Redox reactions of the complexes with cations in higher oxidation states. V.*
Kinetic study of the redox reaction of manganese(III) with oxalic acid in the medium of acetic acid

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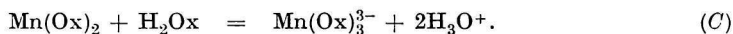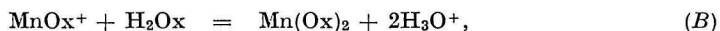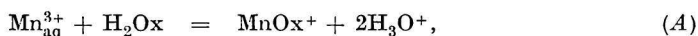*Department of Physical Chemistry, Faculty of Natural Sciences, Komenský University, 801 00 Bratislava*

Dedicated to Professor S. Stankoviansky on his 65th birthday

The kinetics of the redox reaction of manganese(III) with oxalic acid in the medium of 70% acetic acid has been studied. The experimental value of the rate constant (s^{-1}) decreases nonlinearly with increasing concentration of oxalic acid. In the presence of oxalic acid the absorption maximum of Mn(III) shifts by 31 nm towards shorter wavelengths. The redox reaction involves the formation of some intermediary complexes which are analyzed on the basis of kinetic relationships.

The measured value of the activation heat capacity $\Delta C_p^{\neq} = 167 \, \text{cal} \, \text{K}^{-1} \text{mol}^{-1}$ may be in connection with the change in the structure of solvent brought about by the effect of temperature.

The oxidation of oxalic acid with potassium permanganate belongs to the first reactions the kinetics of which has been studied [1]. According to paper [2] the reaction involves the formation of diaquo-dioxalatomanganate(III) as intermediate. The reaction of Mn(III) with oxalic acid has been studied by several authors [3—7]. On the basis of the catalytic effect of Mn(III) ions on the reaction of oxalic acid with chlorine *Taube* [5—7] proposed the following mechanism of the reduction of Mn(III) ions with oxalic acid:

$$\text{Mn}_{aq}^{3+} + \text{H}_2\text{Ox} = \text{MnOx}^+ + 2\text{H}_3\text{O}^+, \tag{A}$$

$$\text{MnOx}^+ + \text{H}_2\text{Ox} = \text{Mn(Ox)}_2 + 2\text{H}_3\text{O}^+, \tag{B}$$

$$\text{Mn(Ox)}_2 + \text{H}_2\text{Ox} = \text{Mn(Ox)}_3^{3-} + 2\text{H}_3\text{O}^+. \tag{C}$$

The structure of dioxalato- and trioxalatomanganate(III) intermediates has been studied in the ultraviolet region of absorption spectrum [4]. The redox system Mn(II)—Mn(III) also plays an important role as a catalyst in many autoxidation reactions. The catalytic activity of manganese is caused by its participation in the oxidation-reduction cycles of some chain reactions. Relatively stable is *e.g.* the solution of the dihydrate of manganese(III) acetate in acetic acid which is a convenient medium for the oxidation reactions of Mn(III).

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* For Part IV see Ref. [11].

Since the redox reaction of manganese(III) acetate with oxalic acid in the acetic acid medium has not been studied up to now, we have decided to study its kinetics and pay special attention to the reaction intermediates.

Experimental

The kinetic measurements of the redox reaction of Mn(III) ions with oxalic acid were carried out in most cases polarographically by recording the time dependences of the limiting diffusion current of Mn(III) ions at the potential -0.3 V to -0.8 V against the potential of 2 M calomel electrode. The dropping mercury electrode with flow rate $m = 1.6$ mg s^{-1} and drop time $t = 3.2$ s at the mercury column height $h = 50$ cm in currentless state served as an indication electrode. A 2 M calomel electrode containing the 2 M solution of sodium chloride was used as the reference part of a Kalousek vessel. A series of kinetic measurements was made spectrophotometrically on a Specord UV-VIS (Zeiss, Jena) spectrophotometer. In both cases the thermostating was provided by connecting the system to a Höppler ultrathermostat. The acidity of the medium with 70% acetic acid and 0.1 M-MnSO$_4$ as a function of oxalic acid concentration was measured on a pH-meter 22 (Radiometer) with a high-ohm resistance glass electrode calibrated by means of the Veibel buffer solution (pH 1.0).

The chemicals used, *i.e.* acetic acid, oxalic acid, manganese(II) sulfate (Lachema, Brno), sodium chloride, and sodium perchlorate (Apolda, GDR) were of anal. grade. Redistilled water was used for the preparation of solutions.

The solution of Mn(III) ions was prepared by the electro-oxidation of 10^{-2} M solutions of manganese(II) sulfate or acetate on a large-surface platinum anode in a 70% aqueous solution of acetic acid. The solution was always prepared before kinetic measurement and the concentration of Mn(III) ions was determined by polarometric titration with the standard solution of oxalic acid. The molar extinction coefficient of the solution thus prepared (orange-red colour) was equal to 1.31×10^2 l mol^{-1} cm^{-1} at the wavelength of 490 nm.

Results and discussion

The order of the studied reaction with respect to the concentration of Mn(III) ions was determined by integral method. In the temperature range from 5 to 50°C the reaction obeys the kinetic equation of the first order from which the value of rate constant was determined with the accuracy of $\pm 5\%$. The experimental value of the rate constant decreases nonlinearly with increasing concentration of oxalic acid (Fig. 1). The pH of the medium depends on the concentration of oxalic acid as illustrated in Fig. 2. The value of the rate constant increases with the concentration of perchloric acid at constant ionic strength $\mu = 1$ (NaClO$_4$) (Fig. 3). The experimental value of the rate constant is also a function of the ionic strength of electrolyte (Fig. 4). Activation parameters of the investigated reaction were obtained by means of the Eyring equation (Fig. 5) from the temperature dependences of the rate constant. These dependences showed a curvature which enabled us to evaluate the dependence of activation enthalpy on temperature (Fig. 6). In this procedure we determined from the values of rate constants at the temperatures T_i and T_j the activation enthalpy $\Delta H_{ij}^{\ddagger}$ for the temperature $(T_i + T_j)/2$ (Table 1). The slope of the linear relationship between activation enthalpy and temperature represents the activation heat capacity $\Delta C_p^{\ddagger} = (\partial \Delta H^{\ddagger}/\partial T)_p$ and is equal to 167 cal K^{-1} mol^{-1}. In a similar way we evaluated the relationship between activation
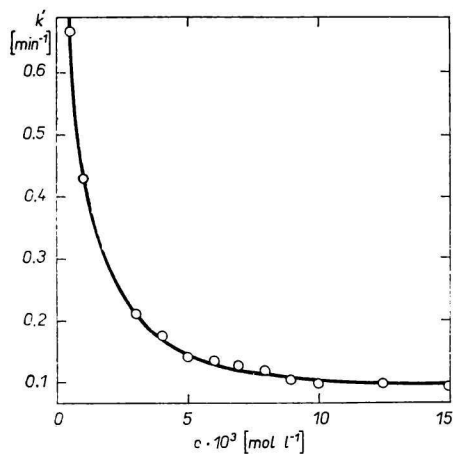
Fig. 1. The experimental value of the rate constant as a function of the concentration of oxalic acid.

3×10^{-4} M-Mn(III); 70% CH₃COOH;
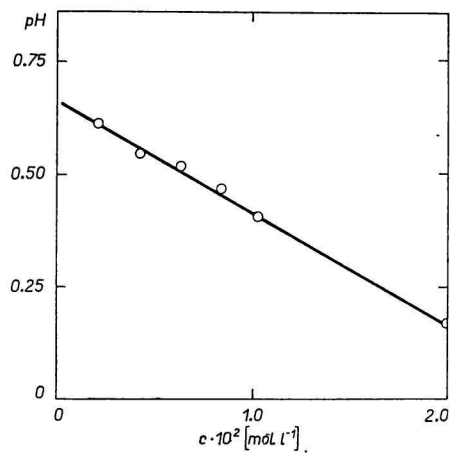$t = 25°C$.

Fig. 2. The pH value of the reaction medium as a function of the concentration of oxalic acid.

Experimental conditions as in Fig. 1.

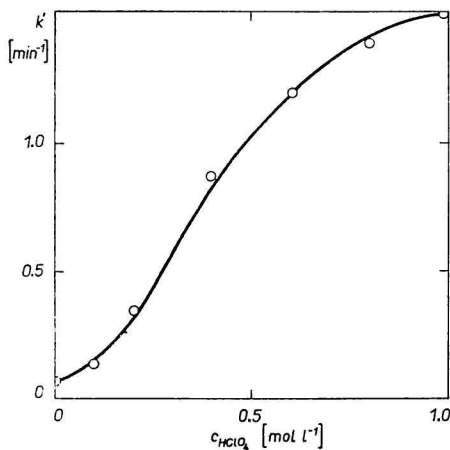*Fig. 3.* The experimental value of the rate constant as a function of the concentration of perchloric acid.

3×10^{-4} M-Mn(III); 70% CH₃COOH;
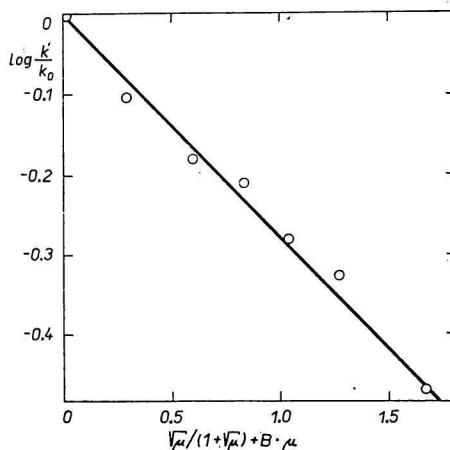$t = 25°C$; 5×10^{-3} M-H₂Ox; $\mu = 1.0$.

Fig. 4. Effect of the ionic strength of electrolyte on the value of the rate constant.

3×10^{-4} M-Mn(III); 5×10^{-3} M-H₂Ox;
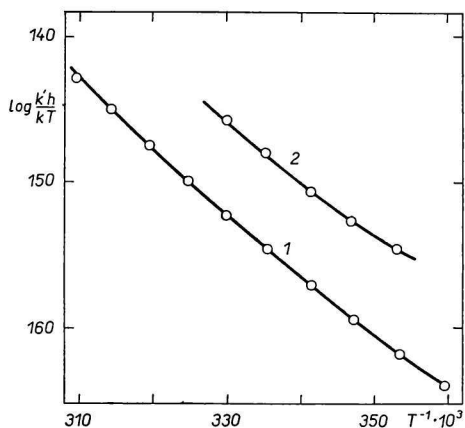70% CH₃COOH; $t = 25°C$; $B = 0.53$.

Fig. 5. The experimental value of the rate constant as a function of the temperature.
3 × 10⁻⁴ M-Mn(III); 70% CH₃COOH;
1. 5 × 10⁻³ M-H₂Ox; 2. 6 × 10⁻⁴ M-H₂Ox
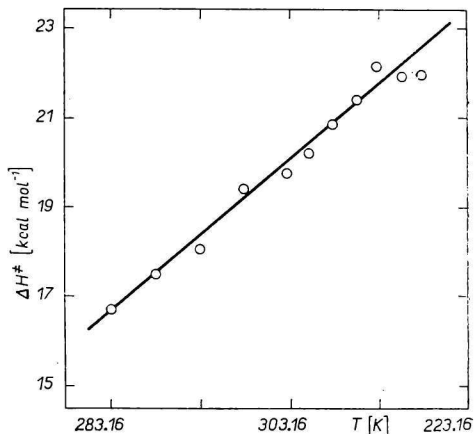(k stands for the Boltzmann constant).

Fig. 6. Activation enthalpy as a function of the temperature.
Experimental conditions as in Fig. 5 (1).

entropy and temperature (Table 2). It is possible to observe a transition from negative to positive values of the activation entropy.

A shift of the absorption maximum by 31 nm towards lower wavelengths (Fig. 7) may be observed in the absorption spectra plotted in the coordinates transparency— —wavelength provided oxalic acid is added into a Mn(III) solution in the medium of 70% acetic acid. In further course of reaction the absorption maximum does not shift any more.

Table 1
Temperature dependence of activation enthalpy

T [°C]	$\Delta H^{\ddagger}$ [kcal mol⁻¹]	T [°C]	$\Delta H^{\ddagger}$ [kcal mol⁻¹]
7.5	14.73	30.0	19.81
10.0	16.75	32.5	20.32
12.5	18.83	35.0	20.92
15.0	17.58	37.5	21.53
17.5	16.36	40.0	22.25
20.0	18.11	42.5	22.00
22.5	19.47	45.0	22.08
25.0	20.00	47.5	21.07
27.5	18.91		

Standard deviation of the values of $\Delta H^{\ddagger} = 0.6$ kcal mol⁻¹. Experimental conditions as in Fig. 5.

Table 2

Temperature dependence of activation entropy

T [°C]	$\Delta S^{\ddagger}$ [cal K^{-1} mol^{-1}]
45.0	+0.6
40.0	+3.2
35.0	+0.3
30.0	−4.9
25.0	−5.6
20.0	−8.4
15.0	−12.2
10.0	−15.9

Standard deviation of the values of $\Delta S^{\ddagger} = 1.5$ cal K^{-1} mol^{-1}.

The nonlinear decrease in the rate constant with increasing concentration of oxalic acid (Fig. 1) may be also explained by successive formation of Mn(III) oxalate complexes the reactivity of which decreases with increasing number of coordinated ligands. The reaction mechanism involving the formation of intermediary complexes is also corroborated by the measured shift of absorption maximum. In the evaluation of the dependence rate constant on the concentration of oxalic acid we proceeded like in the preceding studies of this series [8—11]. On the basis of this idea of the successive formation of manganese(III) oxalate complexes we derived the function

$$\alpha = \left(\frac{k'}{k^x} - 1\right)\frac{a_{H^+}^2}{[H_2Ox]} = K_1 + \frac{K_1K_2[H_2Ox]}{a_{H^+}^2} + \frac{K_1K_2K_3[H_2Ox]^2}{a_{H^+}^4} + \dots ,$$
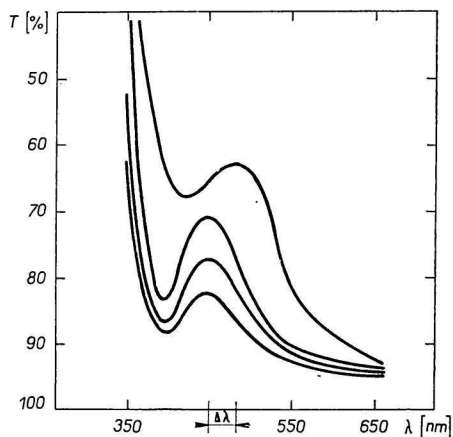

Fig. 7. Absorption spectrum in the course of the studied reaction.
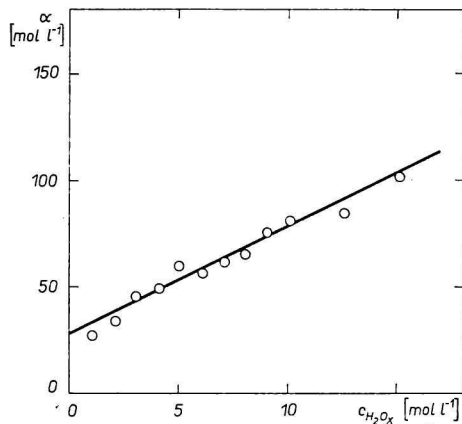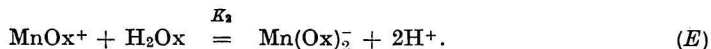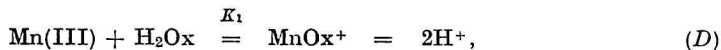3×10^{-4} M-Mn(III); 5×10^{-3} M-H$_2$Ox; 70% CH$_3$COOH; $t = 20$°C.

Fig. 8. Determination of the consecutive constants of complexity.
Experimental conditions as in Fig. 1.

where k' stands for the rate constant at equivalent concentration of both reactants, k^x is the rate constant at a higher concentration of oxalic acid, and K_1, K_2 are the consecutive constants of complexity according to the equations

$$\text{Mn(III)} + \text{H}_2\text{Ox} \overset{K_1}{=} \text{MnOx}^+ = 2\text{H}^+, \qquad (D)$$

$$\text{MnOx}^+ + \text{H}_2\text{Ox} \overset{K_2}{=} \text{Mn(Ox)}_2^- + 2\text{H}^+. \qquad (E)$$

Mn(III) denoting the hydrated manganese(III) acetate which functions as oxidant in the reaction. By the method of least squares we determined $K_1 = 27.4$ and $K_2 = 9.1$ (Fig. 8). The ratio of the determined consecutive constants $K_1/K_2 = 3$ complies well with statistical postulates and the Adams—Wegcheider [12] relationship

$$\frac{K_n}{K_{n+1}} = \frac{n+1}{n} \frac{N-n+1}{N-n},$$

where $N - n$ is the number of unoccupied positions of ligands in central atom and n is the number of ligands already linked. For the investigated reaction it holds $N = 3$ if the oxalate anions are considered to be two-donor ligands.

A relatively small effect of the ionic strength on the rate constant (the value of the product $z_A z_B = -0.23$ calculated by the Bjerrum relation) is in agreement with the idea that the slowest and rate-determining step of the redox reaction is an intramolecular redox process of the intermediate MnOx^+ which shows the character of a monomolecular reaction.

The measured value of the activation heat capacity $\Delta C_p^{\ddagger} = 167 \text{ cal K}^{-1} \text{ mol}^{-1}$ expressing the effect of temperature on the value of activation enthalpy and entropy may be connected with considerable effect of temperature on the structure of solvent used. Further kinetic investigations in this medium will better elucidate this phenomenon.

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Translated by R. Domanský