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SPECTROPHOTOMETRIC STUDY OF THE BrO_3^-/Ce^{4+}/1,3-CYCLOHEXANEDIONE OSCILLATING SYSTEM

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The modified Belousov-Zhabotinskii oscillatory system with 1,3-cyclohexanedione as substrate is described. Oscillations with a decreasing amplitude take place also if the solution is not stirred. Mechanical stirring of the BZ system does not influence the induction period and the period of the first oscillation at various temperatures, however it results in a smoother course of the oscillations.

В статье приведено описание модифицированной системы Белоусова-Жаботинского с 1,3-циклогександионом в качестве субстрата. Колебания с затухающей амплитудой возникают и в не перемешиваемом растворе. Механическое перемешивание системы Белоусова-Жаботинского не оказывает влияния на величину периода индукции и периода первой осцилляции для нескольких значений температуры, однако, оно проявляется в более сглаженной осцилляции.

INTRODUCTION

Janjic and coworkers have shown previously that chemical oscillations could be observed with systems analogous to that of Belousov-Zhabotinskii (BZ), in which malonic acid was replaced by a simple ketonic compound, such as 2,4-pentanedione /1/, fluorinated 2,4-pentanedione, 2,5-hexanedione and acetone /2, 3/, cyclohexanone and cyclopentanone /4–6/ etc. These reaction systems seem to be important in connection with the effect of stirring and that of the presence of oxygen on their oscillating behavior /7–8/. The influence of oxygen and of mechanical stirring on the modified BZ reaction in presence of some ketonic compounds have been studied recently also by us /9–12/.

In the present paper we report our preliminary investigations of the oscillating behavior of the modified BZ reaction system with 1,3-cyclohexanedione as substrate not described yet. Attention has been focused on the effect of mechanical stirring in dependence on the temperature.

EXPERIMENTAL

Reagents

1,3-Cyclohexanedione has been prepared according to /13/. $NaBrO_3$, $Ce(SO_4)_2 \times 4H_2O$, H_2SO_4 pro anal.): Merck A. G.

Spectrophotometric measurements

Spectrophotometric measurements were carried out on a Specord UV–VIS type apparatus (Carl Zeiss, Jena) in 10 mm cuvettes placed in a tempered block connected with a TM 150 type ultrathermostat (Medingen). Reaction course was indicated by the change of the absorbancy at the wavenumber of 28×10^3 cm^{-1} corresponding to the absorption of Ce(IV) ions. The reaction system was stirred by an electromagnetic stirrer /14/.

Activation parameters were evaluated from the logarithmic dependence of the induction period and that of the first oscillation on the reciprocal absolute temperature by the method of least squares.

RESULTS AND DISCUSSION

The oscillating BZ reaction with 1,3-cyclohexanedione as substrate was studied spectrophotometrically. After an induction period, the concentration of Ce(IV) ions begins to oscillate with a decreasing amplitude (Fig. 1). These oscillations take

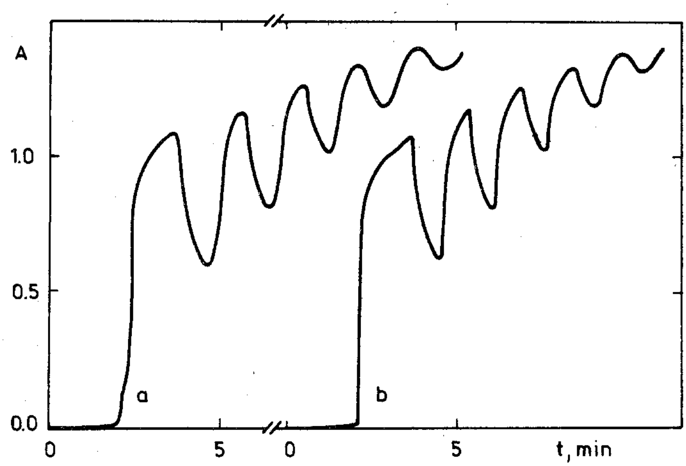

Fig. 1. Oscillations of the BrO_3^-/Ce^{4+}/1,3-cyclohexanedione/H_2SO_4 system. Experimental conditions as in text. Temperature: 40 °C, in presence of air-oxygen, a: no stirring, b: with stirring

Table 1

Induction period and that of first oscillation in absence and presence of mechanical stirring $Ce(SO_4)_2$; 4×10^{-4} mol/dm³ $NaBrO_3$; 6×10^{-2} mol/dm³ 1,3-cyclohexanedione: 6×10^{-3} mol/dm³ 1.24 H_2SO_4, presence of air

Temperature (°C)	τ_{ind} (s) stirring	τ_{ind} (s) no stirring	T_1 (s) stirring	T_1 (s) no stirring
10	2091	2091	1033	1111
20	640	592	408	558
30	272	315	238	291
40	131	121	136	165

place also in the absence of stirring of the solution. The influence of the temperature and stirring on the induction period of the oscillations and on the period of the first oscillation were studied at initial concentrations: 4×10^{-4} mol/dm³ of $Ce(SO_4)_2$, 6×10^{-2} mol/dm³ of $NaBrO_3$, 6×10^{-3} mol/dm³ of 1,3-cyclohexanedione, 1.24 mol/dm³ of H_2SO_4 (Table 1). The logarithmic dependence of the induction period on the reciprocal absolute temperature results the activation energy $E = 64.1 \pm 1.1$ kJ/mol and preexponential term $A = 3.4 \times 10^8$ s^{-1} in absence of stirring, and the activation energy $E = 64.3 \pm 1.1$ kJ/mol and preexponential term $A = 4.3 \times 10^8$ s^{-1} in presence of mechanical stirring. The logarithmic dependence of the period of the first oscillation on the reciprocal absolute temperature results the activatino energy $E = 45.7 \pm 1.1$ kJ/mol and preexpoenntial term $A = 3.2 \times 10^5$ s^{-1} in absence of stirring, and the activation energy $E = 43.9 \pm 1.1$ kJ/mol and preexponential term $A = 1.4 \times 10^5$ s^{-1} in presence of mechanical stirring. Thus we can conclude that a mechanical stirring of the solution has no effect on the corresponding activation parameters, unless it affects the more efficient transport of oxygen into the oscillatory system, as it was observed in Ref. /12/. However, the mechanical stirring of the BZ system with 1,3-cyclohexanedione as substrate manifests itself qualitatively by a smoother course of oscillations, what might be due to a better dispersion of the particles of some less soluble reaction product.

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