Iodide-induced Oscillations in BrO_3^-–Tyrosine–H_2SO_4 System

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The KBO_3–tyrosine(Tyr)–H_2SO_4 system gave rise to sustained uncatalyzed oscillations in a suitable concentration range. Under the case that the reactants' concentrations were out of the oscillating range, initially adding iodide into the above system induced another kind of oscillations with much higher frequency and more oscillation cycles in comparison with the original uncatalyzed oscillations in the absence of iodide.

In the past decades, the chemical oscillations have caused much attentions since such reactions may yield important insights into kinetic and thermodynamic problems, and provided alluring analogues of various biological and biochemical processes.[1] The most thoroughly studied oscillator is the Belousov-Zhabotinskii (BZ) reaction,[2] the homogeneous chemical oscillating reactions in which an organic substrate is brominated and oxidized by bromate ion in aqueous solution. In our previous papers,[3–5] we reported that a number of amino acids could give rise to BZ type oscillations in the presence of Mn^{2+} as a catalyst, known as catalyzed BZ oscillations. Studies on these oscillations may supply valuable information to understand the chemical nature of the periodical phenomena observed in biological and biochemical processes since amino acids are essential for the living bodies. Here we report an uncatalyzed BZ oscillation in the KBO_3–tyrosine(Tyr)–H_2SO_4 system. More surprisingly, addition of iodide could induce a novel kind of oscillations with higher frequency and much greater number of oscillating cycles.

All materials were of analytical grade and used without further purification except for $KBrO_3$, which was recrystallized in hot water to remove Br^- and other impurities. The $Fe(phen)_3{}^{2+}$ was prepared according to the method described in our previous paper.[3] All solutions were prepared with twice-distilled water. The oscillating reactions were carried out in a well stirred 100 cm^3 reaction vessel mounted in a thermostat to keep the reaction temperature at 303 ± 0.2 K. The reactants were added in the following procedure: H_2O, H_2SO_4, Tyr, and finally $KBrO_3$. The potential oscillations were followed by means of a bromide ion selective electrode (Br-ISE) against a mercury (I) sulfate electrode as a reference. The oscillations were recorded as *E-t* curves on a conventional *x-t* recorder. For each oscillatory trace, at least three repetitive experiments were conducted. No significant difference between the recorded oscillatory traces was found, showing the excellent reproducibility of our experiments. According to the results obtained by Ruoff et al.,[6] the I-ISE was not necessary even in the presence of iodide ion since the I-ISE responded exclusively to bromide ion because of the extremely low concentration of iodide under the present conditions.

The BrO_3^-–Tyr–H_2SO_4 system could give rise sustained oscillations only within the concentration range of $[KBO_3]_0 = 0.035$–0.068 M, $[Tyr]_0 = 0.010$–0.025 M, $[H_2SO_4]_0 = 1.08$–1.90 M. Typical oscillatory pattern is shown in Figure 1. One can see an induction period (ca. 16 min) before the oscillations began. During oscillations, the solution color also changed periodically between bright-yellow and brown-yellow. Only a few oscillations were observed. After the oscillations had finished, the oscillations could be restarted by adding Tyr, while no oscillations could be induced when other reactants, $KBrO_3$ or H_2SO_4, were added into the system. These results suggested that Tyr was limited while the other reactants were excess in the present oscillating reaction and thus, the oscillations stopped mainly owing to the exhaustive consumption of Tyr.

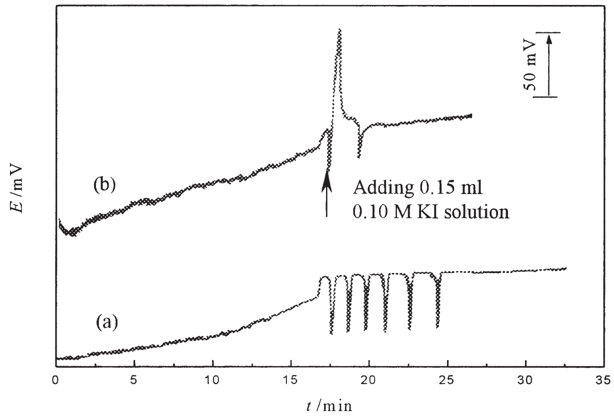

Figure 1. Typical oscillatory trace in the BrO_3^-–Tyr–H_2SO_4 system. Reaction conditions: $[Tyr] = 0.015$ M, $[BrO_3^-] = 0.056$ M, $[H_2SO_4] = 1.40$ M, $T = 303$ K, $V = 50$ ml. (a) No KI was added, (b) 0.15 ml 0.10 M KI solution was added during the oscillations.

Considering two component parts of the Tyr molecule, phenol and phenylalanine (Phe), when Phe was used instead of Tyr, no uncatalyzed oscillations were observed. However, uncatalyzed oscillations could also occur when phenol was used instead of Tyr, indicating that the uncatalyzed oscillations in the present system were mainly attributed to the phenol group rather than the Phe group in the Tyr molecule. The oscillatory pattern in the $KBrO_3$–Tyr–H_2SO_4 system was quite different from that in the $KBrO_3$–phenol–H_2SO_4 system, showing the significant influence of the side group on the oscillatory characteristics.

The mechanism of the uncatalyzed oscillations in the $KBrO_3$–Tyr–H_2SO_4 system could be understood based on OKN mechanism.[7] It is well known that, in the catalyzed BZ oscillations, the organic substrate, such as malonic acid, played the roles of both the bromine acceptor to remove the excess bromine produced during the oscillations and the reducing agent to regenerate the metal ion catalyst. In the uncatalyzed BZ oscillations, OKN mechanism demonstrated that, besides the above two roles, the organic substrate also served as a catalyst instead of the metal ion catalyst used in the catalyzed BZ oscillations which was supported by the following facts. After the uncatalyzed oscillations in the $KBrO_3$–Tyr–H_2SO_4 system had finished, no oscillations could be regenerated by adding either a typical bromine acceptor like acetone or a typical reducing agent like malonic acid which was most frequently used in catalyzed BZ oscillations. However, the oscillations could be successfully reinitiated by adding $Fe(phen)_2{}^{3+}$, a typical metal ion catalyst used in most catalyzed BZ oscillations. These results clearly demonstrated that the cease of the uncatalyzed oscillations in the $KBrO_3$–Tyr–H_2SO_4 system was mainly attributed to the lack of the catalyst owing to the exhaustive consumption of Tyr.

Under the conditions shown in Figure 1, addion of iodide initially or during oscillations caused an abrupt decrease in the oscillation number. The oscillations could be completely inhibited when the initial concentration of iodide exceeded 0.0040 M or when 0.20 ml 0.1 M KI was added during the oscillations. These results implied that iodide was an effective inhibitor for the present uncatalyzed oscillations.

However, surperising phenomena were observed when KI was added initially into the $KBrO_3$–Tyr–H_2SO_4 system with 0.048 M KBO_3, 0.0080 M Tyr, and 1.36 M H_2SO_4. Without iodide, no oscillations occurred since the reactants' concentrations were out of the oscillating regeon descibed above. In the presence of certain amount of iodide (0.0034–0.0042 M), a new kind of oscillations appearred. As shown in Figure 2, nearly 50 oscillating cycles were observed, much more than the pure uncatalyzed oscillations in Figure 1. In addition, the iodide-induced oscillations displayed shorter induction period and higher frequency, implying that the iodide might catalyze the oscillations. With the increase of iodide concentration, the induction period increased while the number of oscillations first increased and then decreased gradually. Maximum number of oscillations was obtained at iodide concentration of 0.0040 M. It seems that the cease of oscillations was mainly due to the extremely decrease in the amplitude of oscillations.

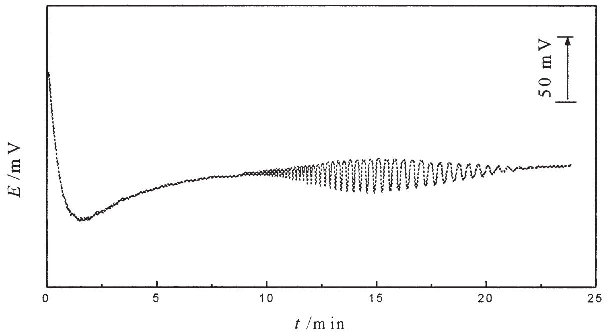

Figure 2. Typical curve of the iodide-induced oscillations in the $BrO_3{}^-$–Tyr–H_2SO_4 system. $[I^-] = 0.0040$ M, $[Tyr] = 0.0080$ M, $[BrO_3{}^-] = 0.048$ M $[H_2SO_4] = 1.36$ M, $T = 303$ K, $V = 50$ ml.

The product analysis revealed that most of I^- ions were oxidized into $IO_3{}^-$ after the oscillations. Before $IO_3{}^-$ was formed as a final product, various intermediates, such as I_2, HOI, HIO_2, and even I^+ in the form of $I^+{\cdot}H_2O$, might be produced.[6] Experiments revealed that addition of iodine in the $KBrO_3$–Tyr–H_2SO_4 system instead of iodide also induced the oscillation similar to that in Figure 2. However, addition of iodate instead of iodide could not induce oscillations. Thus, it might be reasonable to conclude that some intermediates of iodine species played important roles in inducing new kind of oscillations.

Similar phenomena were also observed when $Fe(phen)_3{}^{2+}$ was used instead of iodide. Addition of 0.0020 M $Fe(phen)_3{}^{2+}$ initially into the $KBrO_3$–Tyr–H_2SO_4 system resulted in more than 25 oscillation cycles with high frequency. Thus, we concluded that the iodide ion might play a similar role to that of $Fe(phen)_3{}^{2+}$ as a catalyst in inducing new kind oscillations. A possible mechanism could be described as follows.

According to OKN mechanism, Tyr served as the catalyst instead of metal ion like $Fe(phen)_3{}^{2+}$ to produce $HBrO_2$ via an autocatalytic reaction:

$$BrO_3{}^- + HBrO_2 + H^+ \longrightarrow 2BrO_2{}^{\bullet} + H_2O \qquad (1)$$

$$BrO_2{}^{\bullet} + HAr(OH)R \longrightarrow HBrO_2 + HAr(O^{\bullet})R \qquad (2)$$

Where R represents $-CH_2CH(NH_2)COOH$ group and $HAr(O^{\bullet})R$ is a radical of Tyr which could be further oxidized by HOBr to quinone and other possible products. Unlike the metal ion catalyst in catalyzed BZ oscillations, Tyr could not be regenerated during the uncatalyzed oscillations. Thus, only a few oscillating cycles could be observed because of the rapid consumption of Tyr. In the presence of iodide, it could react with $BrO_2{}^{\bullet}$ to produce $HBrO_2$:

$$2BrO_2{}^{\bullet} + 2I^- + 2H^+ \longrightarrow 2HBrO_2 + I_2 \qquad (3)$$

The iodine (I_2) could also be oxidized to HOI and even I^+ in the form of $I^+{\cdot}H_2O$. However, both HOI and I^+ could react with I^- rapidly to form I_2. As the oxidation of HOI or I^+ by bromate was extremely slow, no iodate could be formed until all iodide ions have been consumed.[8] Iodine might react with Tyr via iodination to regenerate iodide ion. Thus, iodide or iodine could be used repetitively similar to a metal ion catalyst during the oscillations, resulting in much more oscillation cycles since the organic substrate (Tyr) was effectively saved. When the reactants were mixed in the order of H_2O, H_2SO_4, KI, $KBrO_3$, and finally Tyr, no oscillations were observed, possibly owing to the rapid oxidation of iodide to iodate before the addition of Tyr. As mentioned above, adding iodate in the $KBrO_3$–Tyr–H_2SO_4 system could not induce the oscillations. Meanwhile, addition of chloride instead iodide could not induce oscillations, which might be attributed to its higher redox potential ($Cl_2/Cl^- = 1.36$ V) than that of iodide ($I_2/I^- = 0.54$ V). Under the conditions that the $KBrO_3$–Tyr–H_2SO_4 system could give rise to uncatalyzed oscillations (see Figure 1), addition of iodide initially or after occurrence of oscillations may effectively inhibit the oscillations, possibly because of its competitive reaction with $HBrO_2$ against bromide.[9] As well known, both the catalyzed and uncatalyzed oscillations are controlled by the bromide ion which may produced by the reactions between oxybromine species and organic substrates while should be consumed by the $HBrO_2$ oxidation. The presence of iodide could inhibit the reaction between bromide and $HBrO_2$. Thus, oscillations might be suppressed by excess bromide in the system. Detailed studies on the role of iodide are being underway.

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References

1 R. J. Field and M. Burger, "Oscillations and Travelling Waves in Chemical Systems," Willey-Interscience, New York (1985).
2 R. J. Field, E. Körös, and R. M. Noyes, *J. Am. Chem. Soc.*, **94**, 8649 (1972).
3 H. X. Li and J. F. Deng, *Chem. Lett.*, **1996**, 835.
4 H. X. Li, M. H. Wang, and Y. P. Xu, *Chem. Lett.*, **2002**, 754.
5 H. X. Li and M. H. Wang, *Int. J. Chem. Kinet.*, **34**, 405 (2002).
6 P. Ruoff, M. Varga, and E. Körös, *J. Phys. Chem.*, **91**, 5332 (1987).
7 M. Orban, E. Körös, and R. M. Noyes, *J. Phys. Chem.*, **83**, 3056 (1979).
8 R. H. Simoyi, P. Masvikeni, and A. Sikosana, *J. Phys. Chem.*, **90**, 4126 (1986).
9 S. S. Jacobs and I. R. Epstein, *J. Am. Chem. Soc.*, **98**, 1721 (1976).