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A Novel Chemical Oscillator with Tyrosine as the Substrate

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Abstract: A new chemical oscillating reaction system involving the manganese(II)-catalyzed reaction among potassium bromate, acetone and tyrosine in acidic medium was described in this paper. The apparent activation energy of the induction period (E_{in}) and that of oscillation period (E_p) were calculated, E_{in}=110.61KJ/mol, E_p=159.41KJ/mol. The optimum concentration of each reactant was investigated and a steady chemical oscillating system was obtained.

Keywords: Chemical oscillator, tyrosine, substrate, mechanism.

Chemical oscillating reactions have attracted the attention of researchers for many years because of their challenging chemistry and their wealth of dynamic behavior[1-4], Part of the interest in chemical oscillating reaction grew from the study of non-linear dynamics applied to physics[5] and biology [6,7], even meteorology[5] and economic[8].

In a well-stirred chemical oscillator, the concentrations of certain intermediates vary over time, such a system must be thermodynamically far from equilibrium with an overall $\triangle$G which is large and negative. In addition, the rate laws for the reaction must be non-linear, that is, some of the terms must be overall second order, or higher in the concentration of intermediates. Instabilities are usually related to autocatalysis, self-inhibition or delayed feedback. However, it is also important to note that the concentrations of the major reactants in chemical oscillator decrease slowly and continuously during the reaction process without an influx of one or more reagents to sustain oscillating. In consequence, the reaction continuously flows in the direction of decreasing free energy: there is no oscillation in the direction of the overall reaction, which is always moving inexorably towards the chemical equilibrium state.

The instrumental consists of a 50 mL glass reaction vessel fitted with a Model CS-501 thermostat and a magnetic stirrer Model ML-902 for homogenization. The experiments were performed with a CHI832 electrochemical analytical system in a conventional three-electrode cell to record the potential change.

The proposed chemical oscillating system exhibits periodic change both in the potential and in the color of the solution. The color of the solution is light yellow at the minimum of the cycle and brown at the maximum of the cycle. **Figure 1** shows the typical oscillating profile for the new oscillating chemical system. The periodicity in the

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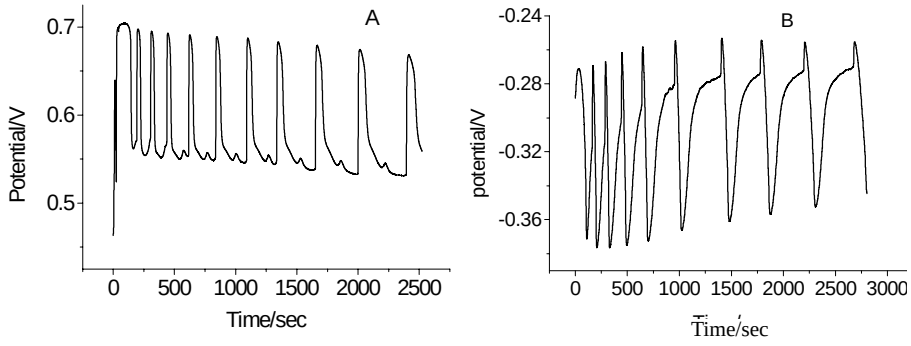
Figure 1 The typical oscillation profile for the proposed oscillating system



(A) platinum electrode as working electrode

(B) bromide ion-selective electrode as working electrode

rate of heat evolution during oscillating in some autocatalytic systems has been described by KÖrÖs *et al* [9].

We also studied the infouence of temperature on the proposed chemical oscillator. The results show that the induction period (t_{in}) and oscillation period (t_p) depend greatly on temperature. Raising the temperature made both the induction period (t_{in}) and oscillation period (t_p) dramatically decrease whereas the oscillation amplitude remained almost constant. In addition, $\ln(1/t_{in})$ and $\ln(1/t_p)$ are linearly proportional to the 1/T (**Figure 2**).

$$\ln(1/t_{in}) = 13.30391(1/T) - 5.53698 \qquad (r=0.9981)$$

$$\ln(1/t_p) = 19.17343(1/T) - 7.03472 \qquad (r=0.9976)$$

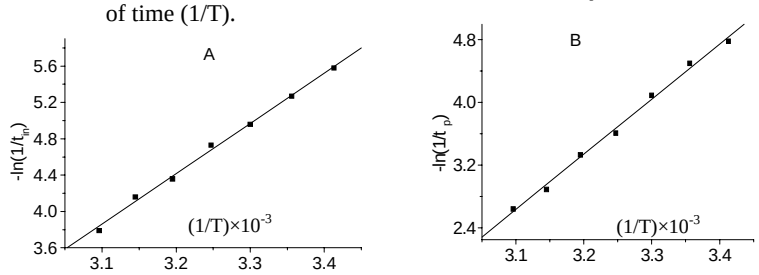
Compared the above described equations with the Arrhenius equation:

$$\ln k = -E_a/RT + A$$

The apparent activation energy (E_{in}) of the induction period and that of the oscillation period (E_p) was calculated, E_{in}=110.61KJ/mol, E_p=159.41KJ/mol. Although they couldn't explain the difficulty degree of each elementary reaction, because of E_{in} is less than E_p, they could illustrate the induction reaction is easier than oscillation reaction.

To obtain stable oscillating system, the effects of the concentrations of tyrosine, potassium bromate, acetone, manganese (II) and sulfuric acid were examined.

Figure 2 Calibration curve of the negative logarithm of the induction period (t_{in}) or the negative logarithm of the oscillation period (t_p) *versus* the reciprocal of time (1/T).



The effect of tyrosine on the oscillating was investigated over the range from 2.0×10^{-4} to 0.2mol/L. As the initial concentration of tyrosine was lower than 4.35×10^{-3}mol/L in the system, no oscillating phenomenon was observed and the potential was low. The lower the concentration of tyrosine, the shorter the duration of the system is. This phenomenon demonstrated that tyrosine was consumed in the process of oscillating. However, a too high concentration of tyrosine made the duration of oscillating short.

The effect of acetone was investigated over the range from 0.017 to 0.13mol/L. If acetone was replaced by equal volume water, the color of solution was light yellow and the system could not oscillate. When the concentration of acetone was decreased, the duration decreased too. So the function of acetone is to remove surplus bromine that was produced in the induction period. Nevertheless, the more acetone was introduced into the system, the larger background noise was obtained.

The effect of potassium bromate in the system was also studied. The results showed that when the concentration of potassium bromate was lower than 0.038mol/L, the same phenomenon was observed just as that of tyrosine. This observation illustrated that lower concentration of potassium bromate leaded to the concentration of Br^- so low to be under the critical value that the system could not oscillate. The concentration of potassium bromate was higher; the color of solution in the induction period was deeper. However, when the concentration of potassium bromate was higher than 0.10mol/L, the oscillating system was unsteady.

The results of studying the influence of manganese (II) showed that potassium bromate cannot oxidize tyrosine without manganese as catalyst, but surplus manganese (II) in the system might have consumed certain crucial intermediate and led to disappear the oscillating.

The effect of sulfuric acid was different from that of tyrosine, acetone, potassium bromate and manganese(II). When the concentration of sulfuric acid was lower than 1.15mol/L, the potential decreased at the minimum of the cycle. With increasing the concentration of sulfuric acid, the amplitude decreased. However, a too high concentration of sulfuric acid led to an unsteady system.

In general, the well-known FKN mechanism[10] can be applied to elucidate the basic mechanism of bromate ion-driven chemical oscillation reaction. Obtaining an exact mechanism was difficult because of the lack of some relevant thermodynamic data. However, computer simulation may be useful for solving the oscillation problem and corresponding studies are in progress.

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