

Radical-controlled Oscillations in BrO_3^- -fructose- Mn^{2+} - H_2SO_4 System

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Abstract: Sustained oscillations were observed in the BrO_3^- -fructose- Mn^{2+} - H_2SO_4 system. Unlike the classical BZ oscillations, the present oscillations might be considered as radical-controlled rather than bromide-controlled since no substance subjected to bromination was present. Addition of acetone induced dual-frequency oscillations comprised of both the radical-controlled and the bromide-controlled oscillations.

Keyword: Radical-controlled, fructose (Fru), BZ type oscillations, dual-frequency oscillations.

The chemical oscillations have caused much attentions since such reactions may provide alluring analogues of various biological and biochemical processes¹. Study on the oscillations with sugars as organic substrates is of special biological significance since these sugars are essential for the living bodies¹. The BZ type oscillations driven by BrO_3^- are most thoroughly studied. According to the widely accepted FKN mechanism², most BZ type oscillations are bromide-controlled in which the brominating reaction is necessary to remove excess Br_2 and regenerate both the Br^- and the oscillating catalyst³. Thus, the organic substrates in BZ oscillations should contain at least one active methylene group for bromination, *e.g.*, malonic acid *etc.* If the organic substrate is non-brominated, such as oxalic acid, amino acid, either a brominating agent like acetone³ or an inert gas like N_2 ⁴ is essential to give rise sustained BZ oscillations. We report here, however, a novel BZ oscillations in the BrO_3^- -fructose (Fru)- Mn^{2+} - H_2SO_4 system, which might be considered as radical-controlled⁵ rather than bromide-controlled since Fru is non-brominated. Addition of acetone could induce the dual-frequency oscillations owing to the coexistence of both the radical- and bromide-controlled oscillations.

Experimental

The oscillating reactions were carried out in a homemade thermostated glass beaker at 303 ± 0.2 K under vigorous stirring. All the reactants were of analytical grade and used without further purification. The reactants were added in the order of H_2O , H_2SO_4 , fructose (Fru), Mn^{2+} , and finally BrO_3^- . The total volume of the reaction solution was

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adjusted to 50 mL with H₂O. The reaction mixture was exposed in ambient air and no special precaution was attempted to exclude oxygen from the reaction mixture. The change in [Br⁻] was followed by monitoring the potential change (E) on a bromide ion-selective electrode (Br-electrode) against a Hg/Hg₂SO₄/K₂SO₄ reference electrode and was recorded as a function of time (E vs. t) on an electrochemical work station (CHI800A). No absolute calibration was attempted.

Results and Discussion

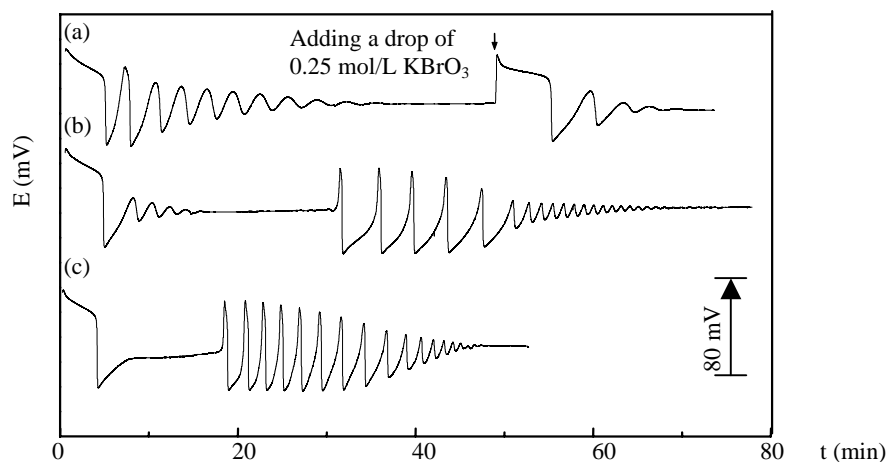
One of the most important findings of the present work was that the BrO₃⁻-Fru-Mn²⁺-H₂SO₄ system could give rise to sustained oscillations even in the absence of either the brominating agent or the inert gas. The suitable concentration range of the reactants for the oscillations is given in **Table 1**. Typical oscillatory pattern is shown in **Figure 1(a)**.

After addition of BrO₃⁻, oscillations started with a short induction period. Besides the oscillations on the Br-electrode, oscillations over the Pt electrode were also observed, showing the periodical change between Mn³⁺ and Mn²⁺, which was consistent with the color change between pink and colorless. The oscillations were strongly damped and only a few of oscillating cycles were achieved. After the oscillations died, addition of small amount of BrO₃⁻ may restart the oscillations while addition of other reactants could not regenerate the oscillations, indicating the stop of oscillations was mainly attri-

Table 1 Concentration range of reactants for oscillations (mol/L)

[BrO ₃ ⁻]	[Fru]	[Mn ²⁺]	[H ₂ SO ₄]
0.0035 ~ 0.038	0.025	0.040	1.0
0.020	0.010 ~ 0.25	0.040	1.0
0.020	0.025	0.0082 ~ 0.43	1.0
0.020	0.025	0.040	0.22 ~ 1.95

Figure 1 Typical oscillatory trace in BrO₃⁻-fructose-Mn²⁺-H₂SO₄ system

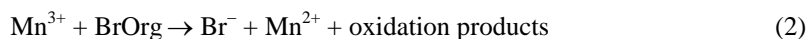


Reaction conditions: [Fru]₀ = 0.025 mol/L, [BrO₃⁻]₀ = 0.020 mol/L, [Mn²⁺]₀ = 0.040 mol/L, [H₂SO₄]₀ = 1.0 mol/L, T = 303 ± 0.2 K, V = 50 mL. (a) [acetone]₀ = 0, (b) [acetone]₀ = 0.050 mol/L, (c) [acetone]₀ = 0.070 mol/L.

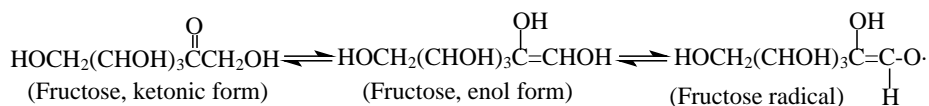
buted to the exhaustive consumption of BrO_3^- in the reaction mixture. During oscillations, bubbles on the electrode surface were observed, indicating the occurrence of the decarboxylation reaction. Besides CO_2 , the other reaction products were analyzed by HPLC with Uv at 210 nm detector under the following conditions: column = Rezex ROA-organic acid, dimensions = 300×7.8 mm, mobile phase = 0.0025 mol/L H_2SO_4 aqueous solution, flow rate = 0.5 mL/min, temperature = 328 K. The products, including arabinose, arabinonic acid, erythrose, formic acid *etc.*, were identified, implying that the oxidation of fructose followed a stepwise mechanism, in which the degradation of fructose and its derivatives occurred. No brominated products were detected throughout the oscillating process due to the absence of brominating reaction since both fructose molecule and its derivatives contain no active methylene groups. The stoichiometric ratio between BrO_3^- and Fru was determined as 3:1 and thus, the general reaction might be described as follows:



Similar to classical BZ oscillations, the present oscillations could also be effectively inhibited by radical scavengers like acrylonitrile and acrylamide, indicating that some radicals were involved in the oscillating mechanism. Meanwhile, the oscillations could also be inhibited by the chloride ion owing to its competitive reaction with HBrO_2 , which is an autocatalyst in most BZ oscillations². The classical BZ type oscillations are bromide-controlled since the autocatalytic reaction could be switched off by Br^- at high concentration. The excess Br_2 produced during the oscillations was consumed *via* brominating reaction with the organic substrate. The resulted brominated substance (BrOrg) was responsible for the regeneration of both the Br^- and the oscillating catalyst (Mn^{2+}) *via* the following reaction:



Unlike the classical BZ type oscillations, the present oscillations in the BrO_3^- -Fru- Mn^{2+} - H_2SO_4 system could not be considered as bromide-controlled since no brominating reaction occurred during oscillations due to the lack of active methylene groups in Fru. In addition, although the potential oscillations on the Br^- -electrode could totally inhibited by adding excess Ag^+ (> 0.0010 mol/L), the oscillations on the Pt electrode could still be observed. This furnished an important evidence that the present BZ oscillations may be not controlled by the bromide ion since, its concentration in the reaction mixture was always less than the critical value ($10^{-5} \sim 10^{-7}$ mol/L) for controlling BZ oscillations, taking into account the formation of the AgBr precipitate with $K_{\text{sp, AgBr}}$ of 5×10^{-13} . Based on above considerations, it was reasonable to conclude that the oscillations in the present system were controlled by radicals. Such radical-controlled oscillations were also observed in the BZ oscillations with malonic acid as an organic substrate when its concentration was extremely high, known as "Racz" reaction⁵. The Fru could be oxidized by Mn^{3+} to form fructose radical (Fru^\bullet) easily since Fru^\bullet was relatively stable owing to the conjugated π bonding (Π_4^5) in the enol form:



The resulted Fru[•] radical controlled oscillations *via* its reaction with HBrO₂. Meanwhile, it also reduced Br₂ to Br⁻, which may remove excess Br₂ produced during oscillations.

Addition of trace acetone resulted in the decrease of both the oscillation number and amplitude, showing the acetone acted as an inhibitor of the present oscillations since acetone could suppress the formation of organic radicals⁶. However, further increasing the acetone concentration from 0.028 mol/L to 0.064 mol/L induced a new type oscillations, resulting in the dual-frequency oscillations, as shown **Figure 1(b)**. When the acetone concentration exceeded 0.064 mol/L, the first type oscillations were totally inhibited and only the second type oscillations were observed, as shown in **Figure 1(c)**. The second type oscillations could be totally suppressed by adding either excess Br⁻ or excess Ag⁺ to remove Br⁻, indicating that such oscillations were bromide-controlled. According to analysis of products, the acetone played a role as a brominating agent to remove excess Br₂ and the resulted bromoacetone was responsible for the regeneration of both the bromide ion and the oscillating catalyst (Mn²⁺), as described in reaction (2). The relatively long induction period for such oscillations could be attributed to the accumulation of enough concentration of the bromoacetone. At very low acetone concentration, the bromide-controlled oscillations could not compete with the radical-controlled oscillations and thus, only the radical oscillations were observed. At very high acetone concentration, the radical-controlled oscillations were totally inhibited since acetone could inhibit the formation of organic radicals⁶, and in turn, only the bromide-controlled oscillations were observed. Within a suitable range of acetone concentration, dual-frequency oscillations appeared due to the coexistence of both these two kinds of oscillations. Detailed studies are being underway to elucidate the reaction mechanism of different oscillations observed in the title system.

Acknowledgments

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