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The Kinetic Study of the Chemical Oscillating System of 1,3-Propanediol/Acetone as the Organic Substrate

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This work was primarily an experimental investigation of the bromate oscillator using 1,3-propanediol and acetone as the mixed organic substrates. The empirical equation of the induction period and oscillating period with the concentrations of the reactants and temperature were obtained. The oscillating characteristic and possible oscillation mechanism were studied.

Key Words: Oscillation, 1,3-propanediol, Acetone, Mixed substrates.

Introduction

The study of oscillating chemical reactions has been dominated by the Belousov-Zhabotinskii (BZ) reaction¹. It is also called the chemical clock, which is similar to the biological clock. When the chemical reaction is far from equilibrium, the concentration of some substances in the reaction system exhibits a regular change with time, a kind of self-regulating function similar to what happens in an organism. During the last 10 to 20 years, vitamin C, glucose, lactic acid, fructose, amino acid, lactose, malic acid and ethanol have been reported²⁻¹⁷ to be very important reaction substrates in oscillation reactions; they also play an important role in the synthesis of cell substances in life¹⁰. As pharmaceutical intermediates and additives, 1,3-propanediol has been used in the pharmaceutical industry and clinically for curing many diseases. In the present work we report a new bromate oscillator using 1,3-propanediol and acetone as the mixed organic substrates. The temperature effects on the oscillations of this system and the initial concentration range of the reactants in the oscillating system have been examined. The relationships between the oscillation periods and the substrate concentrations have been studied. The oscillating characteristic and a cycle oscillating mechanism have been studied.

Experimental

Reagent

Analytical grade 1,3-propanediol, manganous sulfate, sulfuric acid, and acetone were used in the experiments. Analytical grade potassium bromate was recrystallized from water. The water used in the experiments was double deionized.

Apparatus and method

The experiments were performed in a thermostat (the temperature was controlled up to ± 0.1 K). The overall volume of the solution was 50 ml. Sulfuric acid, 1,3-propanediol, manganous sulfate and acetone were added successively under stirring by a magnetic agitator. When the temperature of the reaction mixture became constant (± 0.1 K), the solution of potassium bromate thermostated at the same temperature was instantly transferred into the mixture as the last addition. The oscillating curves of the potential with time were recorded using a table x-t recorder. Smooth bright platinum was employed as the indicator electrode and a 217-Type SCE was used as the reference electrode together with (1 mol dm^{-3} sulfuric acid) a liquid junction having a sintered silica disc at the end dipping in the reaction mixture. Since only the characteristic of the oscillating curve with time was considered in the present work, E was in an arbitrary unit. The typical trace of potential oscillation is shown in Figure 1.

Results and Discussion

Oscillating phenomenon

The Table gives the initial concentration range of the reactants and temperature range in the chemical oscillating system of 1,3-propanediol-Acetone-Bromate-MnSO₄-H₂SO₄.

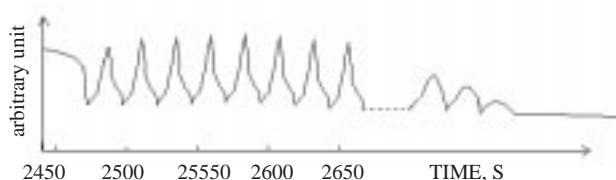


Figure 1. The oscillating curve of the potential with time.

[System: $[\text{Act}]_0 = 1.35 \text{ mol dm}^{-3}$, $[\text{PD}]_0 = 3.30 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{BrO}_3^-]_0 = 0.090 \text{ mol dm}^{-3}$,
 $[\text{Mn}^{2+}]_0 = 6.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4]_0 = 1.80 \text{ mol dm}^{-3}$, Temp. = 298 ± 0.1 K]

Table The initial concentration range of the reactants and temperature range in the oscillating system (Concentration unit: mol dm^{-3}).

$[\text{Act}]_0$	$[\text{PD}]_0 \times 10^2$	$[\text{BrO}_3^-]_0$	$[\text{Mn}^{2+}]_0 \times 10^4$	$[\text{H}_2\text{SO}_4]_0$	T/K
0.750~2.15	3.30	0.090	6.0	1.80	298.0
1.35	2.30~5.80	0.090	6.0	1.80	298.0
1.35	3.30	0.060~0.110	6.0	1.80	298.0
1.35	3.30	0.090	3.00~21.0	1.80	298.0
1.35	3.30	0.090	6.0	1.40~2.40	298.0
1.35	3.30	0.090	6.0	1.80	293.0~323.0

In the concentration range listed in the Table, the color of the solution changed from pink (the color of Mn^{2+}) to brown, and at the same time the potential of the system went up rapidly after KBrO_3 solution was added. After a period of induction, the potential decreased rapidly, and the system exhibited a periodic oscillation between brown and pale yellow. In the latter stage, the solution became light in color, and the oscillating period did not change much during the whole oscillating process. With time, the oscillating

amplitude began to show a slowly increasing trend and after a period of stable amplitude, the amplitude began to decrease gradually until the oscillation stopped.

Effect of temperature and the apparent activation energies

The 1,3-propanediol-Acetone-Bromate-MnSO₄-H₂SO₄ chemical oscillating system is very sensitive to temperature changes. When the temperature increased, the induction period t_i (s) and oscillating period t_p (s) decreased regularly. The composition of the reaction mixture was as follows: $[\text{Act}]_0 = 1.35 \text{ mol dm}^{-3}$, $[\text{PD}]_0 = 3.30 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{BrO}_3^-]_0 = 0.090 \text{ mol dm}^{-3}$, $[\text{Mn}^{2+}]_0 = 6.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4]_0 = 1.80 \text{ mol dm}^{-3}$. A very good linear relationship was obtained when fitting $\ln(t_i^{-1}\text{s})$ and $\ln(t_p^{-1}\text{s})$ with $T^{-1}\text{K}$ (shown in Figure 2), the linear correlation coefficients are greater than 0.997, and the corresponding linear equations are

$$\ln(t_i^{-1}\text{s}) = -E_i/RT + A_i$$

$$\ln(t_p^{-1}\text{s}) = -E_p/RT + A_p$$

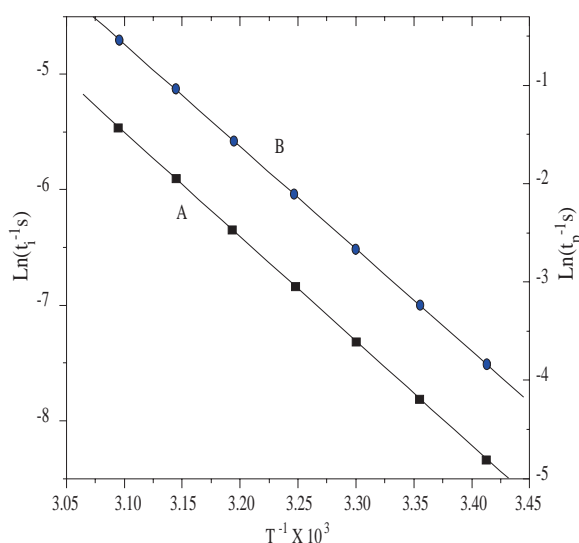


Figure 2. The figure of $\ln(t^{-1}\text{s})$ with $T^{-1}\text{K}$.

A: $\ln(t_i^{-1}\text{s})$ with $T^{-1}\text{K}$; B: $\ln(t_p^{-1}\text{s})$ with $T^{-1}\text{K}$.

[System: $[\text{Act}]_0 = 1.35 \text{ mol dm}^{-3}$, $[\text{PD}]_0 = 3.30 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{BrO}_3^-]_0 = 0.090 \text{ mol dm}^{-3}$,
 $[\text{Mn}^{2+}]_0 = 6.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4]_0 = 1.80 \text{ mol dm}^{-3}$.]

in which A_i and A_p are the intercepts of the lines, and E_i/R and E_p/R are the slopes of the fitting lines. Compared with the Arrhenius equation $\ln(k) = -E_A/RT + A$, t_i^{-1} and t_p^{-1} are very similar to the reaction rate constants, but E_i and E_p should correspond to the activation energies, which are called the apparent activation energies in this paper, and their values are $E_i = 75.2 \text{ kJ mol}^{-1}$ and $E_p = 86.7 \text{ kJ mol}^{-1}$ respectively.

Effects of the reactant concentration

It was found from the experiment that both the induction period t_i (s) and the oscillation period t_p (s) of the chemical oscillating reaction were affected by the concentrations of the reactants, and $\ln(t_i/s)$ and $\ln(t_p/s)$ have a good linear relationship with $\ln([\text{Act}]_0 \text{ mol}^{-1} \text{ dm}^3)$, $\ln([\text{PD}]_0 \text{ mol}^{-1} \text{ dm}^3)$, $\ln([\text{BrO}_3^-]_0 \text{ mol}^{-1} \text{ dm}^3)$, $\ln([\text{Mn}^{2+}]_0 \text{ mol}^{-1} \text{ dm}^3)$, and $\ln([\text{H}_2\text{SO}_4]_0 \text{ mol}^{-1} \text{ dm}^3)$ in the concentration range as shown in the Table. Their linear relationships can be expressed as

$$\ln(t_i/s) = a_i + b_i \ln([\text{Act}]_0 \text{ mol}^{-1} \text{ dm}^3) + c_i \ln([\text{PD}]_0 \text{ mol}^{-1} \text{ dm}^3) + d_i \ln([\text{BrO}_3^-]_0 \text{ mol}^{-1} \text{ dm}^3) \\ + e_i \ln([\text{Mn}^{2+}]_0 \text{ mol}^{-1} \text{ dm}^3) + f_i \ln([\text{H}_2\text{SO}_4]_0 \text{ mol}^{-1} \text{ dm}^3)$$

$$\ln(t_p/s) = a_p + b_p \ln([\text{Act}]_0 \text{ mol}^{-1} \text{ dm}^3) + c_p \ln([\text{PD}]_0 \text{ mol}^{-1} \text{ dm}^3) + d_p \ln([\text{BrO}_3^-]_0 \text{ mol}^{-1} \text{ dm}^3) \\ + e_p \ln([\text{Mn}^{2+}]_0 \text{ mol}^{-1} \text{ dm}^3) + f_p \ln([\text{H}_2\text{SO}_4]_0 \text{ mol}^{-1} \text{ dm}^3)$$

Based on the experimental data, the correlation coefficients in the above two formulae can be determined by multiple linear regression: $a_i = 5.80$, $b_i = -0.58$, $c_i = -0.36$, $d_i = 0.37$, $e_i = -0.25$, $f_i = -2.04$; $a_p = 6.64$, $b_p = -0.86$, $c_p = -1.36$, $d_p = 0.59$, $e_p = 0.46$, $f_p = -1.45$. Therefore the relationship the induction period t_i (s) and oscillating period t_p (s) with the initial concentration of the reactants can be expressed as

$$T_i(\text{s}) = 109[\text{Act}]_0^{-0.58}[\text{PD}]_0^{-0.36}[\text{BrO}_3^-]_0^{0.37}[\text{Mn}^{2+}]_0^{-0.25}[\text{H}_2\text{SO}_4]_0^{-2.04}(\text{mol dm}^{-3})^{2.86}\text{s}$$

$$T_p(\text{s}) = 86.5[\text{Act}]_0^{-0.86}[\text{PD}]_0^{-1.36}[\text{BrO}_3^-]_0^{0.59}[\text{Mn}^{2+}]_0^{0.46}[\text{H}_2\text{SO}_4]_0^{-1.45}(\text{mol dm}^{-3})^{2.62}\text{s}$$

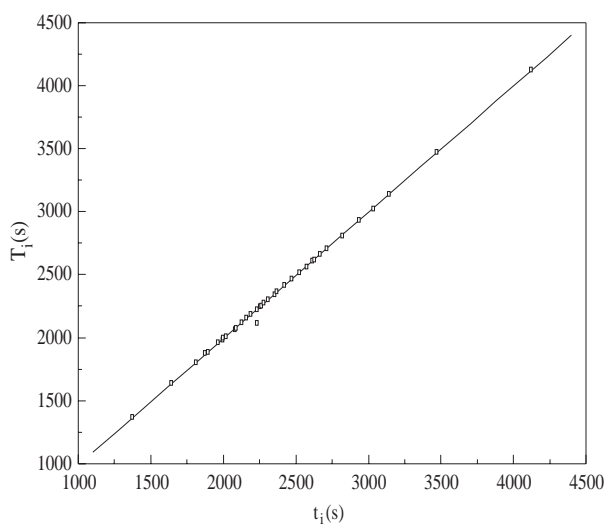


Figure 3. Figure of t_i (s) with T_i (s).

The experimental conditions are listed in the Table. Temp. = 298 ± 0.1 K.

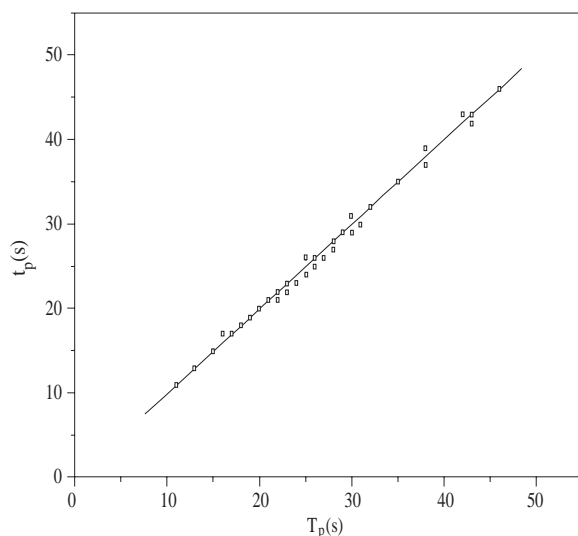


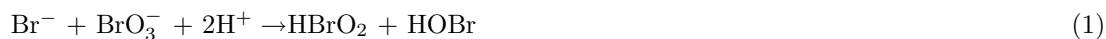
Figure 4. Figure of t_p (s) with T_p (s).

The experimental conditions are listed in the Table. Temp. = 298 ± 0.1 K.

Therefore if T_i (s) and T_p (s) represent the induction period and oscillating period calculated from the above empirical equations, respectively and t_i (s) and t_p (s) represent the induction period and oscillating period measured from the experiments under the same experimental conditions, respectively, two straight lines (Figures 3 and 4) are obtained from t_i (s) with T_i (s) and from t_p (s) with T_p (s), respectively. Each line is composed of 40 points, and each point represents the average of three parallel experimental results. The linear correlation coefficients are 0.998 and 0.997 respectively. The slopes are 0.999 and 0.997, respectively, which are very close to 1. The intercepts are very close to 0. These demonstrate that the above two empirical equations are correct. It can be seen from the above relationships that increasing $[\text{Act}]_0$, $[\text{PD}]_0$, and $[\text{H}_2\text{SO}_4]_0$ can increase the rate and shorten induction period t_i (s) and oscillation period t_p (s); increasing $[\text{Mn}^{2+}]_0$ can shorten the induction period t_i (s) and elongated the oscillating period t_p (s); and increasing $[\text{BrO}_3^-]_0$ can elongate the induction period t_i (s) and oscillating period t_p (s).

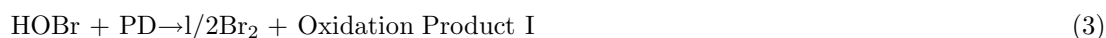
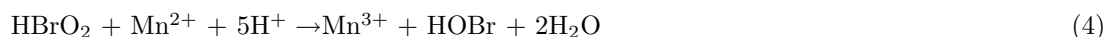
Function of Mn^{2+}

When replacing Mn^{2+} with water, although no oscillation occurred, the color of the solution changed to light brown gradually. This indicates that although there is no Mn^{2+} as the catalyst, BrO_3^- can partly oxidize PD. This is because alcohol is more easily oxidized than homologous acid. This reaction is shown as follows:



This reaction is the side reaction of the oscillating system, and partially consumes PD.

In the presence of Mn^{2+} , $HBrO_2$ and PD reacted rapidly to produce Br_2 , and so the color of the solution changed rapidly to brown. Here Mn^{2+} plays a catalytic role, and the catalytic process is shown as follows:

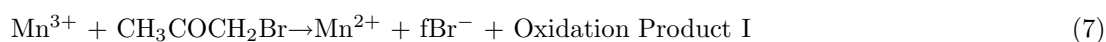
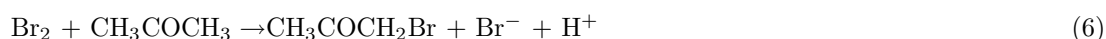


The Br_2 produced was removed in Reaction (6) to produce Br^- at the same time. The Br^- thus formed can be oxidized by BrO_3^- , which is favorable for the accumulation of $HBrO_2$, shown in reaction (1). The existence of an induction period demonstrates that the accumulation process of $HBrO_2$ existed in the oscillating system. Therefore this is an oscillation switch.

At the beginning of the reaction (the induction period), the concentration of Br^- was very low and the catalytic process took place predominately. The increase in the concentration of Mn^{2+} , might have caused Reactions (4) and (3) to proceed very fast, and more Br_2 was produced. This further caused Reaction (6) to produce more Br^- and then Reaction (1) accelerated the accumulation of $HBrO_2$. The time to reach the critical value of oscillating was very short and so the induction period $t_i(s)$ became shorter with the increase in $[Mn^{2+}]_0$. At the beginning of the oscillation, Mn^{3+} returned to Mn^{2+} through Reactions (5) and (7). When $[Mn^{2+}]_0$ was large although the rate of Reaction (5) became faster, every oscillation reaction consumed large amounts of PD, causing $[PD]$ to become lower; and during each cycle the time for Mn^{3+} to return to $[Mn^{2+}]$ for became longer with the increase in $[Mn^{2+}]_0$. Therefore the oscillating period $t_P(s)$ became longer with the increase in $[Mn^{2+}]$.

Function of acetone

While keeping other reaction conditions unchanged, water was added in place of acetone keeping the solution volume constant. It was found in the experiment that adding potassium bromate solution produced large quantities of Br_2 . The system color changed to brown and brown gas was given off. After the induction period, the potential decreased without going up, and the brown color did not disappear, and no oscillating reaction took place. In acidic medium, under the catalytic condition of Mn^{2+} , an oxidation-reduction reaction took place between BrO_3^- and PD producing Br_2 , which caused the color of the solution to change to brown. The brown color disappeared quickly after acetone was added and the oscillation took place. When nitrogen was rapidly bubbled through the system with no acetone added, some oscillations were observed. Therefore one of the main functions of acetone was to eliminate excessive Br_2 and to produce Br^- simultaneously, i.e.



Br^- can be oxidized by Reaction (1). Increasing the amount of acetone increased the accumulation of HBrO_2 , which accelerated the whole oscillating process, and so the induction period and the oscillating period became shorter.

Keeping the other conditions constant, adding a small amount of bromoacetone shortened the induction period. It indicated that the accumulation of bromoacetone was very important during the induction period. Bromoacetone was partly oxidized by Reaction (7) to produce Br^- , which shortened the induction period.

Function of PD

PD played the role of the reductant and participated in the formation of Br_2 at the same time. Therefore, with the increase in the initial concentration of PD, the rate of regeneration of Mn^{2+} through the reduction of Mn^{3+} by PD increased, and the induction period $t_i(\text{s})$ and oscillating period $t_p(\text{s})$ became shorter.

Function of BrO_3^-

Without the catalysis of Mn^{2+} , BrO_3^- can still oxidize part of PD and consume part of PD, which is shown as Reaction (I). Therefore by increasing the concentration of BrO_3^- , more PD was consumed. With the increase in $[\text{BrO}_3^-]$, the induction period $t_i(\text{s})$ and the oscillating period $t_p(\text{s})$ became longer.

Discussion of the Oscillating Mechanism

Based on the above discussions and combined with the life metabolism cycle¹⁸, the following cycle oscillating mechanism was proposed:

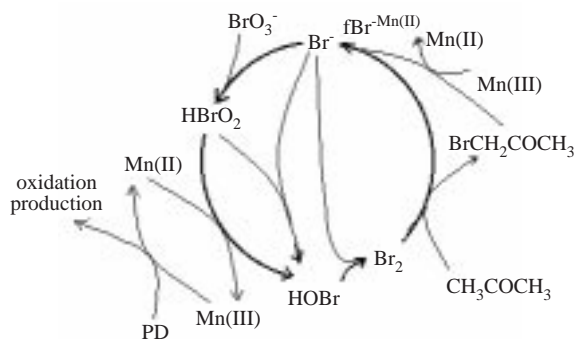


Figure 5. Cycle oscillating mechanism.

The above cycle oscillating mechanism is similar to that of the tricarboxylic acid cycle in the sugar metabolism in the human body¹⁸. A part of PD is consumed in each cycle. When $[\text{Br}^-]$ is concentrated highly enough, reactions took place between Br^- , BrO_3^- and HBrO_2 producing HOBr and Br_2 , which caused the color of the solution to change to brown. At the same time Mn^{2+} was oxidized by HBrO_2 to produce Mn^{3+} . The reaction taking place between Br_2 and acetone produced bromoacetone and reformed Br^- . The bromoacetone was partly oxidized by Mn^{3+} to reproduce Br^- and reform Mn^{2+} simultaneously. These processes go round and round, and the oscillating phenomenon of $[\text{Br}^-]$ or $[\text{Mn}^{3+}]/[\text{Mn}^{2+}]$ begins to take place.

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