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A Vanadium-Based Chemical Oscillator: Identification of Chemical Species Responsible for the Redox Reaction and Construction of a Simplified Model

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Keywords: Oscillation reactions / Vanadium / Redox chemistry / Dichloromethane / Radicals

To identify the chemical species involved in a unique, vanadium-based chemical oscillator reaction, products derived from indole in the oscillation solution were isolated and characterized. NMR and mass spectra showed that 3,3-dichloro-2-oxoindole and isatin were formed during the oscillation process. The formation of these two compounds suggests that peroxo species such as $CHCl_2OO^{\cdot}$ and $CHCl_2OOH$ play a key role in the construction of the oscillation system. A skeletal model for the system is proposed based on these findings.

Introduction

Oscillation phenomena have been a subject of interest in a variety of research fields including physical chemistry,[1,2] materials science,[3] catalysis,[4] and biology.[5,6] Most of the chemical oscillators found so far consist of reductant, oxidant, metal catalyst, acid, and an indicator. Oxidohalogenates such as BrO_3^- are often used as an oxidant. Manganese, cerium, or iron compounds have been used as the metal catalyst, and sulfuric acid is the most commonly employed acid. Oscillation phenomena in general depend on a complicated balance of materials. However, we have recently discovered that oscillating behavior can be observed in simple solutions of certain vanadium compounds, such as $[V^{IV}OCl_2(bpy)]$ or $[V^{III}Cl_3(CH_3CN)(bpy)]$ (bpy: 2,2′-bipyridine), in dichloromethane.[7] The observed color change between pale green and dark orange has been attributed to the V^{IV}/V^{V} redox couple. In this case, the dark orange compound was identified as $[\{V^{V}OCl_2(bpy)\}_2(\mu\text{-}O)]$.[7] Other features of this oscillating system were as follows. First, while the oscillation was aperiodic at constant temperature, a periodic response could be induced by pulsing the temperature of the reaction system. Second, the oscillation system was strongly dependent on the nature of the solvent. Oscillation behavior was observed in dichloromethane but not in other halomethanes. Third, the solution containing the V^{IV} complex exhibited a long induction period that could be significantly reduced by adding benzaldehyde or terephthalaldehyde. Fourth, the oscillation did not occur under anaerobic conditions, indicating that oxygen was indispensable in the oscillation reaction.

The oscillation system described herein is relatively simple. Although vanadium complexes can act as both catalyst and indicator, and atmospheric oxygen could potentially act as an oxidant, one would not expect an oscillation reaction to occur in a solution containing only the vanadium complex. Dichloromethane photochemically decomposes in the presence of a metal catalyst to form several radical species as intermediates, ultimately forming HCl, CO, CO_2, formaldehyde, and phosgene as final products.[8–14] Thus, it is likely that an oscillation system could be self-assembled in situ by employing some of the degradation species of dichloromethane. In this report, we identify the chemical species responsible for the vanadium-based oscillation reaction observed in dichloromethane and construct a simplified mathematical model to simulate the oscillation behavior.

Results and Discussion

One may reasonably assume that some of the degradation products of dichloromethane are involved in the vanadium-based oscillation system in dichloromethane. Many photocatalytic degradation products, shown below, have been proposed for dichloromethane in the presence of a metal catalyst.[8–14]

$$CH_2Cl_2 \xrightarrow{h\nu} {}^{\cdot}Cl + {}^{\cdot}CH_2Cl \quad (1)$$

$${}^{\cdot}Cl + CH_2Cl_2 \rightarrow HCl + {}^{\cdot}CHCl_2 \quad (2)$$

$${}^{\cdot}CH_2Cl + CH_2Cl_2 \rightarrow CH_3Cl + {}^{\cdot}CHCl_2 \quad (3)$$

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$$^{\cdot}CHCl_2 + O_2 \rightarrow CHCl_2OO^{\cdot} \quad (4)$$

$$2\ CHCl_2OO^{\cdot} \rightarrow 2\ CHCl_2O^{\cdot} + O_2 \quad (5)$$

$$CHCl_2O^{\cdot} \rightarrow CHClO + {}^{\cdot}Cl \quad (6)$$

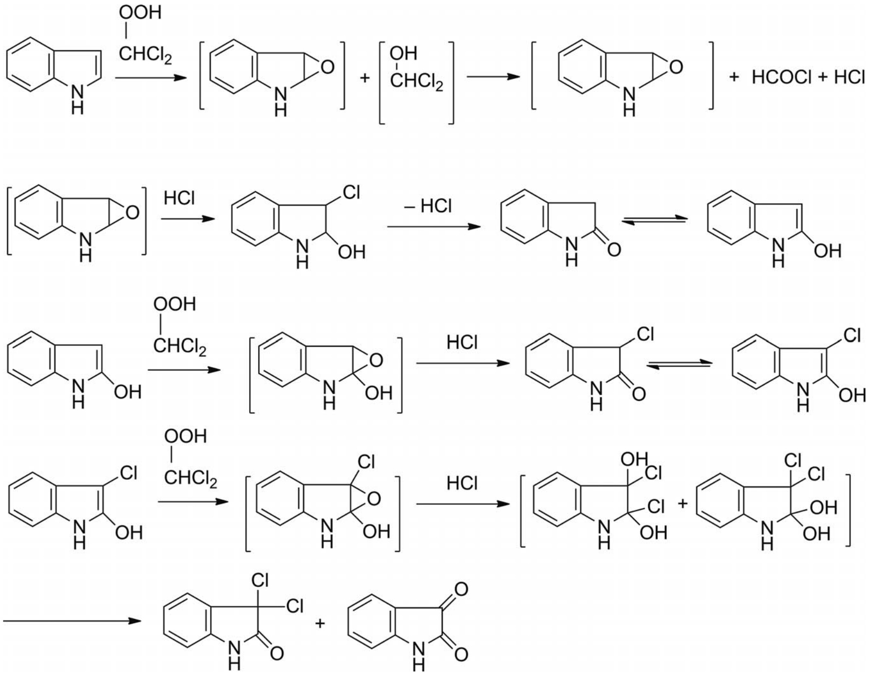
$$CHClO \rightarrow HCl + CO \quad (7)$$

$$CHCl_2OO^{\cdot} + CH_2Cl_2 \rightarrow CHCl_2OOH + {}^{\cdot}CHCl_2 \quad (8)$$

$$2\ CHCl_2OO^{\cdot} \rightarrow CHCl_2OH + CCl_2O + O_2 \quad (9)$$

$$CH_2Cl_2 + H_2O \rightarrow HCHO + 2\ HCl \quad (10)$$

In addition to the above products, phosgene, CCl_4, and CO_2 have also been observed.[10] Since we have found the formation of HCl, CO_2, CO, and phosgene in the oscillation process, the conclusion was made that a similar degradation of dichloromethane must occur at some point during the oscillation reaction.[15] Photoinduced homolytic cleavage of C–Cl bonds in dichloromethane produces $Cl^{\cdot}$ and $^{\cdot}CH_2Cl$ radicals, which then initiate the radical chain reaction as shown above. The buildup of these radical species corresponds to the long induction period observed for the V^{IV} oscillation system.[7] This is consistent with two observations: the oscillation reaction did not occur in the dark, and illumination with UV light significantly shortened the induction period.[15] The induction period was also shortened by the addition of benzaldehyde to the reaction solution or by using the V^{III} complex as a starting material. $PhCO^{\cdot}$ has been proposed to be produced in the oscillatory oxidation of benzaldehyde by air in the presence of a Co^{II} salt.[16] A similar phenomenon would be expected in the present system. The highly reactive V^{III} complex would react smoothly with molecular oxygen, which would then create a superoxide that would lead to the formation of the corresponding V^{IV} complex. Therefore, benzaldehyde and the V^{III} complex reduce the induction period through the formation of $PhCO^{\cdot}$ or $HO_2^{\cdot}$, respectively, which initiates the radical chain reactions that in turn stimulate the buildup of chemical species necessary for the oscillation reaction. This suggests that the stable degradation products of dichloromethane, for example, CO, CO_2, and phosgene, do not contribute to the construction of the oscillation system, which must instead result from the more short-lived radical species. However, it is difficult to identify the radical species responsible for the oscillation behavior directly. Instead, we focused on identifying radical species indirectly by characterizing organic substrates modified by the radical species produced during the oscillation process. Indole was chosen as an organic substrate, because it is moderately reactive toward radical species, and any modifications during the oscillation reaction could be identified relatively easily by NMR spectroscopy. When indole was added to a dichloromethane solution of $[V^{III}Cl_3(CH_3CN)(bpy)]$, the oscillation reaction was completely inhibited, and the induction period lasted for about 1 month. After this long induction period, oscillation behavior was observed as in solutions without indole. This indicates that chemical species required for the oscillation reaction were effectively consumed by indole. The oscillation reaction was able to initiate only after nearly all of the indole molecules had been modified by reactive species in the reaction mixture. Two chemical species were isolated from the reaction mixture after the oscillation reaction had reached completion. Details are given in the Experimental Section. The major and minor species in the reaction residue were 3,3-dichloro-2-oxoindole and isatin (indole-2,3-dione). The compounds were identified by comparing their NMR spectra with those of authentic sam-



Scheme 1. Proposed mechanism for the formation of 3,3-dichloro-2-oxoindole and isatin in the oscillation solution.

ples (see Supporting Information, Figure S1). The ^{1}H NMR spectrum of the reaction mixture (Supporting Information, Figure S2) was dominated by the spectrum of 3,3-dichloro-2-oxoindole, indicating that indole was converted almost quantitatively to 3,3-dichloro-2-oxoindole in the reaction solution. On the other hand, the ^{1}H NMR signals due to isatin were not discerned in the NMR spectrum of the reaction mixture, suggesting that the yield of isatin was very low ($< 10\%$). Scheme 1 shows a probable reaction mechanism, incorporating the degradation products of dichloromethane, for the formation of 3,3-dichloro-2-oxoindole and isatin. The peroxo species are the most likely candidates for the oxidation of indole and would also function as the oxidant in the oscillation reaction [Equations (11) and (12)].

$$\mathrm{CHCl_2OO^{\cdot} + V^{4+} \rightarrow CHCl_2OO^{-} + V^{5+}} \tag{11}$$

$$\mathrm{CHCl_2OOH + V^{4+} \rightarrow V^{5+} + CHCl_2O^{\cdot} + OH^{-}} \tag{12}$$

A similar oxidation reaction has been proposed for the oxidation of $\mathrm{Cu^{I}}$.[8]

Based on the above conclusion, a simplified, theoretical model was constructed to simulate the oscillation behavior. $\mathrm{CHCl_2OO^{\cdot}}$ was employed as the oxidant. A probable reductant could not be identified. Although the proposal has been made that a peroxo species could behave as both the oxidant and reductant,[17] the oscillation reaction could not be reproduced under those conditions in the current model. Therefore, the tentative assumption was that the $\mathrm{V^{V}}$ complex was reduced photochemically with visible light. This assumption is supported by an intense band at 447 nm in the absorption spectrum of the $\mathrm{V^{V}}$ complex,[7] and data that show an enhancement in the reduction of $\mathrm{V^{V}}$ when irradiated with visible light.[15] Upon light irradiation, the decomposition of the $\mathrm{V^{V}}$ complex is followed by the reaction of intermediate species with dichloromethane to yield a single radical species, $\mathrm{CHCl_2^{\cdot}}$, and the reduced $\mathrm{V^{IV}}$ complex [Equation (13)].

$$\mathrm{CH_2Cl_2 + V^{5+} \rightarrow CHCl_2^{\cdot} + H^{+} + V^{4+}} \tag{13}$$

However, the possibility of a chemical reductant cannot be fully excluded. For example, it has been proposed that $\mathrm{PhCO^{\cdot}}$ or $\mathrm{H^{+}}$ may act as an autocatalytic species in the reduction process of $\mathrm{Co^{III}}$ for the oscillatory oxidation of benzaldehyde by air in the presence of a $\mathrm{Co^{II}}$ salt.[16] In this autocatalytic process, HBr or $\mathrm{Br^{-}}$ is assumed to form a bromide complex of $\mathrm{Co^{III}}$ as an intermediate. HBr or $\mathrm{Br^{-}}$ is then reproduced at the end of the autocatalytic sequence. A similar reduction process as shown by Equation (14) may occur in the vanadium system since HCl has been experimentally detected in the reaction mixture by FTIR spectroscopy.

$$\mathrm{V^{5+} + CH_2Cl_2 + CHCl_2^{\cdot} \rightarrow V^{4+} + H^{+} + 2\ CHCl_2^{\cdot}} \tag{14}$$

The oscillatory oxidation of benzaldehyde by air with a $\mathrm{Co^{II}}$ salt has been simulated by a skeletal model consisting of three independent variables [$\mathrm{PhCO^{\cdot}}$, $\mathrm{O_2}$, and $\mathrm{Co^{III}}$] and four steps: (C1) the constant supply of atmospheric oxygen to the system, (C2) the oxidation of $\mathrm{Co^{II}}$ by air, (C3) the reduction of $\mathrm{Co^{III}}$ by benzaldehyde, and (C4) the mildly autocatalytic reduction of $\mathrm{Co^{III}}$ catalyzed by $\mathrm{PhCO^{\cdot}}$.[18] This skeletal model appears to be valid for the vanadium-based oscillator by replacing $\mathrm{PhCO^{\cdot}}$ and $\mathrm{Co^{III}}$ with $\mathrm{CHCl_2^{\cdot}}$ and $\mathrm{V^{V}}$, respectively, since the vanadium-based oscillator may also proceed through steps analogous to C1–C4 as described above.

Note that some of the characteristic features observed in the vanadium oscillator are qualitatively explainable in terms of the skeletal model. First, phosgene production occurs only during the reduction process and not during oxidation. A study proposed that the formation of phosgene results from the dehydration of hydroperoxide, $\mathrm{CHCl_2OOH}$.[15]

In the skeletal model, the hydroperoxide species participates as a reactant and is consumed in step C2. Therefore, the hydroperoxide may not be available for subsequent conversion to phosgene. However, $\mathrm{CHCl_2OOH}$ does not contribute to the reduction in steps C3 and C4, so no small amount may be available for the phosgene production at these points in the reaction. A similar situation arises in the formation of $\mathrm{H^{+}}$ in the skeletal model. The oxidation step C2 consumes $\mathrm{H^{+}}$ as a reactant, while the reduction step C4 yields $\mathrm{H^{+}}$ as a product. This is consistent with experimental observations, which indicate that more HCl evolved during the reduction than during the oxidation.

Based on these data, a tentative mathematical calculation was performed on the skeletal model for the vanadium oscillator. The model used here consists of the following four steps.

$$\mathrm{O_2(g) \rightleftharpoons O_2(soln)} \tag{V1}$$

$$\mathrm{O_2(soln) + CHCl_2^{\cdot} \rightarrow} g\ \mathrm{V^{5+}} \tag{V2}$$

$$\mathrm{V^{5+} \rightarrow CHCl_2^{\cdot}} \tag{V3}$$

$$\mathrm{V^{5+} + CHCl_2^{\cdot} \rightarrow} m\ \mathrm{CHCl_2^{\cdot}} \tag{V4}$$

Equations (V1)–(V4) correspond to the processes C1–C4, respectively. (V1) shows the supply of atmospheric $\mathrm{O_2}$ to the vanadium system. (V2) represents the oxidation of $\mathrm{V^{4+}}$ by $\mathrm{O_2}$ including the Equations (11) and (12). (V3) is deduced from Equation (13) of the reduction of $\mathrm{V^{5+}}$ by dichloromethane. (V4) represents the mild autocatalytic reduction of $\mathrm{V^{5+}}$ by $\mathrm{CHCl_2^{\cdot}}$ such as Equation (14); g and m are the stoichiometric coefficients introduced to the skeleton model to generate oscillation of this simplified model with the three variables and should be greater than unity.[18]

By substituting for the variable concentrations as $A = P_{\mathrm{O2}}$, $X = [\mathrm{CHCl_2^{\cdot}}]$, $Y = [\mathrm{O_2(soln)}]$, and $Z = [\mathrm{V^{5+}}]$, differential equations were derived from (V1)–(V4) as follows.

$$\mathrm{d}X/\mathrm{d}t = -k_2XY + k_3Z - (m - 1)k_4XZ \tag{15}$$

$$\mathrm{d}Y/\mathrm{d}t = k_1A - k_{-1}Y - k_2XY \tag{16}$$

$$\mathrm{d}Z/\mathrm{d}t = gk_2XY - k_3Z - k_4XZ \tag{17}$$

These equations were integrated with the LSODE package by using the Gear methods.[19] Parameter sets were generated from the rate constants k_i and the stoichiometric coefficients g and m. Although the exact values of the parameters for the vanadium oscillator are currently unknown, some of them could be estimated to an order of magnitude from the experimental conditions ($k_1A = 10^{-2}\ \text{M}\,\text{s}^{-1}$ and $Z_0 = 3.4 \times 10^{-4}\ \text{M}$). Other parameters were deduced from literature values[17,18] and considered adjustable parameters to generate sustainable oscillation. These calculations resulted in the solution for sustained oscillatory behavior shown in Figure 1 with representative values of the parameters ($k_{-1} = 1\ \text{s}^{-1}$, $k_2 = 10^4\ \text{M}^{-1}\,\text{s}^{-1}$, $k_3 = 10^{-2}\ \text{s}^{-1}$, $k_4 = 1\ \text{M}^{-1}\,\text{s}^{-1}$, $X_0 = 10^{-7}\ \text{M}$, $Y_0 = 10^{-4}\ \text{M}$, $g = 2$, and $m = 1.1$).

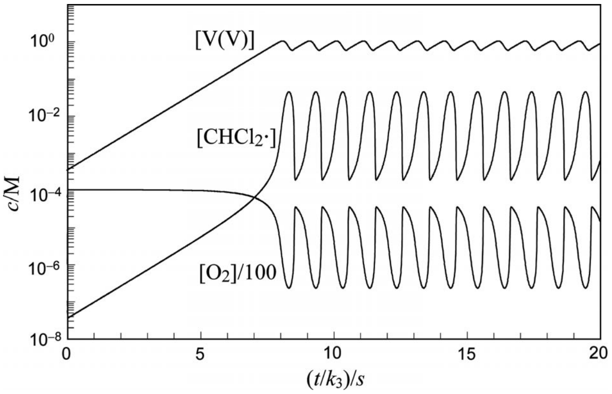


Figure 1. Computed time series shown for the three-variable skeletal model applied to the vanadium oscillator. The values of the rate constants and initial concentrations used were as follows: $k_1A = 10^{-2}\ \text{M}\,\text{s}^{-1}$, $k_{-1} = 1\ \text{s}^{-1}$, $k_2 = 10^4\ \text{M}^{-1}\,\text{s}^{-1}$, $k_3 = 10^{-2}\ \text{s}^{-1}$, $k_4 = 1\ \text{M}^{-1}\,\text{s}^{-1}$, $X_0 = 10^{-7}\ \text{M}$, $Y_0 = 10^{-4}\ \text{M}$, $Z_0 = 3.4 \times 10^{-4}\ \text{M}$.

Conclusions

The result suggests that the mechanism of the vanadium-based oscillator is analogous to that of the benzaldehyde/air/Co^{II} oscillator, although the skeletal model fails to account for some of the experimental observations such as the aperiodic oscillatory behavior, the dependence on the temperature, and the absolute values of the concentrations. Improvements to the skeletal model to better reflect these empirical results are currently under way.

Experimental Section

Characterization of Compounds Modified During the Oscillation Reaction: $[\text{V}^{\text{III}}\text{Cl}_3(\text{CH}_3\text{CN})(\text{bpy})]$ was prepared according to a previously published method.[20] A dichloromethane solution was prepared containing 0.34 mM indole and 0.34 mM vanadium(III) complex in a tightly stoppered Erlenmeyer flask. The resulting solution was stirred at room temperature until the oscillation reaction reached completion (ca. 1.5 months). The solution was concentrated to dryness, and the residue was collected. Dichloromethane (0.5 mL) was added to the residue (0.1 g), and the resulting solution was filtered to remove undissolved material. The filtrate was separated on a silica gel column (length: 30 cm; diameter: 15 cm) by using a mixture of *n*-hexane/ethyl acetate (from 1:0 to 1:1) as the eluent. The crude material separated into two distinct bands (one major and one minor). The compounds obtained from the respective fractions were characterized by NMR and mass spectra.

Measurements: NMR spectra were measured with a JEOL JMN-ECX300 NMR spectrometer by using tetramethylsilane (TMS) as an internal standard. EI and FAB mass spectra were obtained with a JEOL JMS-700V and a JEOL JMS-SX102A mass spectrometer, respectively.

Supporting Information (see footnote on the first page of this article): ^{1}H NMR spectra of the isolated compounds from the reaction mixture (Figure S1) and the spectrum of the reaction mixture (Figure S2).

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[1] F. Sagues, I. R. Epstein, *Dalton Trans.* **2003**, 1201–1217.
[2] R. Toth, A. F. Taylor, *Prog. React. Kin. Mech.* **2006**, *31*, 59–115.
[3] R. Yoshida, *Adv. Mater.* **2010**, *22*, 3463–3483.
[4] V. V. Gorodetskii, V. I. Elokhin, J. W. Bakker, B. E. Nieuwenhuys, *Catal. Today* **2005**, *105*, 183–205.
[5] B. Novak, J. J. Tyson, *Nat. Rev. Mol. Cell Biol.* **2008**, *9*, 981–991.
[6] K. Kruce, F. Juelicher, *Curr. Opin. Cell Biol.* **2005**, *17*, 20–26.
[7] K. Kanamori, Y. Shirosaka, Y. Sakai, T. Kanamori, Y. Mukai, K. Kubo, Y. Nakajima, N. Wada, S. Matsugo, Y. Miyashita, K. Kustin, *Chem. Lett.* **2010**, *39*, 624–626.
[8] K. J. Doyle, H. Tran, M. Baldoni-Olivencia, M. Karabulut, P. E. Hoggard, *Inorg. Chem.* **2008**, *47*, 7029–7034.
[9] L. Sheps, A. C. Crowther, C. G. Elles, F. F. Crim, *J. Phys. Chem. A* **2005**, *109*, 4296–4302.
[10] J. Borisch, S. Pilkenton, M. L. Miller, D. Raftery, J. S. Francisco, *J. Phys. Chem. B* **2004**, *108*, 5640–5646.
[11] L. Pinard, P. Magnoux, P. Ayrault, G. Guisnet, *J. Catal.* **2004**, *221*, 662–665.
[12] V. Catoire, R. Lesclaux, W. F. Schneider, T. J. Wallington, *J. Phys. Chem.* **1996**, *100*, 14356–14371.
[13] E. Sanhueza, J. Heicklen, *J. Phys. Chem.* **1975**, *79*, 7–11.
[14] I. C. Hisatsune, J. Heicklen, *Can. J. Spectrosc.* **1973**, *18*, 77–81.
[15] S. Matsugo, K. Kanamori, *Coord. Chem. Rev.* **2011**, *255*, 2388–2397.
[16] A. J. Colussi, E. Ghibaudi, Z. Yuan, R. M. Noyes, *J. Am. Chem. Soc.* **1990**, *112*, 8660–8670.
[17] C. J. Chang, J. A. Labinger, H. B. Gray, *Inorg. Chem.* **1997**, *36*, 5927–5930.
[18] J. Guslander, R. M. Noyes, A. J. Colussi, *J. Phys. Chem.* **1991**, *95*, 4387–4393.
[19] K. Radhakrishnan, A. C. Hindmarsh, *LLNL report* UCRL-ID-113855, **1993**.
[20] K. Kanamori, Y. Shirosaka, in *ACS Symposium Series 974, Vanadium: The Versatile Metal* (Eds.: K. Kustin, J. Costa Pessoa, D. C. Crans), American Chemical Society, Washington, D.C., **2007**, pp. 424–432.

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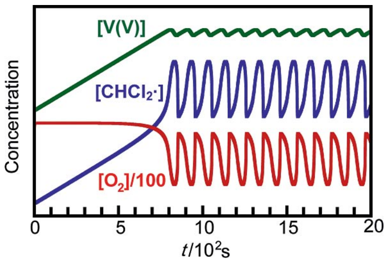
Oscillation Reactions

Products derived from indole in a vanadium-based oscillation solution were identified to be 3,3-dichloro-2-oxoindole and isatin. Peroxo species such as $CHCl_2OO\cdot$ and $CHCl_2OOH$ were found to play a key role in the construction of the chemical oscillation system. A skeletal model for the oscillation reaction is proposed.



K. Kanamori,* H. Kataoka, S. Matsugo **1–5**

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