## The Decomposition of Tris-(Oxalato)-Manganate (III) Complex Ion as the Reaction Suitable for the Laboratory Practice on Chemical Kinetics

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### ABSTRACT

The complex ion  $[Mn(C_2O_4)_3]^{3-}$  is very photosensitive and rapidly decomposes at the daylight even at ambient temperatures. Although the mechanism of this reaction is complicated, its kinetic equation obeys the pseudo-first order. In addition, the tris-(oxalate)-manganate ion has a low thermal stability, and the reaction of its decomposition is highly affected by temperature. This makes this reaction very suitable for demonstrating the laws of chemical kinetics to the students – both the first-order reaction kinetics and the dependency of the rate constant on temperature. The kinetic studies of this reaction using a photocolourimetric method were performed; the influence of the initial concentrations of the reagents and temperature on the rate was studied. The didactic implementation of the reaction was discussed. The methodical instruction for the organization of the laboratory practice is provided.

Keywords: activation energy, Arrhenius equation, chemical kinetics, decomposition, first-order reaction

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#### **INTRODUCTION**

Complex compounds of manganese (III) with various ligands have a very high chemical reactivity. The redox chemistry of Mn<sup>+3</sup> is very diverse and was studied thoroughly.<sup>[1-4]</sup> One of such species of

interest is the complex of tervalent manganese with oxalate-ion. A tris-(oxalate)-manganate (III) complex ion is formed in a solution according to the reaction<sup>[5,6]</sup>:

$$4MnSO_{4}(aq) + KMnO_{4}(aq) + 15H_{2}C_{2}O_{4}(aq) \rightleftharpoons$$
$$\rightleftharpoons 5H_{3}\left[Mn\left(C_{2}O_{4}\right)_{3}\right](aq) + 3H_{2}SO_{4}(aq) + KHSO_{4}(aq) + 4H_{2}O(l) \tag{1}$$

or in ionic form:

$$4Mn^{2+}(aq) + MnO_{4}^{-}(aq) + 15C_{2}O_{4}^{2-}(aq) + 8H^{+}(aq) \rightleftharpoons 5\left[Mn(C_{2}O_{4})_{3}\right]^{3-}(aq) + 4H_{2}O(l)$$
(2)

The complex ion is photosensitive and rapidly decomposes at the daylight even at ambient temperatures.<sup>[7]</sup> A brown solution containing tris-(oxalato)-manganate gradually becomes colourless. Although

this reaction includes several elementary steps, and its mechanism is complicated, <sup>[8–17]</sup> it may be described by the following generalized equation:

$$2H_{3}\left[Mn(C_{2}O_{4})_{3}\right](aq) \rightarrow 2MnC_{2}O_{4}(aq) + 3H_{2}C_{2}O_{4}(aq) + 2CO_{2}(g), \qquad (3)$$

or, in ionic form:

$$2\left[Mn(C_{2}O_{4})_{3}\right]^{3-}(aq) \rightarrow 2Mn^{2+}(aq) + 5C_{2}O_{4}^{2-}(aq) + 2CO_{2}(g)$$
(4)

The reaction obeys the first-order kinetic equation.<sup>[8,9,13,14,16]</sup> In addition, the complex ion  $[Mn(C_2O_4)_3]^{3-}$  has a very low thermal stability and the reaction is strongly affected by the temperature.<sup>[18,19]</sup> This makes the reaction (4) very suitable for the laboratory practice on chemical kinetics for undergraduate students in chemistry. Possible implications are the determination of the reaction order, the study of the first-order reaction kinetics and the study of the temperature influence on the reaction rate. The purpose of this study is to verify the suitability of the tris-(oxalato)-manganate (III) decomposition reaction for the laboratory practice and to develop the methodical recommendations for the students.

#### **EXPERIMENTAL PROCEDURE** Reagents and Equipment

The manganese (II) sulphate pentahydrate, potassium permanganate and oxalic acid dihydrate of analytical grade. commercially available from Peaxum<sup>TM</sup> were used for preparation of the stock solutions. The stock solutions of 0.1 M MnSO<sub>4</sub>, 0.1 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and 0.1 M KMnO<sub>4</sub> were prepared by accurate weighting the corresponding masses of the reagents using the analytical balance ВЛ-120М  $Госметр^{TM}$ , (produced by accuracy  $\pm 0.0001$  g) and dissolving in 0.5 L volumetric flasks. The concentration photocolourimeter K $\Phi$ K-2 (produced by Загорский оптико-механический

завод<sup>TM</sup>) was used for kinetic experiments at ambient temperature, and the spectrophotometer ПЭ-5300В (produced by Промэколаб<sup>TM</sup>) connected to the PC with a special software was used for the experiments at elevated temperatures. The quartz cuvettes with a pathlength of 10 mm were used in both cases. The water bath LT-2 (produced by LabTex<sup>TM</sup>) was used for thermostating the solutions.

### The Experiments at Ambient Temperature

In the first series of experiments the effect of initial concentration of the reagent on the reaction rate at ambient temperature was studied. Since the initial reagent  $[Mn(C_2O_4)_3]^{3-}$ , is formed in situ according to the reaction (2), its initial concentration cannot be controlled directly. Therefore, four series of solutions containing the same quantities of MnSO<sub>4</sub> and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, but different quantities of KMnO<sub>4</sub> were prepared according to Table 1.

### **Table 1.** The preparation of solutions for the study of the effect of initial

concentration on the reaction rate.				
No	of	Concentration of the solution, M		
series		MnSO <sub>4</sub>	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	KMnO <sub>4</sub>
1		0.10	0.10	0.10
2		0.10	0.10	0.05
3		0.10	0.10	0.02
4		0.10	0.10	0.01

For each series of experiments 5 mL of  $MnSO_4$  solution and 35 mL of  $H_2C_2O_4$  solution are mixed in a beaker and 10 mL of KMnO<sub>4</sub> solution are added in another

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beaker. Both beakers are thermostated at the ambient temperature during 15 minutes and then mixed together. A brown complex ion forms immediately and begins to decompose. A quartz cuvette is filled with the reaction mixture and placed into photocolourimeter K $\Phi$ K-2. The clock are started, and the intensity of the light transmission (T, %) of the reaction mixture relative to the distilled water at the wavelength of 540 nm was measured every 60 seconds until the solution become colourless. In this way, the kinetic curves were obtained for each series of experiments. The experiment was repeated three times for the each series.

# The Experiments at Elevated Temperature

In the second series of experiments the effect of temperature on the reaction rate was studied. The initial reagents were prepared analogously to the series No. 1 in Table 1. The beakers with the reagents were placed in the water bath and thermostated at the desired temperature for 15 minutes. Since, the reaction at elevated

temperatures proceeds very fast, the kinetic curves were obtained using the spectrophotometer  $\Pi$ Э-5300B with automatic fixation of the light transmission values. The period between the consecutive measurements was reduced to 2 seconds.

#### **RESULTS AND DISCUSSION**

# The Effect of Initial Concentration on the Reaction Rate

The typical kinetic curves (in coordinates optical density A versus time t) for the reaction mixtures with the various initial concentrations of potassium permanganate presented in Figure 1. are The determination of the rate constant of the reaction first-order with colorimetric control of concentrations can be performed according to equation<sup>[20]</sup>:

$$k = \frac{1}{t} \cdot \ln \frac{A_0}{A},\tag{5}$$

where  $A_0$  is the optical density of the solution at the initial moment of reaction.



Fig. 1. The typical kinetic curves for the reaction with various initial concentration of reagents:  $1 - 0.10 M KMnO_4$ ;  $2 - 0.05 M KMnO_4$ ;  $3 - 0.02 M KMnO_4$ ;  $4 - 0.01 M KMnO_4$ .



**Fig. 2.** The determination of the rate constants for the first-order reaction with various initial concentration of reagents:  $1 - 0.10 \text{ M KMnO}_4$ ;  $2 - 0.05 \text{ M KMnO}_4$ ;  $3 - 0.02 \text{ M KMnO}_4$ ;  $4 - 0.01 \text{ M KMnO}_4$ .

The graphs in coordinates  $\ln \frac{A_0}{A} = f(t)$  are shown in Figure 2. As can be seen at Figure 2, the dependencies of  $\ln \frac{A_0}{A}$ versus *t* are linear and have the almost identical slope regardless of the initial concentration.

It confirms that the reaction (4) obeys the first-order reaction kinetics. The average

experimental value of the rate constant is  $k = (19 \pm 5) \cdot 10^{-4} \text{ s}^{-1}$ .

# The Effect of Temperature on the Reaction Rate

Figure 3 shows the graphs in coordinates  $\ln \frac{A_0}{A} = f(t)$  for the reaction at various temperatures. The dependency is linear for all studied temperatures in the temperature interval 25–60°C. The calculated rate constants are listed in Table 2.



*Fig. 3.* The determination of the rate constants for the first-order reaction at various temperatures: 1–25; 2–30; 3–40; 4–50; 5 – 60°C.

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τ, °C	<i>Т</i> , К	$k \cdot 10^3$ , s <sup>-1</sup>	<u>T – 298.15 K</u> 10 K	$\lg \frac{k}{k_{_{298.15\mathrm{K}}}}$	$\frac{1}{T} \cdot 10^3$ , K <sup>-1</sup>	ln k	$\ln \frac{k}{T}$
25	298.15	3245	0.0	0.000	3.354	-5.731	-11.428
30	303.15	4300	0.5	0.122	3.299	-5.449	-11.163
40	313.15	8097	1.5	0.397	3.193	-4.816	-10.563
50	323.15	11,202	2.5	0.538	3.095	-4.492	-10.270
60	333.15	21,879	3.5	0.829	3.002	-3.822	-9.631

 Table 2. The rate constants of the reaction (4) at various temperatures and the parameters of van't Hoff, Arrhenius and Eyring–Polanyi equations.

An empirical rule was proposed by J. van't Hoff,<sup>[21]</sup> which states that for many reactions the rate constant increases in  $\gamma$  times upon increasing the temperature by 10 K, where  $\gamma = \frac{k_{T+10}}{k_T}$  is a temperature coefficient of the reaction.

For the arbitrary temperature difference the equation can be rewritten in the following form:

$$\frac{k_T}{k_{200,15\,K}} = \gamma^{\frac{T-298.15\,K}{10K}},\tag{6}$$

$$\lg \frac{k_T}{k_{208,15 \text{ K}}} = \frac{T - 298.15 \text{ K}}{10 \text{ K}} \cdot \lg \gamma$$

The corresponding values of  $\lim_{\substack{k_T \\ k_{298,15 \, \mathrm{K}}}} (7)$  and

 $\frac{T-298.15K}{10K}$  are presented in Table 2. The

dependency is shown in Figure 4. It was processed by the less squares method, and, according to it,  $\lg \gamma = (233 \pm 7) \cdot 10^{-3}$ , which leads to the value  $\gamma = 1.71 \pm 0.03$ .



Fig. 4. The determination of the temperature coefficient of the reaction (4).

S. Arrhenius, basing on van't Hoff equation, proposed an equation for the dependency of the rate constant on temperature<sup>[22]</sup>:

$$k_T = A \cdot e^{-\frac{E_a}{R \cdot T}},\tag{8}$$

where A is a pre-exponential factor,  $E_a$  is an activation energy, and R is the universal gas constant. This equation can be linearized in the form:

$$\ln k_T = \ln A - \frac{E_a}{R} \cdot \frac{1}{T} \,. \tag{9}$$

The corresponding values of  $\ln k_T$  and  $\overline{T}$  are presented in Table 2. The Arrhenius plot is shown in Figure 5. The dependency

was processed by the less squares method, and, according to it,  $\ln A = 11.9 \pm 0.9$  and  $\frac{E_a}{R} = 5250 \pm 310$ , K, which gives the values of the activation energy  $E_a = 43,560 \pm 2560$  J/mol and the preexponential factor  $A = (144 \pm 12) \cdot 10^3$  s<sup>-1</sup>.



Fig. 5. The Arrhenius plot for the reaction (4).

Eyring, Evans and Polanyi<sup>[23–25]</sup> developed an equation that describes the dependency of the rate constant on temperature in terms of the transition state theory:

$$k_T = \frac{k_B \cdot T}{h} \cdot e^{\frac{\Delta G^{\ddagger}}{R \cdot T}} = \frac{k_B \cdot T}{h} \cdot e^{\frac{\Delta H^{\ddagger}}{R \cdot T}} \cdot e^{\frac{\Delta S^{\ddagger}}{R}}$$
(10)

where  $k_B$  is the Boltzmann constant, h is the Planck constant, and  $\Delta G^{\ddagger}$ ,  $\Delta H^{\ddagger}$  and  $\Delta S^{\ddagger}$  are, respectively, the Gibbs free energy, the enthalpy and the entropy of activation.

This equation can be linearized in the form:

$$\ln \frac{k_T}{T} = -\frac{\Delta H^{\ddagger}}{R} \cdot \frac{1}{T} + \left( \ln \frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R} \right).$$
(11)

The corresponding values of  $\ln \frac{k_T}{T}$  and  $\frac{1}{T}$ are presented in Table 2. The Eyring-Polanyi plot is shown in Figure 6. The dependency was processed by the less squares method, and, according to it,  $\left(\ln\frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R}\right) = 5.1 \pm 0.9$ and  $\Delta H^{\ddagger} = 4940 \pm 310$ , K, which gives the values R enthalpy of the of activation  $\Delta H^{\ddagger} = 41,030 \pm 2560 \text{ J/mol}$  and the entropy of activation

$$\Delta S^{\ddagger} = -155 \pm 7 \text{ J/(mol} \cdot \text{K})$$



Fig. 6. The Eyring–Polanyi plot for the reaction (4).

### Discussion

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The data, presented in Table 2 and in Figures 2–6 show that both concentration and temperature dependence of the reaction (4) rate are reproduced satisfactory. All the dependencies  $\ln \frac{A_0}{A} = f(t)$  at the various temperatures,

$$\log \frac{k_T}{k_{298.15 \text{ K}}} = f\left(\frac{T - 298.15 \text{ K}}{10 \text{ K}}\right), \quad \ln k_T = f\left(\frac{1}{T}\right) \text{ and }$$

 $\ln \frac{k_T}{T} = f\left(\frac{1}{T}\right)$  have the linear correlation

coefficients  $R^2$  close to unity. This allows to assume that the reaction of tris-(oxalate)-manganate (III) decomposition is very suitable for the kinetic studies by the students during the laboratory practice lesson on chemical kinetics.

### THE METHODIC RECOMMENDATIONS FOR STUDENTS

This section contains the methodic recommendation for students. It can be used by the instructors of the laboratory practice lesson as the students' handouts.

### **Reagents and Equipment**

- An analytical balance
- A photocolourimeter or a spectrophotometer
- Two quartz cuvettes, 10 mm
- A water bath with the heating ability up to 60°C
- Beakers, 100 mL
- Volumetric pipettes, 5, 10 and 25 mL
- A graduated cylinder, 50 mL
- Volumetric flasks, 50 mL
- KMnO<sub>4</sub>, 0.1 M solution
- MnSO<sub>4</sub>, 0.1 M solution
- $H_2C_2O_4$ , 0.1 M solution

### **Performing the Experiment**

- Prepare the photocolourimeter or the spectrophotometer and warm it up during 15 minutes. Set the wavelength to 540 nm. Fill one quartz cuvette with distilled water.
- Prepare 0.05 M, 0.02 M and 0.01 M solutions of KMnO<sub>4</sub> by diluting a 0.1 M stock solution. Use a volumetric flask, 50 mL and the volumetric pipettes, 5, 10 and 25 mL.

- Add 5 mL of 0.1 MnSO<sub>4</sub> solution to the beaker using a pipette. Add 35 mL of 0.1 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution to the same beaker using a graduated cylinder.
- Add 10 mL of 0.1 M KMnO<sub>4</sub> solution to another beaker. Thermostate both beakers at the temperature of the environment during 15 minutes.
- Pour the content of one beaker into another. The brown complex ion solution forms. Fill the quartz cuvette, 10 mm by the reaction mixture and place it into the photocolourimeter.
- Start measuring the light transition intensity every 60 seconds until the reaction mixture becomes discoloured. Record the dependency T, % versus t, s.
- Repeat the experiment three more times, replacing 0.1 M KMnO<sub>4</sub> solution by previously prepared 0.05, 0.02 and 0.01 M solutions.
- Repeat the experiment with 0.1 M KMnO<sub>4</sub> solution four more times at the temperatures 30, 40, 50 and 60°C. Use the water bath to thermostat the beakers with the initial reagents at these temperatures. At the elevated temperatures the period between the consecutive measurements of the light transition intensity can be reduced to 5 s.

### **Processing the Experimental Data**

• For each experiment enter the experimental data into the table (see Table 3).

**Table 3.** The data for calculating the rate constants of the first-order reaction.

<i>t</i> , s	T, %	A	$\ln \frac{A_0}{A}$
0		$A_0$	0

• For each experiment plot the graphs  $\ln \frac{A_0}{A} = f(t)$  (see Figures 2 and 3) and using the less squares method determine the rate constant of the reaction.

- Calculate the average value of the rate constant at the ambient temperature and its uncertainty.
- Collect the rate constant value at the elevated temperatures and the parameters of van't Hoff, Arrhenius and Eyring–Polanyi equations into the table (see Table 2).
- Plot the graph  $\lg \frac{k_T}{k_{298.15 \text{ K}}} = f(T - 298.15 \text{ K}/10\text{ K})$ (see

Figure 4) and using the less squares method determine the temperature coefficient of the reaction  $\gamma$  and its uncertainty.

- Plot the graph ln k<sub>T</sub> = f(1/T) (see Figure 5) and using the less squares method determine the activation energy E<sub>a</sub> and the pre-exponential factor A for the reaction and their uncertainties.
- Plot the graph  $\ln \frac{k_T}{T} = f(1/T)$  (see Figure 6) and using the less squares method determine the enthalpy  $\Delta H^{\ddagger}$  and the entropy  $\Delta S^{\ddagger}$  of activation for the reaction and their uncertainties.

### CONCLUSIONS

kinetics of The the tris-(oxalate)manganate (III) decomposition reaction at the various concentrations of the reagents studied photocolourimetric was by method. The first order of reaction was confirmed and the average value of rate  $k = (19 \pm 5) \cdot 10^{-4} \text{ s}^{-1}$ constant was estimated. The dependency of the rate constant on temperature was studied. The temperature coefficient of the reaction, the activation energy, the pre-exponential factor and the enthalpy and the entropy of activation were estimated:  $\gamma = 1.71 \pm 0.03$ .  $E_a = 43,560 \pm 2560 \text{ J/mol},$  $A = (144 \pm 12) \cdot 10^3 \text{ s}^{-1}$ 

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 $\Delta H^{\ddagger} = 41,030 \pm 2560 \text{ J/mol},$  $\Delta S^{\ddagger} = -155 \pm 7 \text{ J/(mol} \cdot \text{K}).$ 

The reaction was found very suitable for the laboratory practice on chemical kinetics for the students. The methodical recommendations were developed.

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