Kinetic study of the oxidation of malonic acid by the manganese(III) ions

Ľ. TREINDL and M. MRÁKAVOVÁ

Department of Physical Chemistry, Faculty of Natural Sciences
and *Institute of Chemistry, Komenský University,*
842 15 Bratislava

The oxidation of malonic acid by the Mn(III) ions in the solution of sulfuric acid is an important constituent of the Belousov—Zhabotinskii oscillating system. It is an inner-sphere redox reaction the first step of which is the formation of an intermediary complex. It is followed by the slow and rate-determining step

$$[(SO_4)_n\text{---}Mn^{III}\text{---}Ma] \quad \rightleftharpoons \quad \bullet CH(COOH)_2 + H^+ + [Mn^{II}\text{---}(SO_4)_n]$$

which is very likely reversible owing to the retardation effect of the Mn(II) ions.

In this paper, the influence of the presence of oxygen on the value of activation parameters is described and analyzed in more detail.

Окисление малоновой кислоты ионами Mn(III) в растворе серной кислоты, как важная составная часть осцилляционной реакции Белоусовой—Жаботинского, является внутрисферной окислительно-восстановительной реакцией, на первой стадии которой образуется промежуточный комплекс. Затем следует медленный, скорость определяющий процесс

$$[(SO_4)_n\text{---}Mn^{III}\text{---}Ma] \quad \rightleftharpoons \quad \bullet CH(COOH)_2 + H^+ + [Mn^{II}\text{---}(SO_4)_n],$$

который, в связи с замедляющим действием ионов Mn(II), скорее всего, является обратимым.

В работе описано более подробно влияние присутствия кислорода на величину параметров активации.

The oxidation of malonic acid by the Ce(IV) ions was studied under different conditions in the solution of sulfuric acid [1, 2] and perchloric acid [3, 4]. *Barkin et al.* [5] investigated it again thoroughly in the presence of oxygen the influence of which had escaped the attention of preceding authors. The influence of oxygen on the oxidation of malonic acid and other substrates by the Ce(IV) ions in connection with the Belousov—Zhabotinskii reaction was recently described by us [6]. The

kinetics of the oxidation of malonic acid by manganese(III) pyrophosphate was described by *Kemp* and *Waters* [7]. As for the oxidation of malonic acid by the Mn(III) ions in the solution of sulfuric acid, only the stoichiometry and elementary kinetic data have been given [8] up to now.

Since malonic acid is frequently used as a substrate in the presence of the Mn(III)—Mn(II) catalysts in the Belousov—Zhabotinskii oscillating system, we have studied the kinetics of its oxidation by the Mn(III) ions in the solution of sulfuric acid from the view-point of the influence of the presence of oxygen as well.

Experimental

The kinetics of the oxidation of malonic acid by the Mn(III) ions was studied polarographically by investigating the time dependence of the limiting diffusion current of the Mn(III) ions on a mercury dropping electrode at the potential of -0.2 V against the potential of a $Hg|Hg_2SO_4$ electrode in 1.5 mol dm^{-3} solution of sulfuric acid. The presented values of rate constants are always the mean of four independent measurements.

The solution of the Mn(III) ions was prepared by 10 min electrooxidation of a 5×10^{-4} mol dm^{-3} solution of manganese(II) sulfate in a 1.5 mol dm^{-3} solution of sulfuric acid on a large-area platinum electrode in nitrogen atmosphere (electric bulb industry nitrogen).

The chemicals used were anal. grade reagents. The solutions were prepared with redistilled water.

Results

The authors of paper [8] have proved that the reaction stoichiometry in inert nitrogen atmosphere obeys the following equation

$$6Mn^{3+} + CH_2(COOH)_2 + 2H_2O \rightarrow 6Mn^{2+} + HCOOH + 2CO_2 + 6H^+ \qquad (A)$$
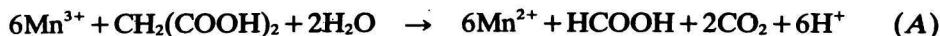
while the reaction in the presence of oxygen is nonstoichiometric. We verified stoichiometric equation (A) by polarimetric titration and ascertained the consumption of six Mn(III) ions for a molecule of substrate in the absence of oxygen.

The oxidation of malonic acid by the Mn(III) ions is a reaction of the first order with respect to concentration of the oxidant. The dependence of the logarithm of the numerical value of limiting diffusion current on time is linear in the first two half-lives of the reaction (Fig. 1). The rate constant k_{exp} in s^{-1} is a nonlinear function of concentration of the substrate (Fig. 2). By using the logarithmic analysis of this relationship, we found that the corresponding partial reaction order was equal to 0.8. The value of the experimental rate constant decreases with increasing concentration of the Mn(II) ions (Fig. 3). The logarithmic analysis of this relationship has shown that the partial reaction order with respect to concentration
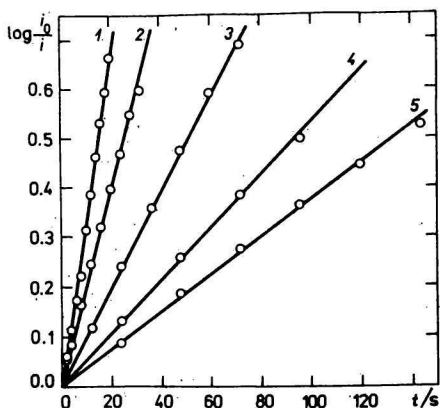
Fig. 1. Evidence of the first reaction order with respect to concentration of the Mn(III) ions.
1.5 mol dm^{-3} H$_2$SO$_4$,
5×10^{-4} mol dm^{-3} Mn(III).
Concentration of malonic acid/mol dm^{-3}:
1. 5×10^{-2}; 2. 2.5×10^{-2}; 3. 10^{-2}; 4. 5×10^{-3};
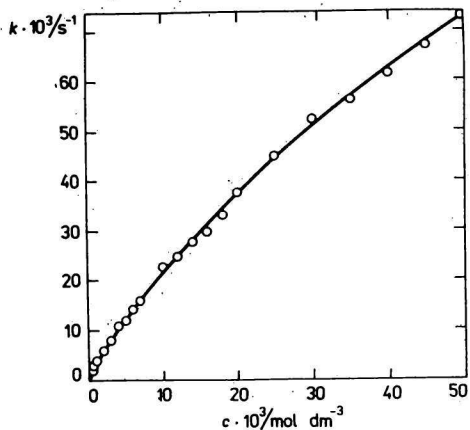5. 3×10^{-3}; temperature 20°C.

Fig. 2. Variation of the experimental rate constant with concentration of the substrate.
1.5 mol dm^{-3} H$_2$SO$_4$,
5×10^{-4} mol dm^{-3} Mn(III), temperature 20°C.
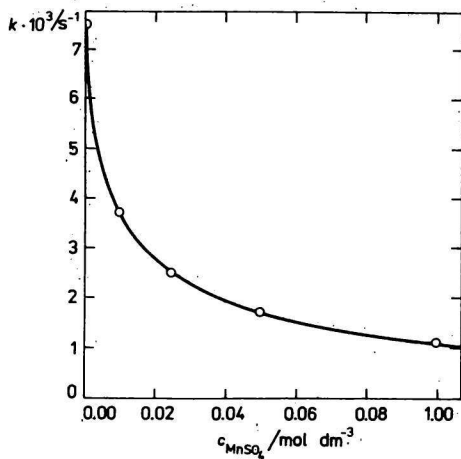
Fig. 3. Retardation effect of the Mn(II) ions.
1.5 mol dm^{-3} H$_2$SO$_4$,
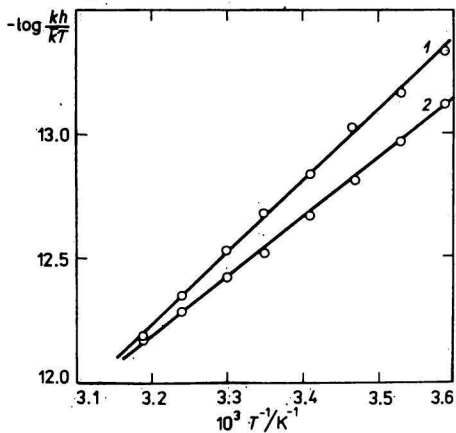5×10^{-4} mol dm^{-3} Mn(III), 10^{-3} mol dm^{-3}
malonic acid; temperature 30°C.

Fig. 4. Temperature dependence of the experimental rate constant k'.
$k' = k/[\text{Ma}]^{0.8}$, 1.5 mol dm^{-3} H$_2$SO$_4$,
5×10^{-4} mol dm^{-3} Mn(III), 10^{-3} mol dm^{-3}
malonic acid.
1. In the absence of oxygen; 2. in the presence of oxygen.

Table 1

Influence of oxygen on the value of activation parameters

	ΔH^{*}/kJ mol^{-1}	ΔS^{*}/J K^{-1} mol^{-1}
With oxygen	44.5	−78.8
Without oxygen	53.6	−51.4

of the Mn(II) ions is equal to -0.5. Hence, the rate equation assumes the form (the brackets denote relative concentrations)

$$- d[Mn(III)]/dt = k^*[Mn(III)][CH_2(COOH)_2]^{0.8}[Mn(II)]^{-0.5} \qquad (1)$$

The influence of temperature on reaction rate was investigated in the temperature interval 5—40°C in the presence as well as absence of oxygen and evaluated on the basis of the Eyring equation (Fig. 4). By using the method of least squares, the corresponding activation parameters, *i.e.* activation enthalpy and activation entropy, were calculated (Table 1).

Discussion

The Belousov—Zhabotinskii oscillating reaction aroused uncommon interest in the seventieth years [9] and for this reason, great attention is given to the study of its partial reaction steps, too. Such a step is also the oxidation of malonic acid by the Mn(III) ions which is the topic of this study.

The first reaction order with respect to concentration of the Mn(III) ions is fulfilled in the course of the first two reaction half-lives if we use a stoichiometric excess of the substrate. The partial reaction order 0.8 may be related with the formation of an intermediary complex Mn^{III}—Ma, *i.e.* in principle with a mechanism of the Michaelis—Menten type (Ma = malonic acid or its anion). We were no longer able to measure further part of the dependence of reaction rate constant on the substrate concentration which was likely to approach the limit because the reaction rates were too high.

Similarly, the authors of paper [10] regard the formation of an intermediary complex as the first step of the reaction mechanism involved in the oxidation of formic acid by the Mn(III) ions. The second step in our scheme is an intramolecular redox stage giving rise to a free radical

$$[(SO_4)_n—Mn^{III}—Ma] = \bullet CH(COOH)_2 + H^+ + [Mn^{II}—(SO_4)_n] \qquad (B)$$

The retardation effect of the Mn(II) ions indicates a reverse step of reversible stage (*B*). The fractional reaction order with respect to concentration of the Mn(II) ions

may be explained by the fact that, besides the reverse step of reversible stage (B), a shift in equilibrium in favour of the Mn(III) ions is to be expected

$$2Mn(III) \rightleftharpoons Mn(II) + Mn(IV) \tag{C}$$
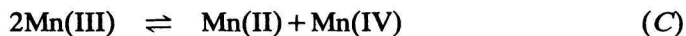
The free radicals $\cdot$ CH(COOH)$_2$ are evidently consumed in the subsequent step in the oxidation by the Mn(III) ions. In the first step, the oxidation product of malonic acid is tartronic acid and provided the concentration of Mn(III) ions is sufficient, the following substances arise in subsequent steps: glyoxylic acid, formic acid, and carbon dioxide — like in oxidation of malonic acid by the Ce(IV) ions [5].

According to our results, the presence of oxygen in the reaction system affects not only the reaction stoichiometry [8] but also the reaction kinetics. In the presence of oxygen, the value of activation enthalpy decreases by 9.1 kJ mol^{-1} and the negative value of activation entropy increases by 27 J K^{-1} mol^{-1}. The significant influence of oxygen on the value of activation parameters may be so interpreted that the dissolved oxygen reacts with the intermediary radicals [5] and thus catalyzes the oxidation of malonic acid by the Mn(III) ions

$$Ma \cdot + O_2 \rightleftharpoons MaOO \cdot \tag{D}$$

$$MaOO \cdot + Ma \rightarrow Ma \cdot + MaOOH \tag{E}$$

$$MaOOH + Mn^{3+} \rightarrow MaOO \cdot + Mn^{2+} + H^+ \tag{F}$$

where Ma $\cdot$ is the original radical $\cdot$ CH(COOH)$_2$, MaOO $\cdot$ is peroxoradical, Ma is malonic acid, and MaOOH is peroxomalonic acid. Besides, we may attribute the irreversible consumption of oxygen to some parallel step as it is indicated by the change in reaction stoichiometry in the presence of oxygen.

In the oxidation of malonic acid by the Ce(IV) ions [5] the reaction in the first step, i.e. the oxidation of substrate to tartronic acid is also considerably slower than it is in further steps.

References

1. Sengupta, K. K. and Aditya, S., Z. Phys. Chem. (Frankfurt) 38, 25 (1963).
2. Kasperek, G. J. and Bruice, T. C., Inorg. Chem. 10, 382 (1971).
3. Jwo, J. J. and Noyes, R. M., J. Amer. Chem. Soc. 97, 5422 (1975).
4. Amjad, Z. and McAuley, A., J. Chem. Soc., Dalton Trans. 1977, 304.
5. Barkin, S., Bixon, M., Noyes, R. M., and Bar-Eli, K., Int. J. Chem. Kinet. 10, 619 (1978).
6. Treindl, Ľ. and Fabian, P., Collect. Czech. Chem. Commun. 45, 1168 (1980).
7. Kemp, T. J. and Waters, W. A., J. Chem. Soc. 1964, 1489.
8. Barek, J., Berka, A., and Hladíková, A., Microchem. J. 24, 323 (1979).

9. Tyson, J. J., *The Belousov-Zhabotinskii Reaction*, *Lecture Notes in Biomathematics*, Vol. *10*. Springer, Berlin, 1976.
10. Kemp, T. J. and Waters, W. A., *J. Chem. Soc. 1964*, 339.

Translated by R. Domanský