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Effect of temperature in cerium-ion-catalyzed bromate-driven oscillators

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Abstract

The influence of substrate composition and initial reagent concentrations on activation energies in closed Ce-ion catalyzed Belousov–Zhabotinsky (BZ) reactions is reported. While changes in the initial concentrations of organic substrate, bromate ion or sulfuric acid showed different changes in activation energies for the various organic substrate BZ systems, for all systems it was found that lowering the Ce-ion concentration leads to a significant decrease in the overall activation energy of the oscillator. When comparing the performance of a malonic acid oscillator run in a batch or in a continuous stirred flow reactor (CSTR), it was found that under CSTR conditions Q_{10} values may become as low as 1.3, while for the batch system the corresponding Q_{10} values are about 2.3.

1. Introduction

Bromate-driven chemical oscillatory reactions, namely the oxidation and bromination of an organic substrate by acidic bromate continues to attract both experimental and theoretical interest [1,2]. Some systems require a one-electron catalyst (as eg., Ce^{4+}/Ce^{3+}, Mn^{3+}/Mn^{2+}, Fe^{3+}/Fe^{2+} or Ru^{3+}/Ru^{2+} complexes) in order to exhibit temporal periodicity. Some others, mostly with aromatic substrates oscillate even in the absence of a catalyst. Catalyzed bromate-driven oscillators are generally termed as Belousov [3] –Zhabotinsky [4] reactions because the first discovery of such a system was due to Belousov, while further more systematic studies with different organic substrates and catalysts were performed by Zhabotinsky and co-workers.

The detailed mechanism of the Belousov–Zhabotinsky reaction was described by Field, Körös and Noyes (FKN) [5] where oscillations are explained as a switching between an oxidizing and reducing state with bromide-ion as the intermediate that controls the switch [2]. A simple mathematical model of the FKN mechanism, the so-called Oregonator [6], was later formulated by Field and Noyes and can describe many of the rather complex dynamic behaviors [7] of the system including excitability [8,9] bistability [10], target or spiral patterns [11,12] in a thin unstirred reaction layer, stirring effects [13,14], or even chaos [15].

Temperature is one of the environmental factors that has a pronounced effect on bromate oscillators: an increase in temperature leads generally to an increase in the frequency of the oscillations. The

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temperature dependence for a variety of catalyzed and uncatalyzed bromate oscillators has been characterized [6,16–24].

Previously [17] it has been found that the activation energy of the classical BZ oscillators (i.e. those composed of bromate ion, malonic acid, sulfuric acid and catalyst) was independent of the nature of the catalyst (Ce^{3+}, Mn^{2+}, respectively $Ru(dipy)_3^{2+}$). Later [19] the dependence of the frequency of the BZ oscillators has been thoroughly analyzed for eight different solutions and it could be concluded that the calculated activation energies covered a narrow range. Performing a numerical analysis by considering the BZ reaction scheme the authors claimed that the frequency of oscillations was controlled to a significant extent by the rate of reaction between bromide ions and bromate ions to form hypobromous acid and bromous acid, and that other reactions which consume bromide ions should be considered too.

Since some essential points remained to be clarified we have performed experiments with BZ systems by varying not only the concentration of the reactants but also using different organic substrates, and examining the effect of added anions that show different coordinative ability towards the metal ion catalyst. In this Letter we present our experimental data obtained so far.

2. Material and methods

The systems presented here were studied in batch or in a continuous-flow stirred tank reactor (CSTR) at different constant temperatures. In the batch system, solutions of sulfuric acid, malonic acid and catalyst were mixed in a vessel equipped with ground glass joints for the electrodes. The mixture was stirred with a magnetic stirrer (500 rpm) and thermostatted (Thermostat Haake DC1) to the required temperature within ±0.02°C. The reaction volume was 50 ml and the reaction initiated by the addition of the sodium bromate solution. In some experiments the reaction mixture contained also $(NH_4)_2SO_4$ or $NaNO_3$. The temporal course of the reaction in batch was followed by monitoring the change in the redox potential using a smooth platinum electrode and/or the change in the bromide ion concentration applying

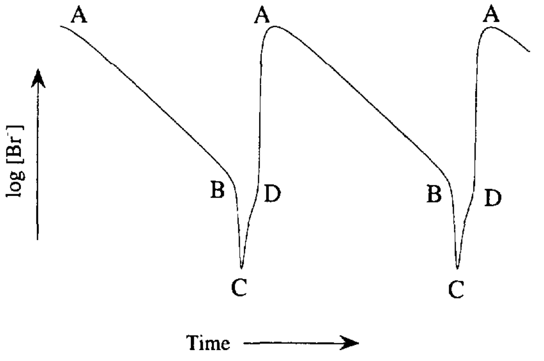

Fig. 1. Oscillations in bromide-ion concentration in the Belousov–Zhabotinsky reaction calculated with the Oregonator model [25]. Interval AB is the slow bromide-ion removing period (SBRP), while CD is the slow bromide-ion producing period (SBPP). BC and DA are rapid transitions whose temperature dependence is not considered here. The shape of the experimental SBPP is somewhat variable and found to depend on the bromide-ion sensor used.

Table 1
Activation energies and influence of temperature on period length in the malic acid BZ system

No.	[Malic acid]$_0$ (M)	[$NaBrO_3$]$_0$ (M)	[$Ce(SO_4)_2$]$_0$ (M)	[H_2SO_4]$_0$ (M)	Period lengths (s) (20.0°C; 25.0°C; 30.0°C; 35.0°C)	E_a (kJ/mol)
1	0.1	0.05	1×10^{-3}	1.0	710; –; 190; 105	98.1
2	0.2	0.05	1×10^{-3}	1.0	235; 135; 90; 55	71.9
3	0.4	0.05	1×10^{-3}	1.0	105; 65; 45; 32	59.3
4	0.2	0.02	1×10^{-3}	1.0	420; 270; 140; 86	92.9
5	0.2	0.1	1×10^{-3}	1.0	180; 115; 80; 52	64.1
6	0.2	0.05	4×10^{-4}	1.0	125; 90; 60; 45	52.0
7	0.2	0.05	5×10^{-3}	1.0	310; 175; 114; 57	85.4
8	0.2	0.05	1×10^{-3}	1.5	150; 125; 72; 47	69.7
9	0.2	0.05	1×10^{-3}	2.0	95; 70; 55; 34	52.6
10	0.2	0.05	1×10^{-3}	2.5	60; 44; 32; 22	49.9

Table 2
Q_{10} values for total period, slow bromide ion removing period (SBRP) and slow bromide ion producing period (SBPP) for malic and malonic acid systems

No.	Q_{10}(SBRP)	Q_{10}(SBPP)	Q_{10}(total period)
malic acid system			
1 [a]	3.0	2.3	2.8
2 [a]	2.6	2.4	2.6
3 [a]	2.4	2.1	2.3
6 [a]	2.5	2.0	2.3
10 [a]	2.3	1.7	2.1
malonic acid system			
6 [b]	2.6	1.9	2.2
7 [b]	3.7	2.2	3.2

[a] Refers to the corresponding systems of Table 1.
[b] Refers to the corresponding systems of Table 3.

a bromide ion selective electrode (Orion model 94-35). As a reference electrode $Hg/Hg_2SO_4/K_2SO_4$ was used and the traces were recorded on a double-pen recorder (Kipp and Zonen BD41).

In the flow experiments a plexiglas CSTR was used with a reaction volume of 57 ml. The temperature inside the reactor was controlled by an outer cooling/heating jacket which was connected to a thermostatted water bath (±0.1°C) where also the (equilibrated) reaction solutions were placed during the experiments. The reaction solutions entered (by means of a peristaltic pump) the reactor from below and were immediately mixed by magnetic stirring. The oscillations were recorded with a Pt electrode against a double-junction Ag/AgCl reference electrode in connection with a conventional strip chart recorder.

The reactants, i.e. organic substrates, sulfuric acid, $Ce(SO_4)_2$, sodium bromate, and ammonium sulfate were of analytical quality. Double distilled water was used.

The variation of period with temperature can be reported as Q_{10} values which are defined by

$$Q_{10} = (\text{period at } T \text{ K})/(\text{period at } T + 10 \text{ K}). \quad (1)$$

Q_{10} values can also be calculated for a temperature interval T_1–T_2 not exactly separated by 10°C. In this case Q_{10} is given by

$$Q_{10} = (P_1/P_2)^{10/(T_2-T_1)} \quad (2)$$

and related to the activation energy E_a by

$$E_a = R(T_1T_2/10)\ln Q_{10}. \quad (3)$$

Activation energies have been determined by an Arrhenius plot by plotting the logarithm of the frequency of the second oscillation against $1/T$.

We have also looked at the reproducibility of the period time/frequency measurements at various temperatures for the determination of E_a values in batch systems. 100 (!) runs with the Ce-catalyzed system gave a 99% confidence level with an uncertainty in the activation energies of ±0.74 kJ/mol.

3. Results

The bromide-ion trace of BZ oscillations consists of a slow bromide-ion removing period (SBRP), a

Table 3
Activation energies and influence of temperature on period length in the malonic acid BZ system

No.	[Malonic acid]$_0$ (M)	$[NaBrO_3]_0$ (M)	$[Ce(SO_4)_2]_0$ (M)	$[H_2SO_4]_0$ (M)	Period lengths (s) (20.0°C; 25.0°C; 30.0°C; 35.0°C)	E_a (kJ/mol)
1	0.1	0.05	1×10^{-3}	1.0	80 [a]; 52.5; 33; 21	66.1
2	0.2	0.05	1×10^{-3}	1.0	115; 80; 50 [b]; 30 [c]	66.1
3	0.4	0.05	1×10^{-3}	1.0	130; 85; 54; 38	61.3
4	0.2	0.02	1×10^{-3}	1.0	45; 30; 19.5; 12.5	64.1
5	0.2	0.1	1×10^{-3}	1.0	55; 34; 22 [d]; 14.5 [e]	67.2
6	0.2	0.05	4×10^{-4}	1.0	55; 35; 25 [f]; 16.5	60.0
7	0.2	0.05	5×10^{-3}	1.0	132; 50; 30; 21	90.8
8	0.2	0.05	1×10^{-3}	1.5	42 [g]; 25; 14; 9.5	76.9
9	0.2	0.05	1×10^{-3}	2.5	33; 22; 12; 8	70.8

[a] 19.8°C. [b] 30.3°C. [c] 35.3°C. [d] 29.4°C [e] 35.5°C. [f] 29.5°C. [g] 20.3°C.

Table 4
Activation energies and influence of temperature on period length in the cyclohexanone BZ system

No.	$[\text{Cyclohexanone}]_0$ (M)	$[NaBrO_3]_0$ (M)	$[Ce(SO_4)_2]_0$ (M)	$[H_2SO_4]_0$ (M)	Period lengths (s) (40.0°C; 45.0°C; 50.0°C; 55.0°C)	E_a (kJ/mol)
1	0.1	0.03	5×10^{-3}	0.5	240; 160; 105; 85	54.5
2	0.2	0.03	5×10^{-3}	0.5	–; 750; 365; 310	75.3
3	0.2	0.05	5×10^{-3}	0.5	87; 57; 45; 13	55.1
4	0.3	0.05	5×10^{-3}	0.5	85; 50; 35; 25	69.2
5	0.1	0.03	5×10^{-3}	1.0	390 [a]; 110; 92.5; 60	57.2
6	0.1	0.03	5×10^{-3}	1.5	155; 78; 62; 40	76.6
7	0.1	0.03	5×10^{-3}	2.0	116; 90 [b]; 42; 32.5	68.6
8	0.1	0.03	1×10^{-3}	0.5	105; 100; 60; 50	42.7

[a] 39.7°C. [b] 44.0°C.

rapid bromide-ion removing period (RBRP), a slow bromide-ion producing period (SBPP), and a rapid bromide-ion producing period (RBPP). Fig. 1 shows a typical bromide-ion concentration profile calculated with the Oregonator model [25]. Because the time scale of the RBRP and RBPP is much shorter compared to the time scale of SBRP and SBPP, the temperature behavior of RBRP and RBPP are ignored.

We will first present results for the malic acid and malonic acid BZ systems. Table 1 shows period lengths and activation energies E_a as a function of initial reactant concentrations and temperature in a batch malic acid BZ system. It is seen that an increase of the initial malic acid, bromate ion, and sulfuric acid concentrations decrease E_a, while an increase in catalyst concentration increases E_a. A closer analysis of the oscillations shows that an increase in temperature leads to a much larger decrease in the SBRP compared to the SBPP. Table 2 shows Q_{10} values of SBRP and SBPP for some of the systems of Table 1. Q_{10} values of the SBPP are found to be significantly lower than for SBRP. The overall period has Q_{10} values between Q_{10}(SBRP) and Q_{10}(SBPP). Table 2 shows that the overall Q_{10} values are almost the arithmetic mean between Q_{10}(SBRP) and Q_{10}(SBPP). Only at higher initial catalyst concentrations (or higher overall activation energies) Q_{10}(SBRP) is more dominating such that

$$Q_{10}(\text{total period}) = 0.5\left[fQ_{10}(\text{SBRP}) + Q_{10}(\text{SBPP})\right], \qquad (4)$$

with f slightly larger than 1.

In the malonic acid Ce-ion system an analogous dependence between activation energy and initial organic substrate and Ce(III) concentrations is found (Table 3). The effects of initial bromate ion concentration and sulfuric acid concentration are opposite compared to a corresponding malic acid system: an increase in sulfuric acid or bromate ion concentration leads to a slight increase in activation energies. However, the most pronounced change in activation energy is found when the catalyst concentration is changed. In the malonic acid system and in the malic acid system we find that a high activation energy corresponds to a long SBRP (data not shown).

Also in other Ce-catalyzed systems we observe a decrease in the overall activation energy when the initial concentration of the catalyst concentration is reduced. Table 4 shows the results for the cyclohexanone system.

Effect of added sulfate, respectively nitrate ions. When the coordinate interaction between added salt and metal-ion catalyst is significant, as it is in the cerium–sulfate system, a considerable increase in the activation energy is found as sulfate ion concentra-

Table 5
Effect of added salt on overall activation energy

c_{salt} (M)	Activation energy (kJ/mol)		
0.0	64.2 [a]	64.2 [b]	64.2 [c]
0.25	73.3 [a]	67.7 [b]	64.1 [c]
0.50	76.2 [a]	65.3 [b]	66.6 [c]
0.75	78.9 [a]	64.8 [b]	67.8 [c]
1.00	86.2 [a]	68.5 [b]	68.0 [c]

[a] 0.20 M malonic acid; 0.05 M $NaBrO_3$; 0.001 M $Ce(SO_4)_2$; 1.0 M H_2SO_4; salt is $(NH_4)_2SO_4$.
[b] 0.20 M malonic acid; 0.05 M $NaBrO_3$; 0.001 M $Ce(SO_4)_2$; 1.0 M H_2SO_4; salt is $NaNO_3$.
[c] 0.20 M malonic acid; 0.05 M $NaBrO_3$; 0.001 M $MnSO_4$; 1.0 M H_2SO_4; salt is $(NH_4)_2SO_4$.

Table 6
Q_{10} values of the malonic acid BZ system in a CSTR [a]

Temp (°C)	Period (min)	Q_{10}
20.3	0.60	1.3
25.4	0.53	1.7
30.7	0.40	1.6
39.7	0.26	-

[a] Input concentrations: [MA] = 0.3 M; $[Ce(SO_4)_2] = 5 \times 10^{-4}$ M; $[NaBrO_3] = 0.1$ M; $[H_2SO_4] = 1.0$M; residence time = 16 min. The overall activation energy over the entire temperature range for the CSTR system is 37 kJ/mol with an overall Q_{10} of 1.6. The corresponding batch system has an overall Q_{10} of 2.3 with an overall activation energy of 63.5 kJ/mol.

tion is increased. Table 5 shows the effect when salts with strong or weak coordinative ability towards the metal ion are added. Cerium ions form complexes with sulfate and hydrogen sulfate ions, however, practically do not coordinate nitrate ions.

Effect of flow in a CSTR. When a malonic acid BZ reaction is run in a CSTR the oscillations become less sensitive towards temperature changes and Q_{10} values as low as 1.3 are found (Table 6).

4. Discussion

Although temperature effects have previously been studied in BZ systems, this is the first report that shows that the overall activation energy is significantly dependent upon the actual BZ system and its composition. For variations in initial concentrations of organic substrate, bromate ion, or sulfuric acid, no general tendency has been found on how overall activation energies will vary. On the other hand, in all systems studied so far, there is a clear correlation between the amount of cerium-ion present and the activation energy of chemical oscillation: decreasing the catalyst concentrations lead to decreasing activation energies while increasing catalyst concentrations lead to higher activation energies.

Both Q_{10} (SBRP) and Q_{10}(SBPP) are affected by the initial catalyst concentration, i.e. both values decrease when the catalyst concentration is decreased. This finding is surprising, because in the FKN mechanism [5] the SBRP is kinetically described by process (5) which is simply the reduction of bromate by bromide with the bromination of the organic substrate RH [2],

$$2Br^- + BrO_3^- + 2H^+ + 3RH \rightarrow 3RBr + 3H_2O. \quad (5)$$

According to process (5), the temperature behavior of the SBRP should therefore be independent of the catalyst. The discrepancy between this prediction and experiments becomes quite obvious in the cerium-catalyzed malonic acid BZ system (Table 2). The results suggest that with increased cerium-ion concentrations additional processes with higher activation energies are induced both for the SBRP and for the SBPP. However, not only plays the amount of the catalyst an important role, it is also of importance what metal-ion-containing species and in what concentrations are present. Therefore coordinative interactions have to be taken into consideration (Table 5).

The nature how the catalyst interacts with process (5) is presently not understood and may involve alternative oxidation pathways of cerium ion by bromate with a subsequent induction of organic or inorganic radical chains and additional production of bromide ion. Such processes would be in agreement with increasing SBRPs at increasing catalyst concentrations (data not shown) and with earlier observations of a nonoscillatory excitable steady state (with bromide-ion concentrations higher than $[Br]_{crit}$) at high cerium ion concentrations [26]. Concerning the question how activation energy (Q_{10} values) may dependent upon the amount of catalyst, it seems that for higher cerium ion concentrations oligomeric cerium-species [27] may lead to lower reactivities (i.e. higher activation energies) compared with the situation when the monomeric form is present at lower total catalyst concentrations.

Matsumura-Inoue and co-workers have studied the catalytic behavior of a variety of synthesized ruthenium(II) polypyridine complexes [28] in the BZ reaction. These systems make a nice example showing that activation energies in the BZ system decrease with increasing efficiency of the type of ruthenium complex considered as catalyst [29].

Flow reactor. A new result is that in a CSTR the malonic acid oscillator becomes significantly less sensitive to temperature changes as in a corresponding batch system (Table 6). Interestingly, due to a suggestion by Rössler [30] adding flow to a closed system may play an important role to achieve temperature compensation in homogeneous chemical oscillatory reactions. In relation to temperature-compensated biological oscillators, where Q_{10} values may be as low as 1.1 [31–33], it appears interesting to investigate how low Q_{10} values may actually get for chemical oscillators, and what importance pumping [34] has for temperature-compensation in biological systems. Further work along these lines is in progress.

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