

Kinetics of the Oxidation of Tris(oxalato)chromate(III) Ion by Manganese(III) Ions

^aM. FICO and ^bL. TREINDL

^a*Institute of Chemistry, Komenský University,
Bratislava 1*

^b*Department of Physical Chemistry, Faculty of Natural Sciences, Komenský University,
Bratislava 1*

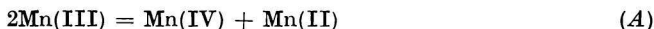
Received February 24, 1971

The kinetics and mechanism of the oxidation of $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$ ions by $\text{Mn}(\text{III})$ ions have been studied. The rate equation has the form $v = 2k'[\text{Mn}(\text{III})][\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}]$. The measurements have shown that the rate constant k' is a linear function of the concentration of H_3O^+ ions. The reaction mechanism is proposed according to which the oxidation of protonized $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$ ions takes place in two parallel steps. Analysis of the results, based on the relationship between the rate constant and concentration of H_3O^+ ions at various temperatures enables us to determine the values of rate constants and activation parameters for both these steps corresponding to $\text{Mn}_{\text{aq}}^{3+}$ and $\text{MnOH}_{\text{aq}}^{2+}$, respectively. Either reaction step may very likely be based on a mechanism involving internal spheres.

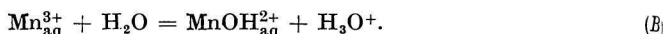
In recent years, a great attention has been paid to the reactivity of coordinately linked ligands, especially with respect to homogeneous catalysis [1]. In particular, this attention is concentrated upon the redox reactions of coordinated ligands [1, 2]. In this case, the reaction systems involving a stable complex ion containing a ligand which undergoes oxidation or reduction by an external agent are to be studied.

The oxidation kinetics of the oxalate ions coordinately linked in inert complexes was investigated in the papers [3–6]. *Saffir* and *Taube* [3] studied the kinetics of the oxidation of complex ion $\text{Co}(\text{NH}_3)_5(\text{C}_2\text{O}_4)^+$ by hydrogen peroxide. The kinetics of the oxidation of $\text{Rh}(\text{C}_2\text{O}_4)_3^{3-}$ ions [4] as well as of mono-, bis-, and tri(oxalato)chromate(III) ions by $\text{Ce}(\text{IV})$ ions was studied, too [4–6]. According to [5], the rate of $\text{Cr}(\text{H}_2\text{O})_4(\text{C}_2\text{O}_4)^+$ ion oxidation by $\text{Ce}(\text{IV})$ ions is considerably low in comparison with $\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2$ and $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$ ions. The paper [4], published recently, points out some vague questions relative to the kinetics and mechanism of the $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$ ion oxidation, as for instance the temperature dependence of activation enthalpy. A kinetic study of the $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$ ion oxidation by another one-electron oxidizing agent should contribute to the elucidation of oxidation mechanism of coordinately linked oxalates. That is why we went into the kinetic study of the $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$ ion oxidation by $\text{Mn}(\text{III})$ ions.

$\text{Mn}(\text{III})$ ion is a relatively strong one-electron oxidizing agent which is, however, subject to disproportionation [7]



and according to [8] it hydrolyzes even in strong acid solutions



The value of equilibrium hydrolysis constant measured at the ionic strength of 4.00 at 25°C equals $K_h = 0.93$ [9]. The kinetics of the oxalic acid oxidation by Mn(III) ions was studied in the papers [10–12]. The kinetics of $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$ ion oxidation has not been studied before and is the subject matter of this publication.

Experimental

The solutions of Mn(III) ions were prepared by the electrooxidation of MnSO_4 in the solution of HClO_4 on a platinum electrode in nitrogen atmosphere [8]. The concentration was estimated by putting the sample into a solution containing an excess of Fe^{2+} and determining Fe^{3+} spectrophotometrically at 260 nm [13], the validity of Lambert–Beer law having been tested beforehand. Owing to the disproportionation of Mn(III), newly prepared solutions of Mn(III) were used for each measurement. To enhance the stability of Mn(III), an approximately hundredfold excess of Mn^{2+} and higher concentrations of H_3O^+ were applied.

$\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ was prepared according to [14]. To identify the substance or test its purity, gravimetric and spectrophotometric analyses were carried out. According to Krishnamurty and Harris [15], the maxima of light absorbance are at 420 and 573 nm what is in agreement with the results of spectrophotometric analysis. The gravimetric analysis gave some data which were consistent with those presented in literature.

The kinetics of $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ oxidation by Mn(III) ions was investigated polarographically by following the dependence of limiting diffusion current of Mn(III) ions on time at the potential of 0.0 V against SCE. Because of possible consecutive reactions, the experimental rate constant was calculated from the 25% advancement of reaction by using the kinetic equation of the first order

$$\log \frac{i_0}{i} = \frac{k_{\text{exp}}}{2.303} t,$$

the accuracy in the determination of individual experimental rate constant being $\pm 6\%$. The measurements were made with a polarograph of the OH-102 type, Radelkis, equipped with a Kalousek vessel which was adapted to kinetic investigations. The temperature of reaction mixture was kept constant with an accuracy of $\pm 0.1^\circ\text{C}$ by means of an ultrathermostat U-10. The individual points of the relationships are the average values of three measurements at least.

Results and Discussion

The overall reaction order was ascertained by the method of half-life at equal molar concentrations of both reactants and was found to equal 2 (Table 1). The reaction order with respect to the concentration of $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$ ions is equal to 1 what follows from the dependence of the measured rate constant on the concentration of complex (Fig. 1). Thus the rate equation assumes the form

$$-\frac{d[\text{Mn(III)}]}{dt} = 2k'[\text{Mn(III)}][\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}], \quad (1)$$

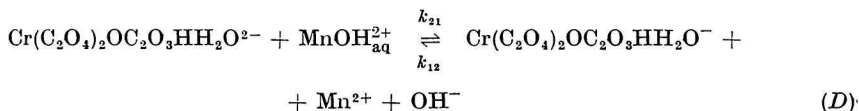
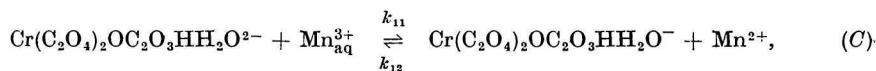
Table 1

Determination of the overall reaction order

No.	[Mn(III)] = [Cr(C ₂ O ₄) ₃ ³⁻] [mole l ⁻¹]	<i>n</i>
1	4 × 10 ⁻⁴	1.78
2	6 × 10 ⁻⁴	2.13
3	8 × 10 ⁻⁴	1.93

1.4 M-HClO₄; *T* = 288 K. $\bar{n} = 1.95$.

where [Mn(III)] denotes the overall concentration of Mn(III) ions in the solution. The rate constant *k'* is directly proportional to the concentration of H₃O⁺ ions (Fig. 2) and changes only slightly with the change of ionic strength (Table 2). In the solution of 0.5–2.2 M perchloric acid the tris(oxalato)chromate(III) complex should be present also in the protonized form Cr(C₂O₄)₂OC₂O₃HH₂O²⁻, in which two C₂O₄²⁻ ions form chelate rings, HC₂O₄⁻ takes the fifth, and H₂O molecule the sixth coordination position [16]. In this solution, the Mn(III) ions must be present in the form of Mn_{aq}³⁺ and MnOH_{aq}²⁺ ions. The redox reaction can therefore proceed in two parallel ways



In these reactions the Mn²⁺ ion and the ion-radical as an instable intermediate product are formed. In the following step the ion-radical is oxidized again in two parallel reactions

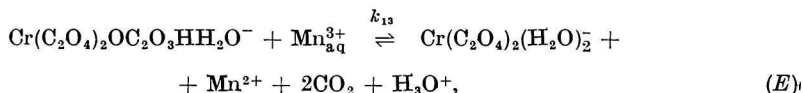
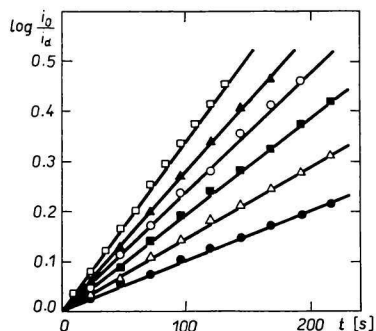
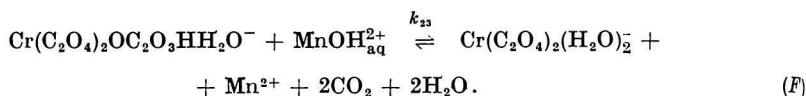


Fig. 1. Dependence of the experimental rate constant *k*_{exp} on the concentration of tris(oxalato)chromate(III) complex.

2.5 × 10⁻⁴ M-Mn(III); *T* = 288 K; 1.4 M-HClO₄.
[Cr(C₂O₄)₃³⁻] = 2, 3, 4, 5, 6, 7 × 10⁻⁴ M.





On the basis of this reaction scheme it may be written

$$-\frac{d[\text{Mn(III)}]}{dt} = k_{11}[\text{Mn}_{\text{aq}}^{3+}][\text{X}] - k_{12}[\text{Mn}^{2+}][\text{Y}] + k_{21}[\text{MnOH}_{\text{aq}}^{2+}][\text{X}] - k_{12}[\text{Mn}^{2+}][\text{Y}] + k_{13}[\text{Mn}_{\text{aq}}^{3+}][\text{Y}] + k_{23}[\text{MnOH}_{\text{aq}}^{2+}][\text{Y}], \quad (2)$$

where $\text{X} = \text{Cr}(\text{C}_2\text{O}_4)_2\text{OC}_2\text{O}_3\text{HH}_2\text{O}^-$ and $\text{Y} = \text{Cr}(\text{C}_2\text{O}_4)_2\text{OC}_2\text{O}_3\text{HH}_2\text{O}^-$. Supposing that the ion-radical Y is in a stationary state, we obtain

$$-\frac{d[\text{Mn(III)}]}{dt} = \frac{2k_{11}[\text{X}][\text{Mn}_{\text{aq}}^{3+}]\{k_{13}[\text{Mn}_{\text{aq}}^{3+}] + k_{23}[\text{MnOH}_{\text{aq}}^{2+}]\}}{2k_{12}[\text{Mn}^{2+}] + k_{13}[\text{Mn}_{\text{aq}}^{3+}] + k_{23}[\text{MnOH}_{\text{aq}}^{2+}]} + \frac{2k_{21}[\text{X}][\text{MnOH}_{\text{aq}}^{2+}]\{k_{13}[\text{Mn}_{\text{aq}}^{3+}] + k_{23}[\text{MnOH}_{\text{aq}}^{2+}]\}}{2k_{12}[\text{Mn}^{2+}] + k_{13}[\text{Mn}_{\text{aq}}^{3+}] + k_{23}[\text{MnOH}_{\text{aq}}^{2+}]}. \quad (3)$$

As the change in the concentration of Mn^{2+} ions has no or very small effect on the reaction rate (Table 3), the term $2k_{12}[\text{Mn}^{2+}]$ in the denominator of the equation (3) may be disregarded and the rate equation assumes the form

$$-\frac{d[\text{Mn(III)}]}{dt} = 2k_{11}[\text{Mn}_{\text{aq}}^{3+}][\text{X}] + 2k_{21}[\text{MnOH}_{\text{aq}}^{2+}][\text{X}]. \quad (4)$$

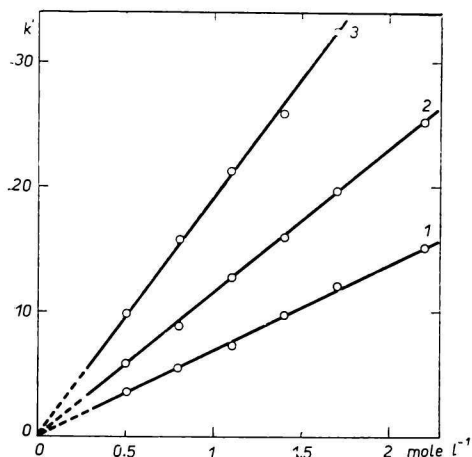


Fig. 2. Effect of the concentration of H_3O^+ ions on the value of rate constant k' .
 $[\text{Mn(III)}] = [\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}] = 2.5 \times 10^{-4} \text{ M}$;
 $I = 4.00$.

1. $T = 293 \text{ K}$; 2. $T = 298 \text{ K}$;

3. $T = 303 \text{ K}$.

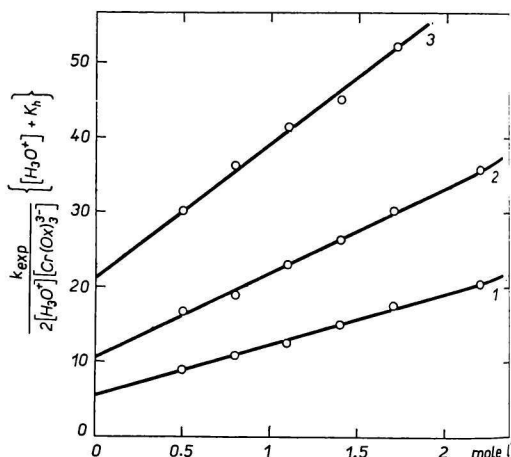


Fig. 3. Variation of the left hand side of the equation (10) with the concentration of H_3O^+ ions.

$[\text{Mn(III)}] = [\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}] = 2.5 \times 10^{-4} \text{ M}$;
 $I = 4.00$.

1. $T = 293 \text{ K}$; 2. $T = 298 \text{ K}$; 3. $T = 303 \text{ K}$.

Since the resulting reaction rate is given by the sum of the rates of side reactions, it holds

$$k_{11}[\text{Mn}_{\text{aq}}^{3+}] + k_{21}[\text{MnOH}_{\text{aq}}^{2+}] = k^0[\text{Mn(III)}] \quad (5)$$

Table 2

Effect of ionic strength on the value of rate constant k'

I	k' [l mole ⁻¹ s ⁻¹]
1.5	7.6
3.0	6.7
4.0	6.0

2.5×10^{-4} M-Mn(III); 2.5×10^{-4} M-Cr(C₂O₄)₃³⁻; 0.5 M-HClO₄; $T = 298\text{K}$.

Table 3

Effect of the concentration of Mn²⁺ ions on the value of experimental rate constant

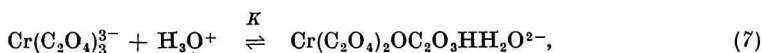
[Mn ²⁺] [mole l ⁻¹]	$10^3 \times k_{\text{exp}}$ [s ⁻¹]
0.05	2.41
0.15	2.23
0.30	2.14
0.45	2.10

2.5×10^{-4} M-Mn(III); 2.5×10^{-4} M-Cr(C₂O₄)₃³⁻; 1.7 M-HClO₄; $I = 3.05$; $T = 291\text{K}$.

and the equation (4) takes the form

$$-\frac{d[\text{Mn(III)}]}{dt} = 2k^0[\text{Mn(III)}][X]. \quad (6)$$

Assuming that the protonized form of complex is in an equilibrium in the solution



it is allowed to write the rate equation (6) in the form

$$-\frac{d[\text{Mn(III)}]}{dt} = 2k^0 K[\text{Mn(III)}][\text{Cr(C}_2\text{O}_4)_3^{3-}][\text{H}_3\text{O}^+] \quad (8)$$

$$-\frac{d[\text{Mn(III)}]}{dt} = 2k'[\text{Mn(III)}][\text{Cr(C}_2\text{O}_4)_3^{3-}], \quad (9)$$

which agrees with the equation (1) obtained experimentally considering $k' = k^0 K[\text{H}_3\text{O}^+]$.

Table 4

Values of $k_{11} K$ and $k_{21} K$ as a function of temperature

T [K]	$k_{11} K$ [l ² mole ⁻² s ⁻¹]	$k_{21} K$ [l ² mole ⁻² s ⁻¹]
293	7.04	6.60
298	11.43	11.31
303	17.64	20.76

2.5×10^{-4} M-Mn(III); 2.5×10^{-4} M-Cr(C₂O₄)₃³⁻; $I = 4.00$.

The reaction scheme proposed is thus in agreement with the rate equation (I) as well as with the first reaction order with respect to the concentration of H_3O^+ ions. Provided only the $\text{Mn}_{\text{aq}}^{3+}$ ion reacted with tris(oxalato)chromate(III) complex, the reaction would have to be of the second order with respect to the concentration of H_3O^+ ions because of a shift of equilibrium in favour of the protonized form of tris(oxalato)chromate(III) complex as well as of the $\text{Mn}_{\text{aq}}^{3+}$ ions. In kinetic studies on Mn(III) ions, some authors [17–20] consider only the $\text{Mn}_{\text{aq}}^{3+}$ ions to be reactive particles in the medium of perchloric acid while others [3, 21–23] take the reaction of either form into consideration.

Table 5

Activations parameters of the parallel elementary steps

$\Delta H_{11}^\ddagger = 15.8 \pm 0.9 \text{ kcal mole}^{-1}$	$\Delta H_{21}^\ddagger = 19.5 \pm 1.2 \text{ kcal mole}^{-1}$
$\Delta S_{11}^\ddagger = -1 \text{ cal K}^{-1} \text{ mole}^{-1}$	$\Delta S_{21}^\ddagger = 12 \text{ cal K}^{-1} \text{ mole}^{-1}$

On rearranging the equation (8) and substituting k_{11} and k_{21} , we obtain the relationship

$$\frac{k_{\text{exp}}}{2[\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}][\text{H}_3\text{O}^+]} \{[\text{H}_3\text{O}^+] + K_h\} = k_{11} K[\text{H}_3\text{O}^+] + k_{21} K K_h, \quad (10)$$

which on the basis of the values of the products $k_{11} K$ and $k_{21} K$ (Fig. 3) and (Table 4) has enabled us to compare the reactivity of both the forms of trivalent manganese at three different temperatures. It follows from the dimensional analysis that the products $k_{11} K$ and $k_{21} K$ have the significance of the rate constants of $\text{Mn}_{\text{aq}}^{3+}$ and $\text{MnOH}_{\text{aq}}^{2+}$ ions at their unit concentrations and at the unit concentration of H_3O^+ and $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$ ions as well.

Since the association constant K depends only slightly on temperature [16], the activation parameters of both parallel elementary steps (Table 5) could be determined from the temperature dependence of the products $k_{11} K$ and $k_{21} K$ by means of the Eyring equation. Both these parallel reaction steps are likely to proceed according to a mechanism involving internal spheres. The Mn(III) ion is evidently able to get linked to a free carboxylic group of oxalate ligand under formation of a transition complex possessing two nuclei, i.e. $[(\text{C}_2\text{O}_4)_2\text{Cr}-\text{C}_2\text{O}_4-\text{Mn}_{\text{aq}}^{3+}]^+$ or $[(\text{C}_2\text{O}_4)-\text{Cr}-\text{C}_2\text{O}_4-\text{MnOH}_{\text{aq}}^{2+}]^0$.

References

1. Jones M. M., *Ligand Reactivity and Catalysis*. Academic Press, New York—London, 1968.
2. Candlin J. P., Thompson D. T., Taylor K. A., *Reactions of Transition Metal Complexes*. Elsevier Publishing Company, Amsterdam, 1968.
3. Saffir P., Taube H., *J. Chem. Soc.* **82**, 13 (1960).
4. Hsu M. W., Kruszyna H. G., Milburn R. M., *Inorg. Chem.* **8**, 2201 (1969).
5. Teggin J. E., Wang M. T., Milburn R. M., *Advances in Chemical Series*, No. 37, 226 (1963).
6. Wang M. T., *Disc. Abstr.* **1965**, 3029.
7. Davies G., *Coord. Chem. Rev.* **4**, 199 (1969).

8. Diebler H., Sutin N., *J. Phys. Chem.* **68**, 174 (1964).
9. Wells C. F., Davies G., *Nature* **205**, 692 (1965); *J. Chem. Soc., A*, **1967**, 1858.
10. Duke F. R., *J. Amer. Chem. Soc.* **69**, 2885 (1947).
11. Taube H., *J. Amer. Chem. Soc.* **69**, 1418 (1947).
12. Murgulescu I. G., Oncescu T., *Proceedings of 8th International Conference on Coordination Chemistry*, p. 301. Springer-Verlag, Wien, 1964.
13. Bastian R., Weberling R., Palilla F., *Anal. Chem.* **28**, 459 (1956).
14. *Inorganic Syntheses, Vol. I*, p. 37. McGraw-Hill, New York, 1939.
15. Krishnamurty K. V., Harris G. M., *J. Phys. Chem.* **64**, 346 (1960).
16. Kelm H., Harris G. M., *Inorg. Chem.* **6**, 1743 (1967).
17. Wells C. F., Mays D., *Inorg. Nucl. Chem. Lett.* **4**, 61 (1968).
18. Wells C. F., Mays D., *J. Chem. Soc., A*, **1968**, 577, 1622.
19. Wells C. F., Mays D., *Inorg. Nucl. Chem. Lett.* **4**, 43 (1968).
20. Wells C. F., Mays D., *J. Chem. Soc., A*, **1968**, 665.
21. Rosseinsky D. R., Nicol M. J., *J. Chem. Soc., A*, **1968**, 1022.
22. Rosseinsky D. R., Nicol M. J., *Trans. Faraday Soc.* **64**, 2410 (1968).
23. Davies G., Kustin K., *Inorg. Chem.* **8**, 484 (1969).

Translated by R. Domanský