1 , I_2 and I_3 be the concentrations of 1:1, 1:2 and 1:3 complexes, then

$$[Mn(III)]_t = I_1 + I_2 + I_3 \quad \dots (6)$$

Since I_1 is negligible under these conditions, Eq. (6) may be approximated to

$$[Mn(III)]_t = I_2 + I_3 \quad \dots (6a)$$

From Eq. (6a) it can be derived that

$$I_2 = \frac{Mn(III)_t}{1 + K_3[C_2O_4^{2-}]} \text{ and } I_3 = \frac{K_3[Mn(III)]_t[C_2O_4^{2-}]}{1 + K_3[C_2O_4^{2-}]} \dots (7)$$

Therefore, $\frac{d[Mn(III)]_t}{dt}$

$$= \frac{k_1 K K_1 K''_a [Mn(II)]_0 [Ox]_0 [H^+] [HCrO_4^-]_0}{[H^+] + K_1 K''_a [Ox]_0}$$

$$- (k'_2 [I_2] + k''_2 [I_3]) \quad \dots (8)$$

Using Eqs (5) and (7), Eq. (8) may be written as

$$\begin{aligned} \frac{d[Mn(III)]_t}{dt} &= \left\{ \frac{k_1 K K_1 K''_a [Mn(II)]_0 [Ox]_0 [H^+] [HCrO_4^-]_0}{[H^+] + K_1 K''_a [Ox]_0} \right. \\ &\quad - \left(\frac{k'_2 [Mn(III)]_t}{1 + K_3 K''_a [Ox]_0 / [H^+]} \right. \\ &\quad \left. \left. + \frac{k''_2 K_3 K''_a [Mn(III)]_t [Ox]_0 / [H^+]}{1 + K_3 K''_a [Ox]_0 / [H^+]} \right) \right\} \quad \dots (9) \end{aligned}$$

which on integration leads to Eq. (10)

$$[\text{Mn(III)}]_t = \frac{k[\text{HCrO}_4^-]_0}{(k_b - k_a)} (e^{-k_a t} - e^{-k_b t}) \quad \dots (10)$$

Equation (10) is the same as the equation for consecutive pathway (Eq. (1)), where

$$k_a = \frac{k_1 K K_1 K''_a [\text{Mn(II)}]_0 [\text{Ox}]_0 [\text{H}^+]}{[\text{H}^+] + K_1 K''_a [\text{Ox}]_0} \quad \dots (11a)$$

and

$$k_b = \frac{k'_2}{1 + K_3 K''_a [\text{Ox}]_0 / [\text{H}^+]} + \frac{k''_2 K_3 K''_a [\text{Ox}]_0 / [\text{H}^+]}{1 + K_3 K''_a [\text{Ox}]_0 / [\text{H}^+]} \quad \dots (11b)$$

In agreement with this rate-law, the results obtained under these conditions (Table 1) show that k_a is directly proportional to $[\text{Mn(II)}]_0$. Further the values of $[\text{Ox}]_0 [\text{H}^+] / ([\text{H}^+] + K_1 K''_a [\text{Ox}]_0)$ were calculated taking the literature values of K''_a and K_1 . A plot of k_a versus $[\text{Ox}]_0 [\text{H}^+] / ([\text{H}^+] + K_1 K''_a [\text{Ox}]_0)$ is linear passing through the origin establishing the validity of the rate-law.

Choosing any two values from Table 1, k'_2 and k''_2 can be calculated from Eq. (11b) using the values of K_3 and K''_a available in the literature; k'_2 and k''_2

have been found to be $1.17 \times 10^{-3} \text{ s}^{-1}$ and $1.52 \times 10^{-3} \text{ s}^{-1}$ respectively at 30°C . Using these data the values of k_b have been calculated for other runs mentioned in Table 1. k_b thus calculated is in good agreement with that obtained from the experimental results, showing the validity of the rate-law under the experimental conditions employed. The values of k'_2 and k''_2 are also in reasonable agreement with those reported in literature^{9,10} ($k'_2 = 8 \times 10^{-4} \text{ s}^{-1}$ at 20°C and $k''_2 = 0.49 \times 10^{-3} \text{ s}^{-1}$ at 25°C).

References

- 1 Rodek J & Fariza H, *J Am chem Soc*, 94 (1972) 9073.
- 2 Bakore G V & Jain C L, *J inorg nucl Chem*, 31 (1969) 805.
- 3 Durham D A, *J inorg nucl Chem*, 31 (1969) 3549.
- 4 Ayyar R V V, Ph D Thesis, Andhra University, Waltair (1966).
- 5 Chakravarty D N & Ghosh S, *Proc Natl Acad Sci, India, Sect A*, 29 Pt. 2 (1960) 199.
- 6 Haight G P (Jr) & Huber C F, *J Am chem Soc*, 68 (1976) 14.
- 7 Jackson W G, Harrofield M & Vowles P D, *Int J chem Kinet IX* (1977) 535.
- 8 Espenson J H in *Chemistry: kinetics and reaction mechanisms* (McGraw-Hill, New York) 1981.
- 9 Duke F R, *J Am chem Soc*, 69 (1947) 2885.
- 10 Adler S J & Noyes R M, *J Am chem Soc*, 77 (1955) 2036.
- 11 Dingle R, *Acta Chem Scand*, 20 (1966) 35-36.
- 12 Buckingham D A, Francis D J & Sargeson A M, *Inorg Chem*, 13 (1974) 2630.