A Vanadium-based Chemical Oscillator

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Nature abounds with examples of aperiodic functions such as hormonal, daily, and seasonal cycles and cardiac rhythms, but establishing a chemical basis of these oscillations has been difficult. Efforts to provide chemical models for the study of oscillating phenomena have focused on halogen-, sulfur-, and manganese-based systems. We show here that a vanadium-based chemical system exhibits oscillatory behavior similar to circadian and other aperiodic rhythms.

We have recently found that a dichloromethane solution of $[V(IV)OCl_2(bpy)]$ (bpy: 2,2′-bipyridyl) or $[V(III)Cl_3(CH_3CN)-(bpy)]$ exhibits aperiodic oscillatory behavior in a closed system.[1] The color of a dichloromethane solution of the vanadium complexes in a closed volumetric flask (with or without stirring) changes from initial pale green to dark orange aperiodically after an induction period at an ambient temperature, then back to pale green, and this pattern repeats for a long period (over a month in some cases). A similar oscillation reaction was also observed when 1,10-phenanthroline analogs were used instead of the bpy complexes.

The dark orange species was successfully isolated as crystals by maintaining a dark orange solution at $-20\,°C$. The isolated complex was found to be $[\{V(V)OCl_2(bpy)\}_2-(\mu\text{-}O)]\cdot2CH_2Cl_2$ by X-ray crystallography (Figure 1).[2] Short V1–O1 and V2–O2 distances (1.586(4) and 1.582(4) Å, respectively) are consistent with V=O, indicating vanadium atoms in the +5 oxidation state. Thus, the observed color change can be attributed to a redox reaction between vanadium(IV) and -(V). The 447-nm absorption band responsible for the dark orange color can be assigned to a CT transition because of lack of a d–d transition for d^0 vanadium(V) (Figure 2).
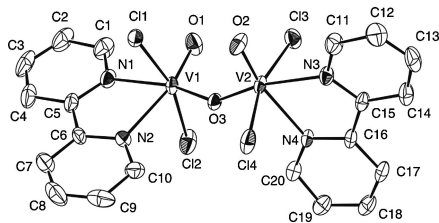

Figure 1. ORTEP of $[\{V(V)OCl_2(bpy)\}_2(\mu\text{-}O)]\cdot2CH_2Cl_2$ (thermal ellipsoids set at 30% probability). Dichloromethane molecules are omitted for clarity.
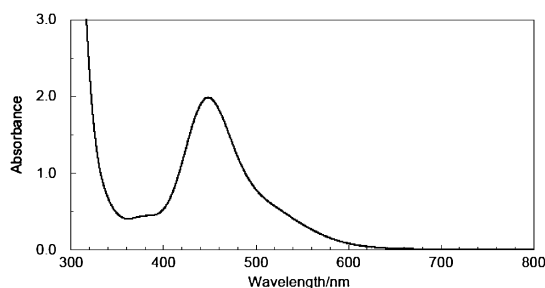

Figure 2. Absorption spectrum of the dark orange species formed in the reaction solution ($[V] = 0.55\,\mathrm{mmol\,dm^{-3}}$).

It should be important to follow the time-course of the color change. At first, we tried to follow the color change spectrophotometrically by circulating a reaction solution into a flow-cuvette with a peristaltic pump, but tubing, viton as well as tygon, could not resist exposure to dichloromethane for a long period. We, therefore, employed a video camera (SONY DCR-HC90) to obtain an oscillatory pattern of the solution. A volumetric flask with a tight plug was used as a reaction vessel to avoid evaporation of volatile dichloromethane. Video frames with a constant time interval of 10 min were captured for several dichloromethane solutions of the vanadium complexes with stirring. The color density (gray scale) of the solutions was converted to a numerical value by analyzing pixels of captured video frames using a graphic software program (Canvas 6.0; DENEBA). Although this technique is of course not as accurate as a spectrophotometric method for color density (absorbance) measurements, it ensures sufficient quality for following color changes of the reaction solutions. As shown in the lower part of Figure 3, in which an oscillatory pattern observed for a dichloromethane solution of $[V(IV)OCl_2(bpy)]$ (0.55 mM) at ambient temperature is shown, numerical values using the above method correspond well to apparent color densities shown by some photos included at several points in this Figure. In spite of the above disadvantage in accuracy, this method has the advantage of convenience. Oscillating patterns can be compared exactly for different solutions since we can measure several solutions simultaneously under the same conditions. Because oscillating reactions are in general very sensitive toward small changes in environmental conditions, this is beneficial for the present system in which the oscillation lasts for a long period of time.
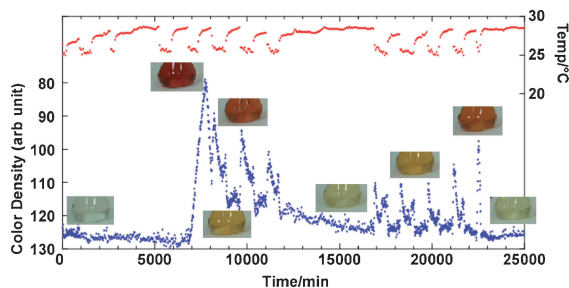
Figure 3. Oscillatory pattern for [V(IV)OCl$_2$(bpy)]. Lower part: Change of the color density of the reaction solution (left scale). Upper part: ambient temperature (right scale).

Figure 4. Oscillating pattern for a dichloromethane solution of [V(IV)OCl$_2$(bpy)].

Figure 5. Oscillating pattern for a dichloromethane solution of [V(III)Cl$_3$(CH$_3$CN)(bpy)].

The present oscillatory system has some features distinct from known chemical oscillators. The most striking feature of the present system is its simplicity. All previously described chemical oscillators essentially contain all or some of the following constituents; metal catalyst (Ce(III), Mn(II), etc.), oxidant (bromate, iodate, H$_2$O$_2$, etc.), reducing substrate (malonic acid, oxalic acid, etc.), and acid (H$_2$SO$_4$, HClO$_4$, etc.).[3–9] On the contrary, the present system only consists of the vanadium complex and dichloromethane as a solvent. This indicates that chemical species formed in situ, namely, degradation products of dichloromethane, would constitute a new oscillatory system, which is fundamentally different from those previously reported. Degradation products of dichloromethane will be discussed later. The oscillation period for the present system is also different from other systems. Chemical oscillators typically have periods from seconds to minutes while the present system has a period of hours, indicating the reactions responsible for the oscillation are slow. It is noteworthy that some biological oscillators have even longer periods. For example, the oscillatory reaction of chondroitin sulfate has a period of ca. 25 h.[10] Finally, while the majority of the chemical oscillations found so far occur in aqueous media, the present oscillation was observed only in dichloromethane.

The present oscillation system shows a strong dependence on solvent as well as ingredient. The oscillation was not observed in other halomethanes including chloroform, 1,2-dichloroethane, and dibromomethane. Interestingly, stabilizers involved in dichloromethane were found to crucially influence the oscillation. In dichloromethane for HPLC (Wako Pure Chemicals, Japan) and that for UV spectrometry (Dojin, Japan), which includes 0.2–0.4% and 0.5% methanol, respectively, the oscillatory reaction does not occur. On the other hand, the oscillation was observed in special-grade dichloromethane including 0.0005–0.005% 2-methyl-2-butene as a stabilizer (Wako Pure Chemicals, Japan) and in dichloromethane from which the stabilizer was removed.[11]

The vanadium system's aperiodic behavior (Figure 3) could arise from uncontrolled environmental perturbations. For example, external forcing or perturbation experiments on oscillating systems have been reported for an electrochemical system[12] and for biological oscillators.[13,14] For this system, an induction period of approximately 7000 min is followed by color change (Figure 3, lower) that seems to correlate with ambient temperature change (Figure 3, upper). This phenomenon is not due to thermochrism, because the color change occurs aperiodically at a constant temperature, 25 °C.[15]
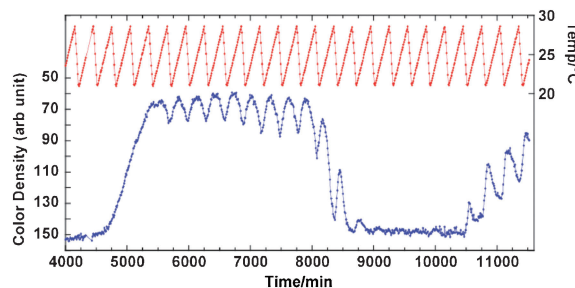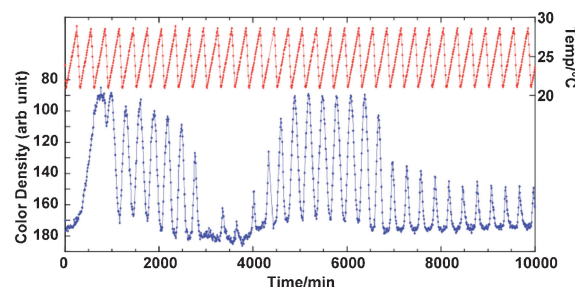
To eliminate this aperiodic effect, oscillating patterns were obtained for reaction vessels placed in a thermocontrolled water bath, in which we can apply temperature pulsing to the vessels. Representative results are shown in Figures 4 and 5. In these experiments, the average temperature was set to 24 °C, the amplitude of temperature pulsing to ±4 °C, and the pulse period to 5 h (descending time 1 h and ascending time 4 h). Figures 4 and 5 show oscillatory patterns observed for dichloromethane solutions of [V(IV)OCl$_2$(bpy)] (0.34 mM) and [V(III)Cl$_3$-(CH$_3$CN)(bpy)] (0.34 mM), respectively. For [V(IV)OCl$_2$(bpy)], after an induction period of ca. 5000 min the reaction solution exhibited oscillations in shades of orange color until ca. 8000 min in resonance with the temperature pulsing. Then, the oscillation was damped to yield a pale green solution, and no oscillation was observed between 9000 and 10500 min. Interestingly, the resonance oscillation was recovered after 10500 min. More distinct resonance phenomena were observed for [V(III)Cl$_3$(CH$_3$CN)(bpy)]. In this case, after the first development of the orange color at ca. 750 min, the color change between pale green and dark orange continued in resonance with the temperature pulsing until ca. 3000 min. The oscillation once dampened between 3000 and 4000 min as in the case of [V(IV)OCl$_2$(bpy)], but the resonance oscillation recovered from 4000 min and lasted for a long period of time though the amplitude of the oscillation was reduced after 7000 min. A similar phenomenon was also observed for a system in which the amplitude of temperature pulsing was set to ±2 °C, but when the amplitude was reduced to ±1 °C the response became remarkably worse and the oscillation tended to be aperiodic. We are now examining in detail effects of the pulse pattern on the oscillatory behaviors.

An early experimental study of chemical resonance was done on the Belousov–Zhabotinsky (BZ) reaction by Buchholtz and Schneider.[16] They applied a sinusoidal modulation on the total flow thorough a continuous-flow stirred tank reactor (CSTR) when the BZ reaction is in the condition of non-oscillatory (steady) state. Application of a periodic perturbation to the influx of an oscillatory component was also conducted on a biological oscillator by Lazar and Ross.[13] There is no example of a temperature-pulse-inducing oscillatory behavior as far as we know, though a pressure pulse experiment has been reported for the oscillatory behavior of a catalyst.[17] On the other hand, phenomena illustrating that temperature change induces oscillatory behavior are ubiquitous in nature. For example, the opening and closing of tulip petals can be reproduced by changing the temperature from 5 to 20 °C for opening and 20 to 5 °C for closing.[18]

Although a detailed mechanism underlying the present oscillatory behavior cannot be determined at present, we want to show some insights into important features of the present system here. Recently, photocatalytic degradation of dichloromethane by copper(II) ion has been studied.[11] Aerated dichloromethane solution of $[CuCl_4]^{2-}$ causes the decomposition of dichloromethane by irradiation of near UV light to yield HCl, $C_2H_2Cl_4$, and peroxides. It is certain that a similar degradation of dichloromethane occurs in the present system since a large amount of HCl is produced in the present system after oscillation. The vanadium complexes would work as catalysts in the present system. The photodissociation of a chlorine atom from CH_2Cl_2 initiates a series of radical reactions to accumulate the peroxides, $CHCl_2OO\cdot$ and $CHCl_2OOH$, which are formed by a reaction with dioxygen. The peroxides work as an oxidant to reoxidize copper(I), which is formed by photoreduction of the initial copper(II) species. These reactions allow an explanation of some features of the present oscillatory reaction. This is also consistent with the fact that the present oscillatory reaction does not occur under anaerobic conditions.

The oscillatory reaction was not initiated in the dark, indicating that the photodissociation of a chlorine atom is a requisite for initiation of the oscillatory reaction. As described above, methanol in dichloromethane inhibits the oscillation. This fact would indicate that radical species necessary for the oscillation were not accumulated in dichloromethane containing 0.2–0.5% methanol since methanol can work as a radical scavenger, while 0.0005–0.005% 2-methyl-2-butene does not significantly influence the oscillatory behavior.

Assuming that the peroxides, $CHCl_2OO\cdot$, and $CHCl_2OOH$ function as oxidants for the present system as in the case of the copper system, the induction period before the first development of dark orange color (first oxidation from V(IV) to V(V)) would correspond to a period for accumulating the peroxides. This assumption also explains the observation that the oscillatory behavior does not occur in anaerobic conditions. We presumed at first dioxygen itself works as an oxidant in our preliminary report,[1] but we could not explain the reason why the oscillatory behavior was not observed in other aerobic halomethanes. The above assumption regarding the potential oxidant can explain a strong solvent dependence for the present oscillation.

The induction period is considerably short for the V(III) complex, which is readily oxidized to V(IV) complex in aerobic solution, compared to that for the V(IV) complex. This fact would indicate that species formed in the oxidation of the V(III) complex, such as superoxide, may enhance the accumulation of the peroxides. The feedback route for the present system, namely, reduction of the V(V) complex is not clarified at present though formaldehyde included as a contaminant[1] or produced as a degradation product of dichloromethane[15,19] would potentially work as a reductant. The resonance oscillation with temperature pulsing suggests that gaseous and/or volatile chemical species such as O_2, HCl, CO, and HCHO would play an important role in the oscillation reaction. We are now investigating the identification of chemical species in the system, including radicals conducive to this unique oscillatory reaction.

References and Notes

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