Belousov-Zhabotinsky oscillatory reaction. Kinetics of malonic acid decomposition

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The kinetics of the Belousov-Zhabotinsky (BZ) oscillatory reaction was analyzed. With this aim, the time evolution of a reaction mixture composed of malonic acid, bromate, sulfuric acid and cerium(III) was studied at 298 K. Pseudo-first order kinetics with respect to malonic acid as the species undergoing decomposition with a corresponding rate constant, $k = 7.5 \times 10^{-3}$ min^{-1}, was found.

Keywords: kinetics, non-linear dynamics, oscillatory reaction, Belousov-Zhabotinsky reaction.

INTRODUCTION

In the literature,[1–7] reaction mixtures composed of an organic substrate, bromate, sulfuric acid and a metallic catalyst, which show oscillatory behavior, are referred to as Belousov-Zhabotinsky (BZ) reactions mixtures. The most studied[7–11] and by far the best characterized is the malonic acid, bromate, sulfuric acid and cerium(III) reacting system. This system was also analyzed in this study.

As was explicitly stated by one of the best known scientists in this field, Endre Koros,[7] the species in the BZ system consisting of malonic acid, bromate, sulfuric acid and cerium(III), can be classify into three distinct groups: (a) the reactants (BrO_3^- and malonic acid), (b) the recycling intermediates (*e.g.*, Br^-, BrO_2, $HBrO_2$, Ce^{4+}) and (c) the final products (*e.g.*, CO_2, brommalonic acid). In the mentioned reaction system, the concentrations of recycling intermediates exhibit temporal concentration oscillations, whereas the concentrations of the reactants and the final products exhibit a corresponding stepwise evolution. The stepwise decreasing of the reactant concentrations means that the rate of decomposition periodically changes and that in this reaction system there are at least two kinetic states.

However, bearing in mind that this system can be considered as the decomposition of malonic acid, as well as that decomposition reactions are often first order

with respect to the reactant undergoing decomposition, we decided to analyze the kinetics of the overall reaction as a pseudo-first order reaction with respect to malonic acid.

EXPERIMENTAL

The kinetics of the Belousov-Zhabotinsky oscillatory reaction was analyzed in a well stirred closed reactor (magnetic stirrer of 700 rpm) at a constant temperature $T = 298\pm0.5$ K (25 °C). The time evolution of the reaction was monitored potentiometrically, using a Pt-electrode and a bromide ion-sensitive electrode. Both electrodes were connected to a Ag/AgCl reference electrode by a sulfate bridge.

All experiments were carried out with constant values of the initial concentrations of potassium bromate, sulfuric acid, potassium bromide and cerium(III): $[KBrO_3]_0 = 6.2\times10^{-2}$ mol/dm^3, $[H_2SO_4]_0 = 1.0$ mol/dm^3, $[KBr]_0 = 1.5\times10^{-5}$ mol/dm^3, $[Ce_2(SO_4)_3]_0 = 2.5\times10^{-3}$ mol/dm^3. The initial malonic acid concentration, $[CH_2(COOH)_2]_0$, was varied from 8.0×10^{-3} to 4.3×10^{-2} mol/dm^3.

The introduction of 1 ml of cerium(III) sulfate solution to 50 ml of the standardized mixture of potassium bromate, sulfuric acid, potassium bromide solution was taken as the inital moment of the reaction.

RESULTS AND DISCUSSION

With the aim of analyzing the BZ reaction of malonic acid decomposition in the presence of bromate, sulfuric acid and cerium(III), numerous experiments were performed where only the initial concentration of malonic acid was varied. The emergence of the oscillation evolution and the increasing number of oscillations with increasing initial malonic acid concentration can be seen in Fig. 1. Also, with increasing initial malonic acid concentration, a shortening of the preoscillatory period, τ_1, and a prolongation of the time elapsed from the beginning of the reaction until the end of an oscillatory evolution τ_{end}, were found.

However, in all experiments the type of oscillogram is permanent. Hence, under the considered conditions, it could be supposed that the malonic acid concentration at the end of reaction is approximately constant, independent of the initial malonic acid concentration. With this assumption and the fact that decomposition reactions are often first order with respect to the reactant undergoing decomposition, the kinetic analysis could be begun by considering the overall process as pseudo-first order with respect to malonic acid. In other words, if both assumptions are valid, the equation

$$d[CH_2(COOH)_2]/dt = -k[CH_2(COOH)_2]$$

as well as the integrated form of this equation,

$$\tau_{end} = -(1/k)\ln[CH_2(COOH)_2]_{end} + (1/k)\ln[CH_2(COOH)_2]_0$$

where $[CH_2(COOH)_2]_{end}$ and $[CH_2(COOH)_2]_0$ denote the concentrations of malonic acid at $t = \tau_{end}$ and $t = 0$, must be satisfied.

Indeed, the obtained results obey the last equation under considered conditions very well (Fig. 2). Thus, it is shown that the malonic acid decomposition can be analyzed as a first order reaction with respect to malonic acid.
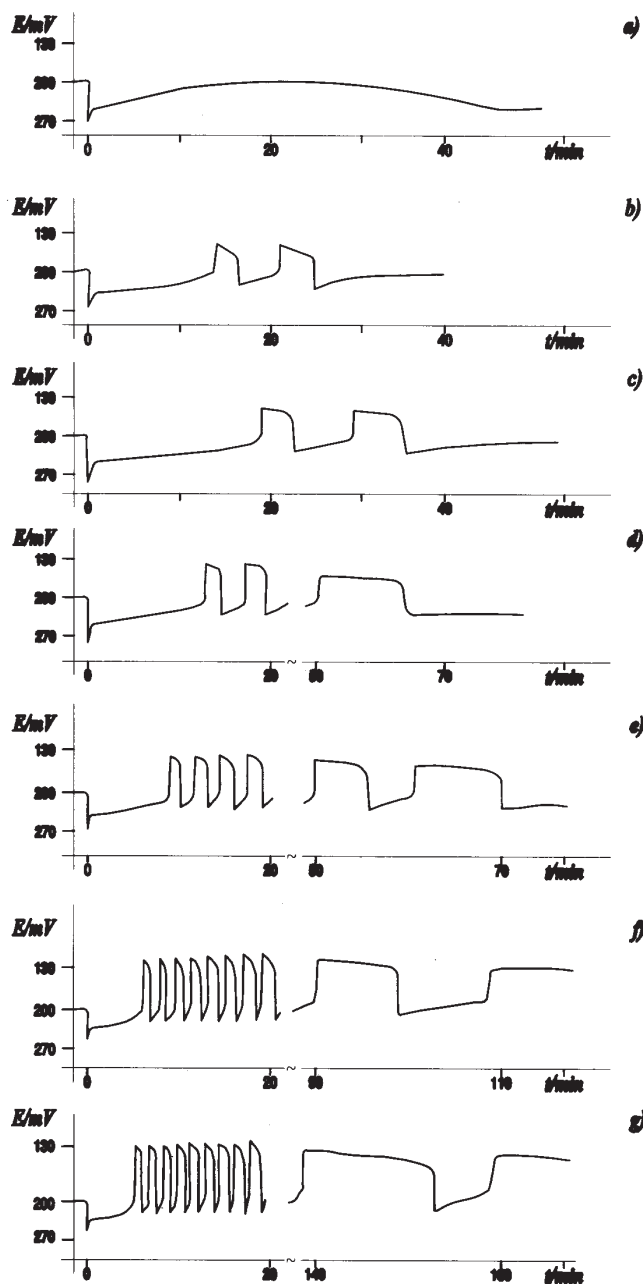
Fig. 1. The potentiometric traces of the BZ reaction, obtained from the Pt-indicator electrode, in order of increasing $[CH_2(COOH)_2]_0$ (in mol/dm^3): a) 8×10^{-3}; b) 9×10^{-3}; c) 1.2×10^{-2}; d) 1.6×10^{-2}; e) 2.2×10^{-2}; f) 3.2×10^{-2}; g) 4.3×10^{-2}; $[KBrO_3]_0 = 6.2\times10^{-2}$ mol/dm^3; $[H_2SO_4]_0 = 1.0$ mol/dm^3, $[KBr]_0 = 1.5\times10^{-5}$ mol/dm^3, $[Ce_2(SO_4)_3]_0 = 2.5\times10^{-3}$ mol/dm^3, $T = 298\pm0.5$ K.
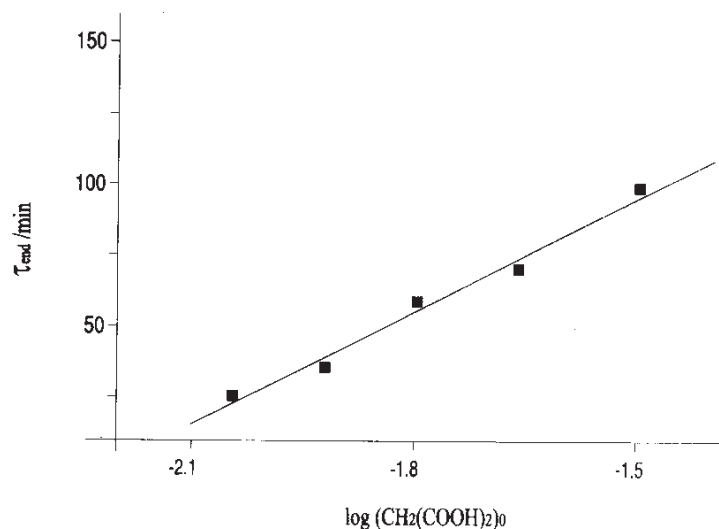
Fig. 2. The time elapsed from the beginning of the reaction until the end of an oscillatory evolution, τ_{end}, as a function of $[CH_2(COOH)_2]_0$ ($[CH_2(COOH)_2]_0$ in mol/dm^3). The concentrations of the other species were the same as in Fig. 1.

The obtained pseudo first order rate constant $k = 7.5 \times 10^{-3}$ min^{-1} for the overall process at 298 K (25 °C) has the expected value. A comment has been made in the literature that this reaction can be analyzed as a kind of monomolecular reaction.[12]

The same method has already been applied to two other well-known oscillatory reactions.[13–16] In Refs. 13–15, where the Bray-Liebhafsky oscillatory reaction was analyzed, it was shown that hydrogen peroxide decomposition in the presence of potassium iodate and sulfuric acid can be considered as a first order reaction with respect to hydrogen peroxide, whereas in Ref. 16, where the Briggs-Rouscher reaction was analyzed, it was shown that hydrogen peroxide decomposition in the presence of potassium iodate, perchloric acid, malonic acid, sulfuric acid, manganese sulfate and starch, can be considered as a first order reaction with respect to hydrogen peroxide as the reactant undergoing decomposition.

CONCLUSION

The postulated method, based on the assumption that the decomposition of any species can be considered as a pseudo-first order reaction with respect to itself, can even be applied to reactant decomposition in an oscillatory reaction system where the reactant decomposition has a cascade time-evolution.

ИЗВОД

БЕЛОУСОВ-ЖАБОТИНСКИ ОСЦИЛАТОРНА РЕАКЦИЈА. КИНЕТИКА РАЗЛАГАЊА МАЛОНСКЕ КИСЕЛИНЕ

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Са циљем да се анализира кинетика Белоусов-Жаботински осцилаторне реакције, проучавана је временска еволуција реакционе смеше која се састоји од малонске киселине, сумпорне киселине и церијума (III) на 298 K. Нађена је кинетика псеудо-првог реда у односу на малонску киселину као врсту која подлеже разлагању и одговарајућа константа брзике, $k = 7.5 \times 10^{-3}$ min^{-1}.

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