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Cu^{2+}-Catalyzed Oscillatory Oxidation of Ascorbic Acid by O_2 Flow

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Abstract: A novel heterogeneous oscillator, the Cu^{2+}-catalyzed oscillatory oxidation of ascorbic acid (Vitamin C) in aqueous solution by O_2 flow was reported. Both the potential oscillations on Pt-electrode corresponding to $[Cu^{2+}]$ and the absorbance oscillations at λ=260 nm corresponding to [ascorbic acid] were observed. Oscillations in the completely homogeneous system were also observed. Effects of several factors on the oscillations were investigated.

Keywords: Organic-O_2 oscillators, heterogeneous and homogeneous oscillators, Cu^{2+}, O_2 flow, ascorbic acid.

The most widely studied oscillatory chemical reactions are based on homogeneous systems, such as the BrO_3^--driven BZ type oscillations[1], the IO_3^--driven BR type oscillations[2], and the ClO_2^- driven oscillations performed in CSTR[3]. Recently, oscillations have also been found in some heterogeneous systems, such as the oscillations across the liquid membrane[4], the oscillations on the electrode[5], and the oscillations in catalysis[6]. The metal-catalyzed oscillatory oxidation of the organic substrate in the liquid solution by O_2 flow was first reported by Jensen in 1983[7]. Up to now, only the benzaldehyde and cyclohexanone have been reported to give rise to sustained oscillations during their oxidation by O_2 flow, in which, only the Co^{2+} ions can be used as metallic catalyst[4-8]. In this paper, we report a new heterogeneous oscillator consisting ascorbic acid (Vitamin C) in an aqueous solution which undergoes the oxidation by O_2 flow catalyzed by the Cu^{2+} ions. Such an oscillator seems useful to elucidate these periodical phenomena in biological processes since all the substances involved are essential for living bodies and oscillations in the concentrations of both the Cu^{2+} ions and ascorbic acid are observed.

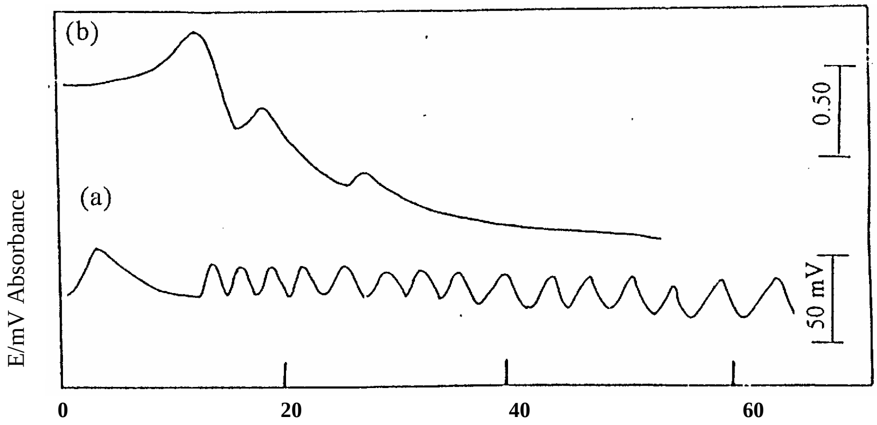
Experimental

All the materials were of analytical reagent grade and used without further purification. All the solutions were prepared in twice-distilled water. The oscillating reactions were performed in a thermostated glass beaker in which desired amount of ascorbic acid, Cu^{2+} catalyst ($CuSO_4$), and NaH_2PO_4-Na_2HPO_4 (buffer solution, pH=6.98) were mixed completely in an aqueous solution. The reaction temperature was maintained at 37 $\pm 0.2^{o}C$. After the temperature was reached a given point, the O_2 flow (99.99%) was introduced into the solution *via* a long glass-tube. During the reaction, the solution was stirred vigorously (*ca.* 200 rpm) and the condensing system was employed to diminish the loss of the solvent in the presence of O_2 flow. The oscillations in $[Cu^{2+}]$ were monitored by measuring the potential change on a bright Pt electrode against a $Hg/Hg_2SO_4/K_2SO_4$ reference electrode, which was recorded as a function of time (E~t) on a XWT x-t recorder. While, the oscillations in [ascorbic acid] were observed by following the change of the absorbance at λ=260 nm corresponding to the maximum wavelength of ascorbic acid on a HP 8451 A UV spectrophotometer.

Results and Discussion

Oscillations in the Cu^{2+}-ascorbic acid-O_2 flow system could be observed in a very narrow range of the reactant's concentrations: [ascorbic acid]=2.5×10^{-6}~3.8×10^{-5} mol/L; $[Cu^{2+}]$=8.5×10^{-7}~5.6×10^{-6} mol/L. **Figure 1a** shows a typical oscillatory curve in redox potential on Pt-electrode corresponding to $[Cu^{2+}]$.

Figure 1 Oscillating Curves in (a)Heterogeneous and (b) Homogeneous Systems



Reaction conditions: $[\text{ascorbic acid}]_0=1.5\times10^{-5}$ mol/L, $[CuSO_4]_0=1.0\times10^{-6}$ mol/L, T=37.0°C, pH=6.98. O_2 flow rate=65 ml/min, (b) $[O_2]_0=5.0\times10^{-4}$ mol/L.

Similar to most of the heterogeneous systems, the reproducity of the present oscillation wave is relatively poor. During the potential oscillations, no change in the solution color was observed, possibly due to the extremely low $[Cu^{2+}]$. The oscillations could last for more than 2.0 h. After the oscillations stopped, addition of small amount of ascorbic acid may restart the oscillations, showing that the disappearance of the oscillations was mainly attributed to the exhaustive consumption of the ascorbic acid in the solution. This could account for the increase in lifetime of oscillations with the increase of [ascorbic acid]. While, the increase of O_2 flow rate could result in the decrease of oscillation lifetime owing to the acceleration of ascorbic acid consumption. No oscillations were observed at $[Cu^{2+}]<8.5\times10^{-7}$ mol/L. Addition of small amount of EDTA could also inhibit the oscillations as shown in **Figure 1a**, possibly due to the formation of Cu^{2+}-EDTA complex. These results demonstrated that the suitable concentration of Cu^{2+} is essential for the present oscillations. However, on the other hand, high concentration of Cu^{2+} is also harmful for the oscillations owing to the rapid consumption of ascorbic acid by O_2 flow. The maximum concentration of Cu^{2+} for the present oscillations was determined as 6.4×10^{-6} mol/L. Increase in the reaction temperature from room temperature to 60°C caused an abrupt decrease in the induction period, the oscillating period and the oscillation lifetime[1], showing that the reaction rates increased with increase of the temperature. According to the effect of the reaction temperature on the oscillation frequency, the apparent activation energy of the present oscillations was determined as 56.52 kJ/mol by using Arrhenius equation. This value was significantly lower than that of the oscillations with cyclohexanone (72.08 kJ/mol). The reason could be that ascorbic acid is more easily oxidized than cyclohexanone.

Although Co^{2+} has been claimed to be the best catalysts in the O_2 flow-driven oscillators[4-8], no oscillations were observed when Co^{2+} was used instead of Cu^{2+} in the present system. On contrary, the ascorbic acid could effectively inhibit these oscillations catalyzed by Co^{2+}. For example, during the oscillations in benzaldehyde-O_2-Co^{2+} system, addition of 5.0×10^{-3} mol/L ascorbic acid could completely inhibit the oscillations. This could be understood by considering the catalytic mechanism. In the Co^{2+}-catalyzed oscillations[5], the catalyst cobalt changed between Co^{3+} and Co^{2+}. As Co^{3+} is a very strong oxidizing agent and it can oxidize the strong reducing agent ascorbic acid, no significant Co^{3+} could be accumulated. Therefore, no oscillations could be observed in Co^{2+}–ascorbic acid-O_2 system. The oscillations could be observed in the presence of Cu^{2+} instead of Co^{2+} since the oxidizing ability of Cu^{2+} is much weaker than that of Co^{3+}.

The oscillations in the ascorbic acid-O_2-Cu^{2+} system could also be found even under the batch-reactor conditions in a completely homogeneous system. Ascorbic acid, Cu^{2+}, and O_2 were dissolved in the aqueous solution previously. Besides the potential oscillations corresponding to $[Cu^{2+}]$ by using the Pt-electrode, the oscillations corresponding to [ascorbic acid] were also observed by measuring the absorbance change of ascorbic acid at λ=260 nm. Under the similar conditions, the oscillatory curve corresponding to [ascorbic acid] is shown in **Figure 1b**. Comparing the experimental results in the homogeneous oscillator with those in the heterogeneous oscillator in the presence of the O_2 flow, the following remarkable differences were obtained. (1) The oscillations in the heterogeneous oscillator could last for very long time and a lot of oscillation cycles could be observed. However, in the homogeneous system, the oscillations damped very rapidly and only less than 5 oscillation cycles were observed; (2) As mentioned above, the lifetime of the oscillations in the heterogeneous oscillator was mainly dependent on the concentration of ascorbic acid. However, in the homogeneous oscillator, after the oscillations finished, addition of ascorbic acid could not restart the oscillations. On contrary, the oscillations could be restarted when O_2 flow was introduced into the system. These results demonstrated that the exhaustive consumption of the dissolved O_2 in the liquid solution was the essential factor of the disappearance of the oscillations in the homogeneous oscillator. Therefore, the lifetime of the oscillations was also mainly dependent on the concentration of O_2 in the homogeneous solution.

The present oscillator seems helpful to understand the periodical phenomena in the biological processes. All the substances involved in the present oscillator are essential for the living materials and the oscillations in [ascorbic acid] observed in the present oscillator are reasonable to explain the periodical change of the concentration of vitamin C observed in the biological processes. Obviously, the oscillating mechanism in the ascorbic acid-O_2-Cu^{2+} system was very complicated and quite different from all other organic substrate-O_2 oscillators reported so far. Not only the potential oscillations are dependent on the concentration of the metallic ions, but also on the concentration of the organic substrate itself. To explain these new oscillating phenomena, the oscillating mechanism proposed previously by Reolofs and co-workers[6] should be revised. The studies on the reaction kinetics, such as the rate equations, the reaction products and various intermediates resulted from the oxidation of ascorbic acid by O_2, the effects of various factors on the oscillation characteristics are being underway.

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