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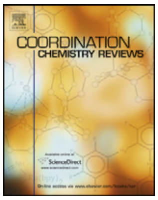

Review

Chemical oscillation of vanadium complexes: Simple and aperiodic systems

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ABSTRACT

An oscillatory chemical reaction is an intriguing phenomenon subject to various and often uncontrollable factors. Many oscillatory systems consist of a strong acid, metal ion and an additional species with accessible oxidation states, and restrictive temperature conditions. Thus, an oscillatory system in which all the factors are understood would be useful. In this paper, we describe the first such system based on vanadium chemistry. The V(IV) complex (pale green color) turns dark orange with the production of a V(V) complex. This reaction is affected by many factors such as oxygen, ultraviolet (UV) irradiation, visible irradiation, and aldehyde addition. This oscillation reaction occurs only in a dichloromethane solution, suggesting that the solvent intervenes in the reaction. Examination of the gas phase during the oscillation reaction revealed the formation of carbon monoxide, carbon dioxide, hydrogen chloride, and phosgene. Based on these observations, we propose a plausible oscillation reaction mechanism.

The results of this study contribute to the field of nonlinear dynamics. Additionally, this work offers new insights into vanadium chemistry because this oscillation phenomenon is strongly correlated with the electron transfer reaction of the vanadium complex. Moreover, studies using vanadium complexes may help in understanding vanadium-mediated electron transfer systems *in vivo*, such as vanadium accumulation and storage observed in marine organisms.

1. Introduction

Many electronic devices, such as personal computers and GPS, enable us to control information electronically. However, there are sudden thunderstorms, tsunamis, and earthquakes. We cannot predict the exact time when cherry blossoms will come out

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$$V^{3+} + e^{-} \rightleftharpoons V^{2+} \qquad E^{\circ} = -0.26\ V$$

$$VO^{2+} + 2H^{+} + e^{-} \rightleftharpoons V^{3+} + H_2O \qquad E^{\circ} = 0.36\ V$$

$$VO_2^{+} + 2H^{+} + e^{-} \rightleftharpoons VO^{2+} + H_2O \qquad E^{\circ} = 0.999\ V$$

Scheme 1. Standard electrode potential of vanadium species (H. Sakurai (Ed.), The Encyclopedia of Bio-elements, Ohmsha, Tokyo, Japan, 2006, p. 63).

and in which direction a typhoon and hurricane will move. We do not know when it will start snowing, or when cicadas will come out from the earth. Although four seasons come periodically and repeatedly, we live with many aperiodical phenomena. Many people look to science to provide answers for all phenomena occurring in the world. However, there is only so much modern science can provide.

In this meaning, the oscillation reaction is an attractive field to inspire the interest of basic chemical researchers. Review articles have dealt with the oscillation reaction mainly based on the physical dynamics including nonlinear chemical dynamics, oscillation and patterns and chaos [1,2].

The chemical oscillation reaction of vanadium proposed here is simple; however, we recognize the complexity of the chemical reaction. The color change of the vanadium solution corresponds to the change in oxidation states of vanadium from V(V) (dark orange) to V(IV) (pale green). We introduce this new oscillation reaction and propose a reaction mechanism.

2. Vanadium

Vanadium is a metal that changes color based on its oxidation state. When vanadium was first discovered by Del Rio in 1813, it was named panchromium because of its variety of colors [3]. In 1831, the Swedish chemist Sefström rediscovered vanadium and gave it the current name for the Scandinavian Venus (Vanadis). Vanadium complexes have attracted attention because their color changes are quite obvious. Additionally, there is evidence that vanadium plays an important role in the lives of various organisms. Thus, much research in the chemical, biological, and physiological fields has focused on vanadium. Although the importance of vanadium is well known, its necessity as a fundamental element in the human body is still unclear; thus, vanadium complexes have been widely investigated. Vanadium complexes can act as strong dehydration catalysts [4], oxidizing agents [5–7], and insulin-mimicking drugs [8,9]. Vanadium complexes have also shown haloperoxidase activities [10,11] and accumulation in marine organisms [12,13]. The wide variety of vanadium activities is due to its ability to exist in a variety of oxidation states. Vanadium forms complexes in which its oxidation state can range from −2 to +5, with +3, +4, and +5 being found in living organisms. Thus, a variety of functionalities may be present in vanadium complexes. The change in the oxidation state between V(IV) and V(V) occurs readily because the oxidation–reduction potential of these two states is quite low, as shown in the following equations (Scheme 1).

The visible color change that occurs when V(IV) (typically green or blue) transitions to V(V) (typically yellow or colorless) corresponds to the oxidation state. This transition between oxidation states is explained by the electrode potential difference between V(V) and V(IV) (0.999 V), resulting in the color change that occurs readily in vanadium complexes. Marine ascidians accumulate vanadium in its reduced form as V(III), even against an energy potential. Thus, there is interest in examining this accumulation mechanism. In this study, we developed vanadium chemistry that mimics the natural reduction process carried out by ascidians.

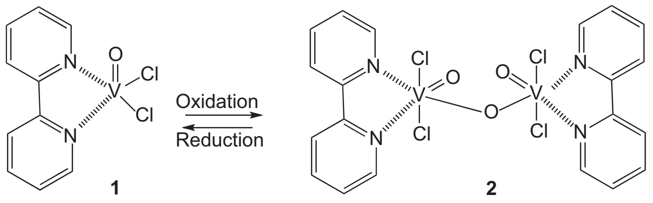


Fig. 1. Oscillation reaction profile.

3. Vanadium-based oscillation

We followed the reactions of specific vanadium complexes and found that the color change occurred repeatedly for standing solutions of the samples over a period of time [14]. The color change occurred aperiodically and was strongly dependent on the experimental conditions. To understand this unique phenomenon, we examined the reaction mechanism in detail.

3.1. Color change

We found that [V(IV)OCl_2(bpy)] and [V(III)Cl_3(CH_3CN)(bpy)] (bpy: bipyridyl) were oxidized to V(V), as indicated by the color change from pale green to dark orange under mild reaction conditions [14]. This reaction occurred aperiodically over time (Fig. 1).

For this reaction, V(IV) or V(III) complexes were dissolved in dichloromethane at room temperature. The pale green color of the V(IV) complex gradually changed to dark orange due to formation of the μ-oxo dinuclear vanadium(V) complex. The structure of this dinuclear complex was confirmed by X-ray crystallography (Fig. 2) [15].

The color change was temperature-dependent. However, there are many other factors that can affect this oscillation reaction. In this paper, we analyzed the factors that have the potential to control the oscillatory reaction.

3.2. Solvent effect

The oscillation reaction was carried out using polar and nonpolar solvents, along with protic and nonprotic solvents. Our results showed that the oscillation reaction occurred only in dichloromethane. Although the color change occurred in other solvents, such as chloroform, it did not occur repeatedly. Thus, the use of dichloromethane was crucial for this oscillation reaction. We also examined the effect of solvent stabilizers added to the dichloromethane. The inclusion of methanol inhibited the reaction completely, while 2-methyl-2-butene (0.0005–0.005%) in dichloromethane did not affect the reaction [15]. Furthermore, during dichloromethane production, a small amount of formaldehyde is thought to be produced; thus, we investigated the effect of formaldehyde on this oscillation reaction. The oscillation reac-

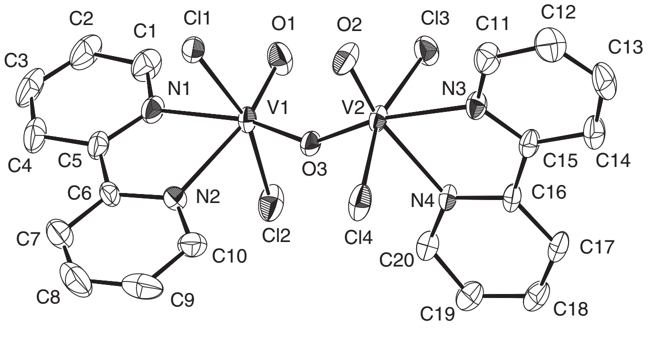


Fig. 2. ORTEP of [{V(V)OCl_2(bpy)}$_2$(μ-O)].

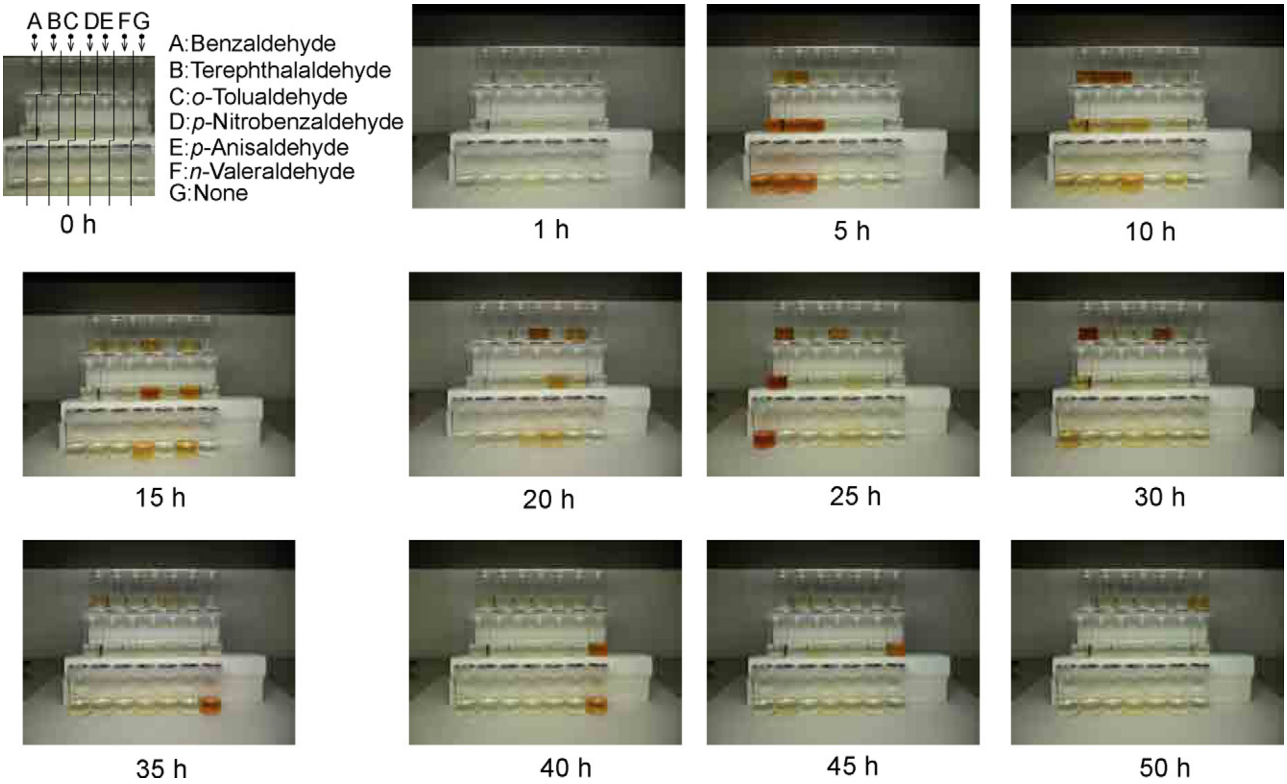


Fig. 3. Time-dependent oscillation reaction of the vanadium complex. (a) Control, (b) 1 h, (c) 5 h, (d) 10 h, (e) 15 h, (f) 20 h, (g) 25 h, (h) 30 h, (i) 35 h, (j) 40 h, (k) 45 h, (l) 50 h samples: from left to right, V(IV) complex + benzaldehyde; V(IV) complex + terephthalaldehyde; V(IV) complex + ortho-tolylaldehyde; V(IV) complex + para-nitroaldehyde; V(IV) complex + para-anisaldehyde; V(IV) complex + n-valeroaldehyde; V(IV) complex (alone).

tion occurred in the presence of formaldehyde, especially in the first oxidation stage. Thus, the intervention of a carbonyl moiety or aldehyde moiety may have affected the oscillation reaction. Based on this hypothesis, we examined the effects of aldehydes using various aromatic aldehydes, because small aliphatic aldehydes, such as formaldehyde, are usually volatile, making quantitative analysis difficult. Additionally, aromatic aldehydes were useful for investigating steric effects on the oscillation reaction. An ortho-substitution of the aldehyde group would not have resulted in a useful ligand for the aromatic aldehyde. Furthermore, information about the electronic effects on aldehyde groups can be obtained by varying the para- or meta-position substituents.

3.3. Aromatic aldehyde effects on the oscillation reaction

The oscillation reaction was carried out in the presence of various aromatic and aliphatic aldehydes. As shown in Fig. 3, color change occurred in all samples; however, the induction period before the first color change was highly dependent on the nature of the aldehyde.

The induction period was shorter for benzaldehyde and terephthalaldehyde, whereas it was longer in the presence of aliphatic aldehydes, such as n-valeroaldehyde, compared with the control solution. The first color change following the induction period was a trigger for the oscillatory reaction but did not correspond to a specific stage of the reaction. Thus, the oscillation reaction was triggered within a short time in the presence of the benzaldehyde and terephthalaldehyde. However, it is unclear why the reaction was not triggered by the other aldehydes. Ortho substituents hindered the aldehyde coordination to the vanadium center. In certain stages of the oscillation reaction, this kind of coordination was necessary for the reaction to proceed. Additionally, we carried out experiments using nitro or methoxy substituents in the para-position on the aromatic ring to examine electronic effects. The results showed that neither substituent reduced the induction period. In fact, they increased the induction period compared with those of benzaldehyde or terephthalaldehyde. Thus, in the oscillation reaction induced by the vanadium complexes observed here, the electronic effect of the substituents on the aromatic aldehyde was negligible; however, the steric effects may have initiated the reaction and controlled the reaction rate. To confirm the possible coordination of the aldehyde moiety to vanadium complexes, we examined the products of the oscillation reaction in the presence of terephthalaldehyde.

3.4. Product analysis

After the oscillation reaction was carried out with the addition of terephthalaldehyde in dichloromethane at room temperature for a few days, the solution was poured into methanol to generate high yields of dimethyl phthalate and para-fomyl benzoic acid (∼90%). The formation of both compounds can be explained by the oxidation of terephthalaldehyde. The formation of dimethyl phthalate occurred due to nucleophilic attack of the methanol moiety towards the carbonyl moiety coordinated to the vanadium. Another possibility would be acid-catalyzed esterification of terephthalic acid by methanol. However, the yield would have been expected to be lower than what was observed here because the acid-catalyzed esterification reaction is an equilibrium reaction; thus, it would have been difficult to achieve high yields of dimethyl phthalate. When ethanol was used instead of methanol, we obtained ethyl 4-formyl benzoic acid diethyl acetal and diethyl phthalate in high yields. These products were also the result of carbonyl intervention (Fig. 4).

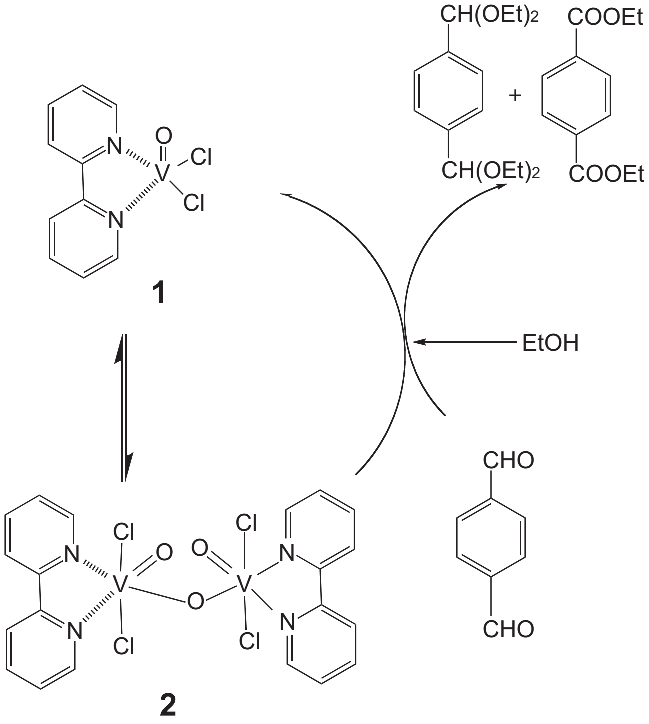


Fig. 4. Isolation and characterization of the oscillation reaction products for the solution containing terephthalaldehyde.

3.5. UV irradiation

Initially, we carried out the oscillation reaction at room temperature in dichloromethane in the presence or absence of benzaldehyde (aromatic aldehyde) without considering the effect of light. The experiments showed that the oscillation reaction typically occurred readily, but in some cases the reactions were extremely slow. It was apparent that light was an important variable in the oscillation reaction because the brightness surrounding the reaction vessel varied during the reaction. To investigate the effect of light on the reaction, we prepared samples containing the vanadium complex and benzaldehyde and carried out the reaction with and without UV irradiation. One sample was irradiated by UV light (302 nm) and the other was kept in the dark at room temperature. The oscillation reaction did not proceed in the absence of photoirradiation. UV irradiation in the presence of benzaldehyde shortened the induction period markedly. UV irradiation has been reported to induce decomposition of the substrate, including solvents such as dichloromethane, for metal complexes [16,17]. In the presence of UV irradiation, the induction period was shortened markedly, clearly demonstrating the effect of UV irradiation (UV light) on the oscillation process (Fig. 5).

3.6. Oxygen effect

The vanadium complex starting material was in the V(IV) state, and it was readily oxidized to the μ-oxo-vanadium(V) complex. In the oxidation stage, we did not add any oxidant, such as hydrogen peroxide. The only oxidizing source available for this system was molecular oxygen in the air. To determine the role of oxygen, we examined the reaction in a closed system to control the amount of oxygen in the reaction vessel. When the vanadium complex with benzaldehyde in dichloromethane was irradiated with UV light, the solution turned dark orange within 5 min. When left standing at room temperature for 8 h, the dark orange color disappeared completely. For this experiment, we initially used a 10 mL flask (flask A) and transferred the solution to a 100 mL flask (flask B). In a short period of time, the color of the solution turned dark orange, and we returned the solution to the 10 mL flask. The dark orange color slowly disappeared. This phenomenon was observed in every case (Fig. 7). These results clearly demonstrated the effect of oxygen on the conversion of V(IV) to V(V). UV irradiation may have resulted in an excited state of the vanadium(IV) complex, which reacted with molecular oxygen to form the μ-oxo-vanadium(V) complex as a stable end-product (Fig. 6).

3.7. Visible irradiation effect on the oscillation reaction

Because the μ-oxo-vanadium(V) complex has an absorption band near 450 nm, it absorbs visible light. Thus, visible light irradiation may affect the stability of this complex or the reduction stage of the oscillation reaction. To confirm this, we examined the visible irradiation effect on the reduction stage using the same procedure shown for the UV irradiation (see Fig. 7). After the V(IV) complex was irradiated with UV light, it was oxidized to the V(V) complex. Then, the solution was irradiated with visible light and was immediately reduced to the V(IV) complex. Solutions of A and B both contained V(IV) and a large amount of benzaldehyde. As discussed earlier, UV irradiation made the solution turn orange, resulting in V(V). Visible light irradiation caused the orange color to disappear, whereas the orange color did not disappear in the absence of visible light. Thus, the visible irradiation effect reduced the V(V) complex. Spectroscopic measurements revealed a decrease in the 450-nm absorption band due to the presence of the V(V) complex formed by visible light irradiation.

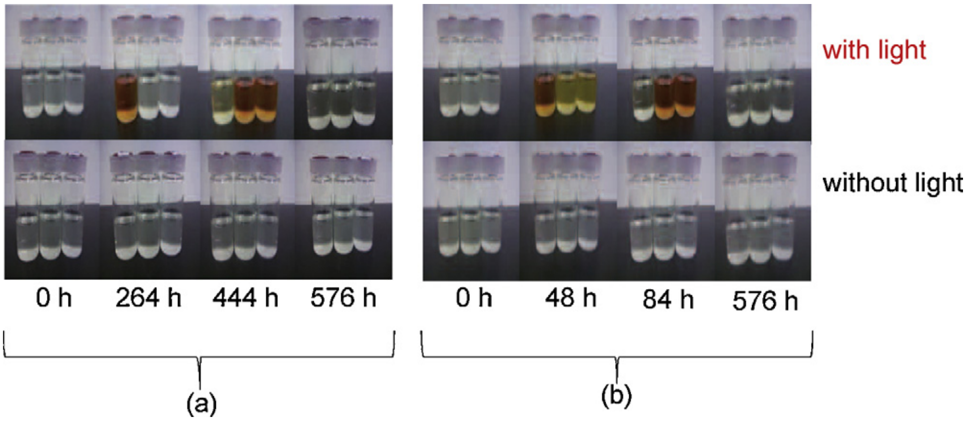


Fig. 5. UV-irradiation effect on the oscillation reaction.

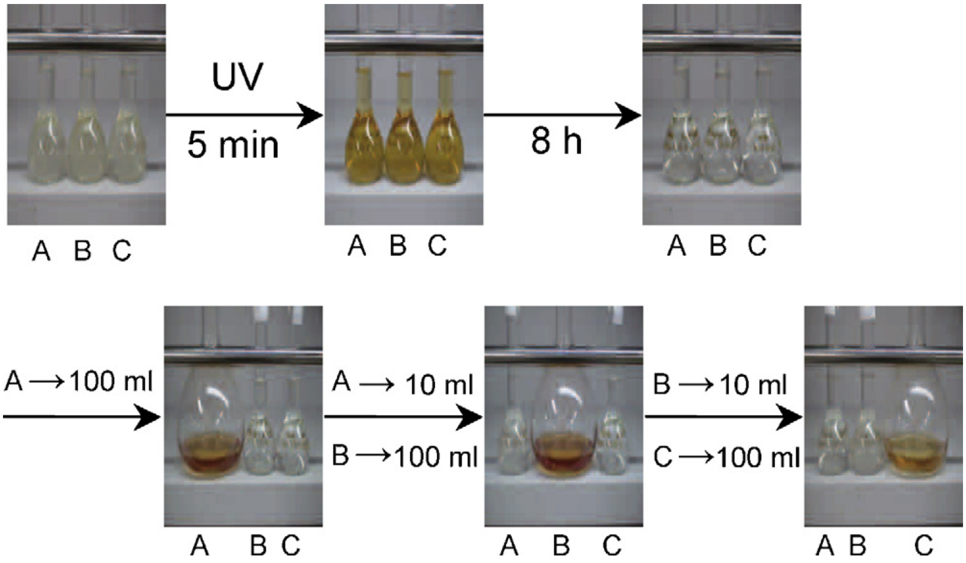


Fig. 6. Oxygen effect on the oscillation reaction.

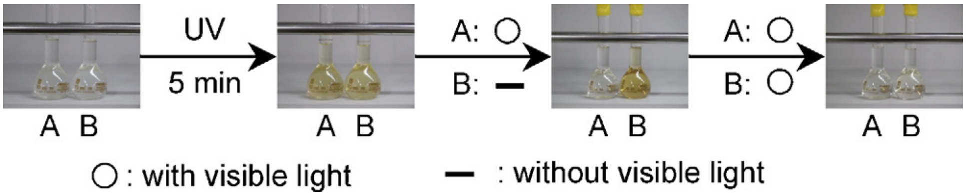


Fig. 7. Visible-irradiation effect on the oscillation reaction.

3.8. *Aldehyde effect on the reduction stage*

To maintain the oscillation reaction, an oxidizing agent and a reducing agent were added to the system. The only available oxidizing reagent in this system was oxygen. However, this does not necessarily imply that molecular oxygen itself directly oxidized the V(IV) complex. We suggest that a peroxyl radical formed *in situ* and acted as the oxidant. However, the identity of the reducing agent is unknown. The molar ratio of the vanadium complex and benzaldehyde (aromatic aldehyde) was sufficient for the aldehyde to act as the reducing agent. We observed the aromatic aldehyde effect on the oscillation reaction as the oxidized products were generated in the presence of terephthalaldehyde. We applied the system shown in Fig. 9, in which the upper column is the time course showing the effect of benzaldehyde on the disappearance of the orange color. In this figure, circles denote the presence of benzaldehyde and minus signs denote the absence of benzaldehyde. The orange color disappeared much faster in the presence of benzaldehyde than in the absence of benzaldehyde. The lower column in Fig. 8 shows the profile of the benzaldehyde effect on the oxidation stage. The orange color appeared much faster in the absence of benzaldehyde than in the presence of benzaldehyde. Thus, aromatic aldehydes, such as benzaldehyde, can act as reducing agents to promote the oscillation reaction. Based on these results and the product analysis, we suggest that aldehyde may have played a variety of roles, including acting as the reducing agent.

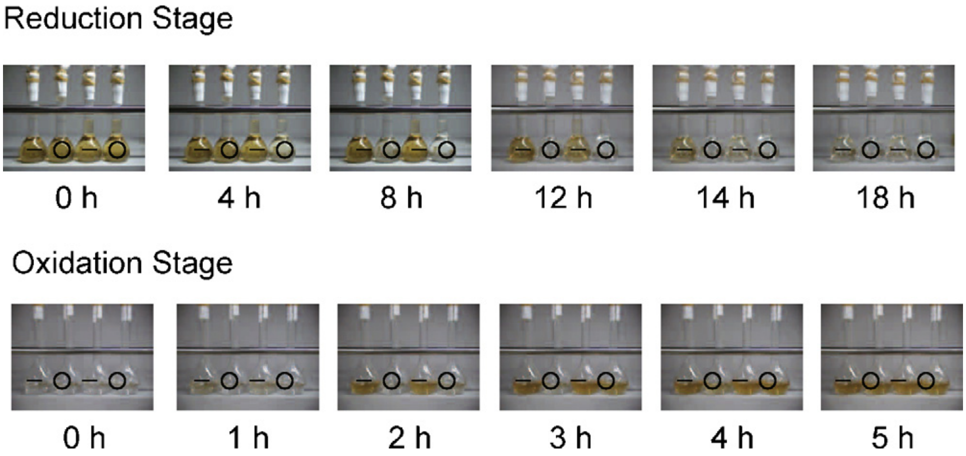


Fig. 8. Effects of aldehydes on the oscillation reaction.

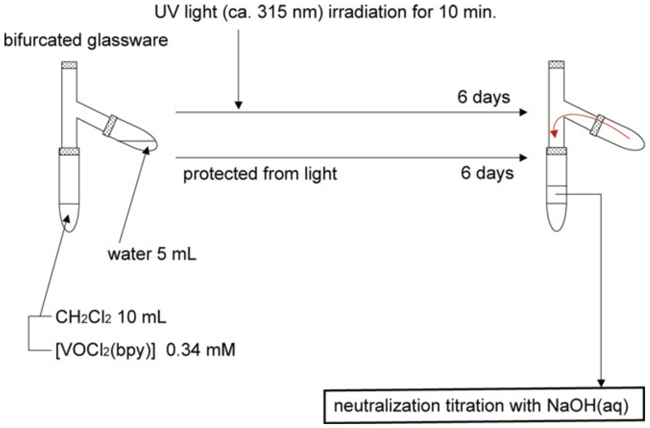


Fig. 9. Titration procedure for acidic gas produced in the reaction system.

3.9. Acidic gas evolution in the oscillation reaction

During the reaction, we observed the production of acidic gas, which was confirmed by pH analysis. Hydrogen chloride originated from the decomposition of dichloromethane. To quantify the amount of hydrogen chloride produced in the reaction, we assembled the apparatus shown in Fig. 9. The oscillation was initiated in a branched flask by UV irradiation. After the solution stood for 6 days at room temperature, water was poured into the reaction mixture. The water phase was extracted and titrated with a dilute sodium hydroxide solution using phenolphthalein as an indicator. The quantification of acidic gas revealed the formation of a large amount of hydrogen chloride (200–300 times more than the content of the vanadium complex). In the absence of the vanadium complex, only a small amount of hydrogen chloride was produced in the reaction. Thus, hydrogen chloride produced in the oscillation reaction originated from the decomposition of dichloromethane catalyzed by the vanadium complex.

3.10. Fourier-transform infrared (FT-IR) analysis of gases produced in the oscillation reaction

We qualitatively analyzed the gases produced during the oxidation and reduction stages of the oscillation reaction. The oscillation reaction was initiated by UV irradiation. During this stage, the gas products were sampled from the gas phase of the reaction vessel using a syringe. The sample was analyzed using Fourier-transform infrared (FT-IR) spectroscopy. The FT-IR spectrum shown in Fig. 10a compares the results from the orange sample to those of the control (UV irradiation without the vanadium complex). This FT-IR spectrum had three characteristic bands corresponding to hydrogen chloride, carbon dioxide and carbon monoxide. During the oscillation reaction, the color of the solution changed back to pale green, and we extracted a sample of the gas phase at this stage. We observed a new band in addition to the three bands observed for the oxidation stage; this new characteristic band corresponded to phosgene. Because phosgene was not observed for the oxidation stage, it is thought that the formation of phosgene only occurred during the reduction stage and originated from the decomposition of dichloromethane in the presence of the V(V) complex.

3.11. Carbon monoxide effects on the oscillation reaction

FT-IR analysis revealed the formation of carbon monoxide, carbon dioxide, hydrogen chloride and phosgene. UV irradiation of a dichloromethane solution containing metal complexes has been reported to produce these gases [17–19]. In our oscillation system, it was unclear whether these gases resulted from an intervention of the oscillation reaction. We focused on carbon monoxide because it is related to carbonyl moieties of aldehydes. Carbon monoxide was not sterically hindered; thus, it was readily oxidized and reduced. Carbon monoxide was formed from the dichloromethane used in the reaction medium. If large amounts of carbon monoxide participated in the oscillation reaction, it was likely that carbon monoxide enhanced the reduction stage because aromatic aldehydes can act as reducing agents. To confirm this, we purged the vessel with carbon monoxide and examined the effect on the oscillation reaction. Carbon monoxide was generated in the present system by decomposition of formic acid catalyzed by sulfuric acid. No color change was observed in the purged sample or the unpurged sample up to 500 min. However, after 500 min, the color of the purged solution began to change and became distinct after 1000 min. Thus, carbon monoxide enhanced the reduction of the V(V) species (Fig. 11).

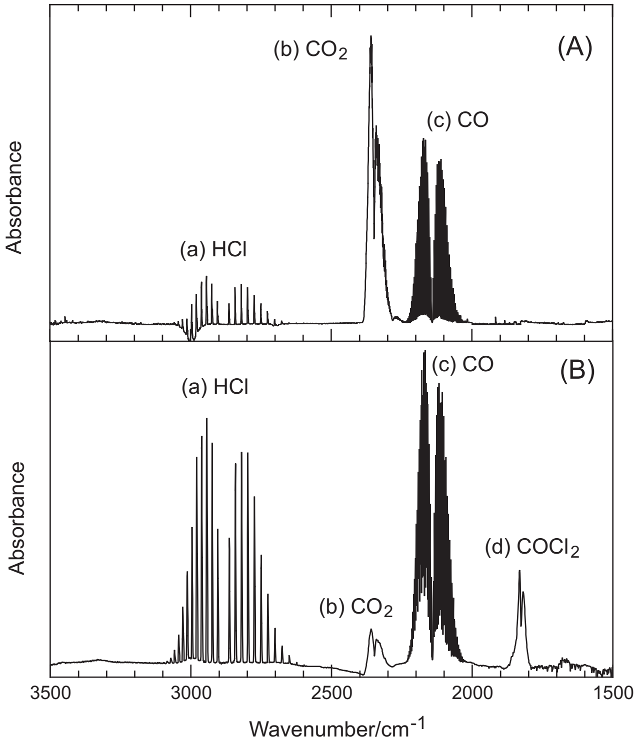


Fig. 10. FT-IR spectra of gas phase products formed during the oscillation reaction. Products formed during the oxidation of V(IV) to V (V). Products formed during the reduction of V(V) to V(IV).

3.12. Reaction mechanism

We confirmed the fundamental factors that were likely responsible for the oscillatory redox reaction between the V(IV) and V(V) species. The trigger of the oscillatory reaction is unclear, but we showed that a simple solution containing only the V(IV) complex required a long induction period, whereas oscillation behavior with the addition of an aromatic aldehyde, such as benzaldehyde, reduced the induction period considerably.

Initially, the effect of light was not considered, but the experimental conditions revealed that the induction period was significantly shorter than the control conditions when the V(IV) solution was irradiated with UV light. In contrast, visible light irradiation enhanced the reduction from V(V) to V(IV).

An oxidizing agent was required for the oscillation reaction to proceed. We examined the effect of solvent stabilizers and found that they did not influence the oscillation reaction. To confirm this,

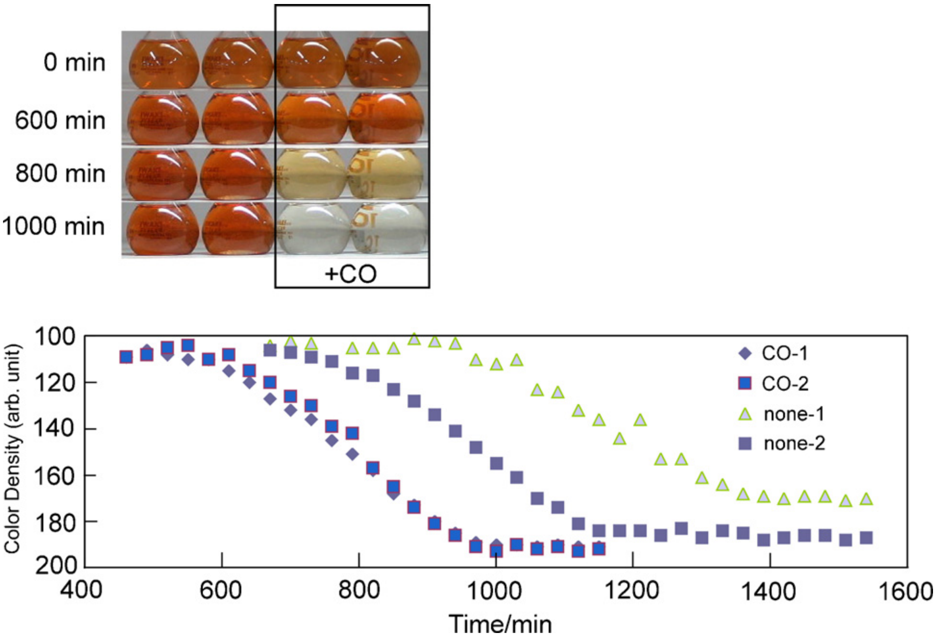
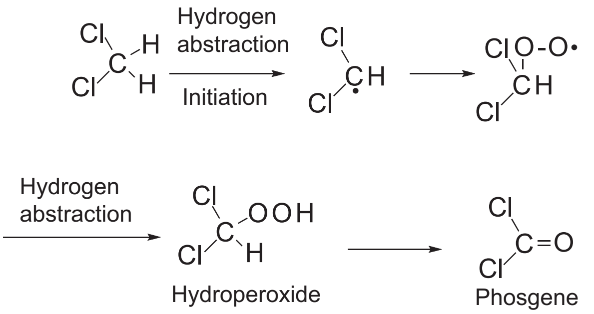


Fig. 11. Effect of carbon monoxide on the oscillation reaction.



Scheme 2. Proposed mechanism for formation of phosgene from dichloromethane.

dichloromethane was also redistilled; however, this did not affect the oscillation reaction. The presence of oxygen molecules in the reaction vessel indicated that oxygen may have acted as the oxidizing agent. The reduced form of V(IV) must be oxidized to form the μ-oxo-dinuclear vanadium(V) complex. To identify the oxidizing agent, we carried out experiments using a small flask (10 mL) and a large flask (100 mL) while keeping the solution volume constant (10 mL). The color change did not readily occur in the 10 mL flask. However, the color change from dark orange to pale green occurred after some time in the 10 mL flask, and the reaction mixture was transferred to the 100 mL flask where the color change to dark orange occurred readily, corresponding to formation of the V(V) complex. Thus, molecular oxygen was required for the oscillation reaction to proceed under these conditions.

Aromatic aldehydes, specifically benzaldehyde and terephthaldehyde, significantly shortened the induction period of the oscillation reaction. That is, addition of aldehydes accelerated the initial oxidation of the V(IV) complex. Aldehydes have diverse func-

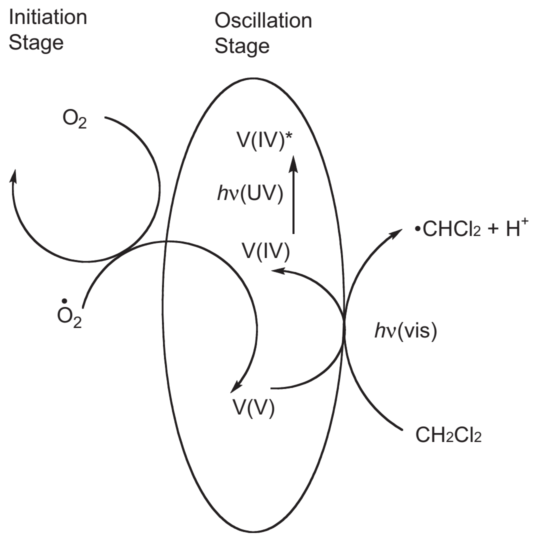
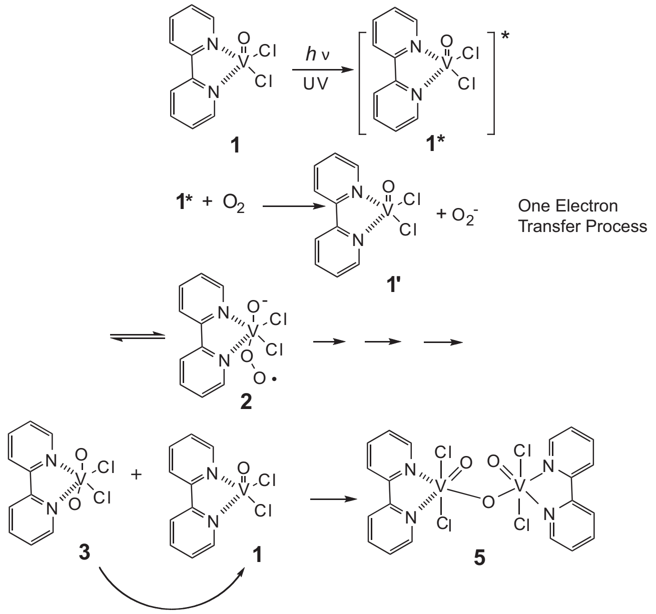


Fig. 12. Brief profile of the oscillation reaction.

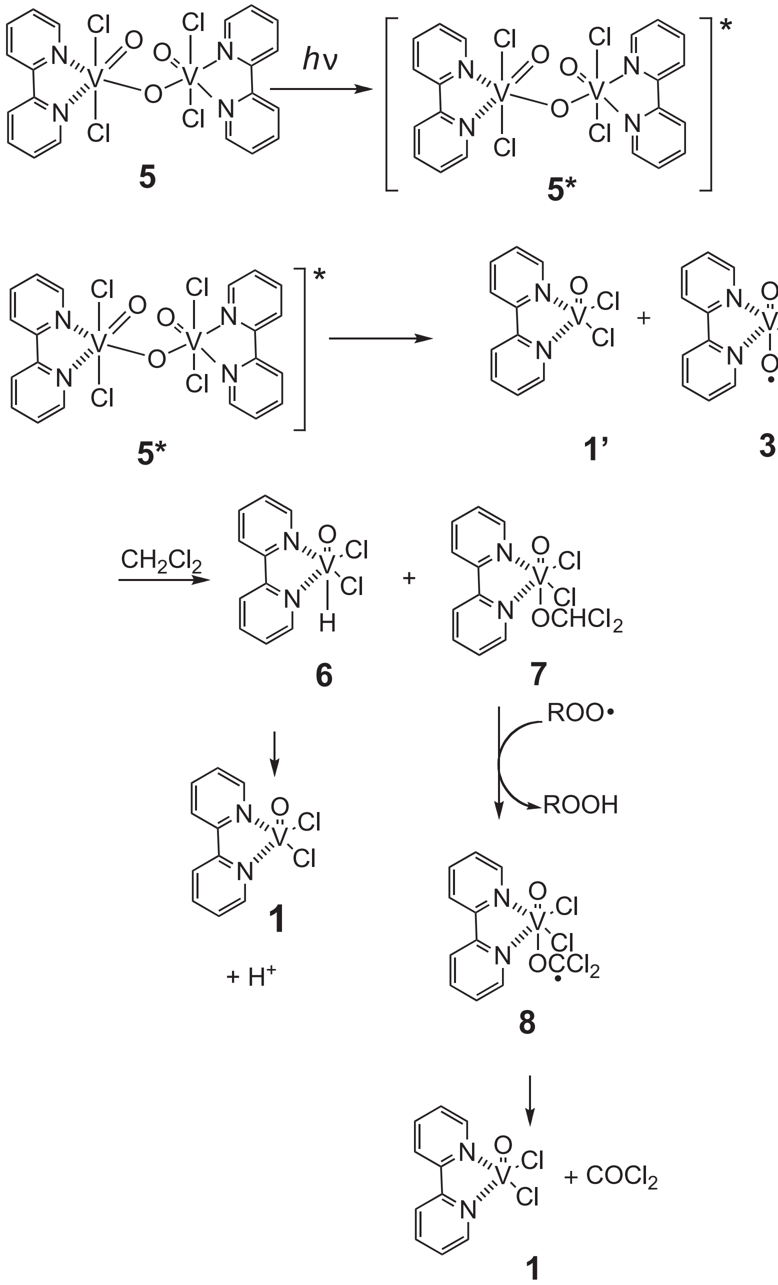


Scheme 3. Possible reaction mechanism for the oxidation stage in the oscillation reaction.

tional groups and are not only readily oxidized to carboxylic acids but are readily reduced to form alcohols. The role of the aldehyde during the induction period of the oscillation reaction was unclear. After the oscillation reaction occurred, the vanadium(V) complex was readily reduced by addition of the aromatic aldehyde (Fig. 9). Thus, it seems likely that the aromatic aldehydes played a role in the reduction of the vanadium complex. To determine the mechanism, we formed dimethyl phthalate by adding methanol to the oscillated reaction solution. During the oscillatory reaction, the aromatic aldehyde was oxidized to yield carboxylic acid derivatives. Thus, aromatic aldehydes acted as reducing agents and were oxidized during the reduction of V(V) to V(IV).

We carried out the oscillation reaction in nonpolar, polar, protic and nonprotic solvents. However, the oscillation reaction only occurred in dichloromethane. Thus, it is important to understand the role of dichloromethane. There are several physical properties of dichloromethane, such as boiling point, polarity, and viscosity that affected the reaction. It is known that UV irradiation of methane in the presence of chorine initiates a substitution reaction between hydrogen and chloride [20]. The end-product in this photoreaction is carbon tetrachloride. Dichloromethane is also produced as an intermediate and reacts with chlorine to form chloroform and carbon tetrachloride. Dichloromethane is vulnerable to radical reactions and reacted readily with radical species present in the reaction medium, allowing an easy abstraction of hydrogen from dichloromethane. Thus, the radical reaction involving oxygen and dichloromethane must be included in the present reaction mechanism.

If dichloromethane participated in the oscillation reaction, decomposition products of dichloromethane would have been produced. Thus, FT-IR was used to identify gases produced during the reaction. Large amounts of hydrogen chloride, carbon dioxide, and



Scheme 4. Photochemical decomposition of dichloromethane.

carbon monoxide were detected during the oxidation of V(IV) to V(V). In the reverse process, V(V) to V(IV), we detected the formation of phosgene, which is the oxidized form of dichloromethane, in addition to those three compounds. During the reduction of V(V) to V(IV), an oxygen atom from the μ-oxo dinuclear vanadium(V) complex was removed. The oxygen atom in phosgene may have originated from the oxygen atom bridging two vanadium(V) centers. The formation of phosgene resulted from the dehydration of hydroperoxide, CCl_2HOOH, as shown in Scheme 2. Hydroperoxide was produced by the reaction between a radical and dichloromethane; specifically, hydrogen was removed following the reaction with oxygen to produce a peroxyl radical. Hydrogenation of the peroxyl radical formed hydroperoxide. Because of its instability, hydroperoxide decomposed to form a carbonyl compound product. The oxygen atom of the μ-oxo complex led to the decomposition of the μ-oxo vanadium(V) complex to the vanadium(IV) complex and an oxo-vanadium(V) complex (radical form), which reacted with dichloromethane to form the dichloromethane radical shown below (Fig. 12).

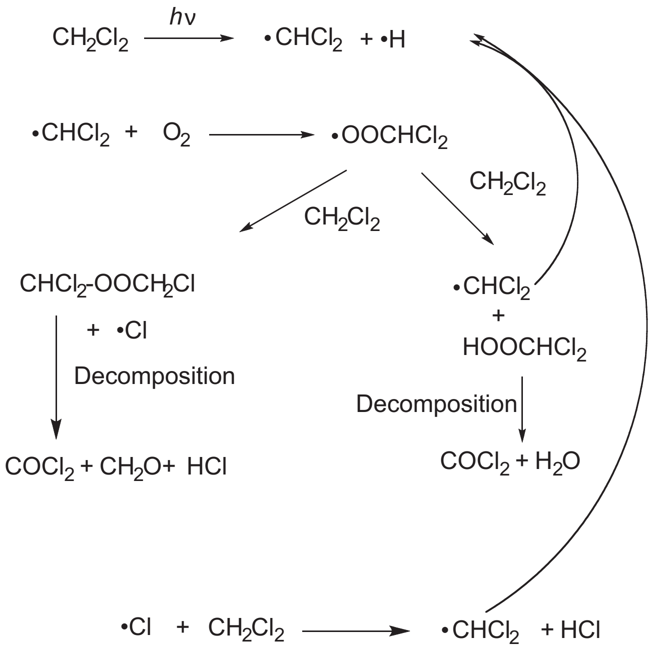
Addition of the aldehyde enhanced the reduction stage, which consisted of the reduction and deoxygenation of vanadium(V) and the oxidation of other substrates, including gases. This was shown by purging ambient air, which contained molecular oxygen, with carbon monoxide. The carbon monoxide enhanced the reduction of the V(V) dinuclear complex.

Based on our results, the following reaction mechanism for the vanadium oscillation reaction is proposed. Initially, UV irradiation formed a radical species in the reaction medium. The generated radical reacted with molecular oxygen in the reaction vessel to form a peroxyl radical. Dichloromethane promoted the removal of hydrogen from the peroxyl radical. The addition of benzaldehyde reduced the induction period due to the oxidation of benzaldehyde. It is unclear whether hydrogen atoms from the aldehyde moiety participated in the initiation of the reaction. The effects of aldehyde addition suggest a mechanism in which aromatic aldehydes intervene in the initial stage of the radical reaction (Fig. 8).

The oscillation reaction can be divided into two parts, an induction period and an oscillation period. UV irradiation and the addition of an aromatic aldehyde initiated the oscillation reaction; however, the role of oxygen in the initiation is unclear. UV irradiation produced a vanadium complex that reacted with benzaldehyde to form a PhCO radical, which decomposed to CO and a Ph radical, with the removal of a hydrogen atom from dichloromethane to give the dichloromethyne radical. The reaction of the dichloromethyne radical with molecular oxygen produced the peroxyl radical, as shown in Scheme 3. To produce the μ-oxo vanadium(V) complex, electron transfer from the V(IV) complex was necessary. Molecular oxygen was the only available oxidizing agent.

If this electron transfer mechanism occurred during the reaction, superoxide and/or hydrogen peroxide would have been produced. However, no measurement, including ESR spectroscopy, detected superoxide in the reaction. Additionally, no reaction was observed in the absence of oxygen. For the conversion of **2** to **5** in Scheme 3, various radical chain reactions were anticipated, including radicals derived from dichloromethane, as depicted in Scheme 4. This radical chain reaction was controlled by the amount of oxygen dissolved in the medium and also the amount of molecular oxygen present in the gas phase in the reaction vessel.

The oscillation reaction is not a one-way reaction. For the oscillation reaction to proceed, the V(IV) complex should be recovered during the reverse reaction. FT-IR analysis of the gas phase during reduction from V(V) to V(IV) indicated the formation of phosgene. The carbon atom of phosgene most likely originated from the carbon atom of dichloromethane; thus, the formation of phosgene resulted from the oxidation of dichloromethane by reactive oxygen species. It is unclear whether the oxygen atom in the μ-oxo vanadium(V) complex participated in the oscillation reaction. We suggest a possible reaction mechanism based on these data and the observation that the visible light irradiation induced the reduction process efficiently.



Scheme 5. Possible reaction mechanism for the reduction stage in the oscillation reaction.

The visible light irradiation of **5** generated the excited state of **5***, which readily decomposed to give **1**′ and oxo-radical **3**. Hydrogen removal from dichloromethane by **1**′ occurred, followed by deprotonation of **6** to produce a proton and **1** as final products. The oxo-radical **3** reacted with the dichloromethyne radical to produce the adduct **7**. Hydrogen removal from **7** by other radicals, including species derived from aromatic aldehydes, generated the carbon-centered radical **8**. Radical decomposition followed by one-electron transfer produced the starting material **1** and phosgene as final products. UV irradiation of dichloromethane in the presence of metal complexes has been reported to produce radicals that correspond to the decomposition of dichloromethane [21]; thus, we suggest the photodecomposition of dichloromethane, based on the irradiation of metal complexes. However, the amount of radicals produced by the decomposition of the solvent was not negligible. That is, the radicals shown in Schemes 4 and 5 resulted from the radicals formed from the photoreaction of the vanadium complex and from the photodecomposition of dichloromethane, as shown in Scheme 4 [22].

No difference was detected among the gases produced in the oxidation and reduction stages. However, phosgene gas was formed during the reduction stage, but not during the oxidation stage. Thus, the photodecomposition path, including solvent decomposition, was not the primary pathway in this oscillation reaction.

If hydrogen abstraction was a driving force in the oscillation reaction, significant isotope effects should have been observed. Thus, we carried out the oscillation reaction in deuterated dichloromethane and compared the reaction profiles to those of the original solution. The reaction was initiated with UV irradiation in the presence of the V(IV) complex and benzaldehyde. Although the first oxidation of the V(IV) complex occurred in both solvents, it took longer in deuterated dichloromethane. Although the first oscillation reaction occurred in dichloromethane, the second cycle

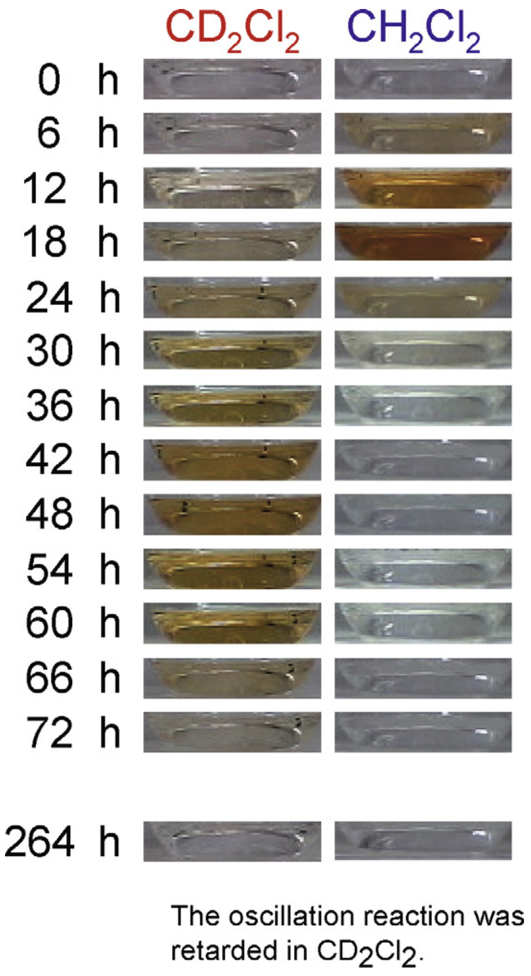


Fig. 13. Deuterium isotope effect on the oscillation reaction.

was blocked in deuterated dichloromethane, and precipitation was observed. A distinct isotope effect was observed in this oscillation reaction, demonstrating the importance of the hydrogen abstraction reaction.

All these results do not exclude the possibility of autocatalytic process or auto-inhibitory process. For example, the $CHCl_2$ radical produced in the reaction course can easily react with molecular oxygen to produce peroxo-radical, which further reacts with dichloromethane to produce the $CHCl_2$ radical again. The clear isotope effect observed in dichloromethane and deuterated dichloromethane showed the importance of the hydrogen atom of dichloromethane in the reaction course. Further studies are necessary to clarify these points (Fig. 13).

4. Conclusion and perspective

The Belousov–Zhabotinsky (BZ) reaction, a well-known oscillation reaction [23,24], includes many components of this oscillation reaction system. Here, the oscillation reaction occurred within several minutes and was finished within 1 h. Severe reaction conditions are required for the BZ oscillation reaction. In contrast, the oscillation reaction reported here contained only the vanadium complex and a dichloromethane solvent. The reaction conditions were mild, and no technical difficulty was present in this system, although the mechanism of the reaction was unclear. Further studies are necessary to clarify the reaction mechanism and to explore the possibility of using this oscillation reaction for molecular sensing probes.

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