October, 1988] © *1988 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***61***, *3467—3470 (1988)*

A New Permanganate-Nitrite-Formic Acid-Methanol Oscillator

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(Received June 3, 1988)

Sustained oscillation and birhythmicity have been observed when aqueous solutions of potassium permanganate, potassium nitrite, formic acid, and methanol were mixed in a continuous-flow stirred tank reactor. A detailed phase diagram is shown. This new oscillator is composed of non-halogen compounds and the first example of the nitrogen-based oscillator.

In recent years much attention has been attracted to oscillators in chemical reactions,[1)] and a number of examples of oscillations and related phenomena, e. g., multiple stationary states,[2—4)] simple and complex oscillations,[5,6)] aperiodic oscillation (chaos),[6,7)] and the growth of traveling waves,[8,9)] suggest that these dynamical phenomena are not exceptional but universal behavior sufficiently far from equilibrium. The majority of known oscillators are based on the reactions of oxohalogenate anions, which have been studied mainly by Epstein and co-workers.[10)] Examples are the chlorite-bromate-iodide reaction,[11)] the bromate-iodide reaction,[12)] the arsenite-iodate reaction,[2,3)] and the chlorite-thiosulfate reaction.[6)]

On the other hand, there are some oscillators without oxohalogenate compounds, examples of which are the oxidation of benzaldehyde by oxygen in glacial acetic acid with $CoBr_2$ catalyst,[13)] the oxidation of Methylene Blue by oxygen in a strongly alkaline medium in the presence of sulfite and sulfide,[14)] the oxidation of sulfide ion by hydrogen peroxide in nearly neutral solutions,[15)] the reduction of permanganate by hydrogen peroxide in phosphoric acid,[16)] and the oxidation of oxalate[17,18)] or ninhydrin[19)] by permanganate. Many efforts have been made to find new oscillators, because discovery of a new chemical oscillator brings further understanding of the mechanism of chemical oscillation.

We have checked the reaction mechanisms of known chemical oscillators and noticed that these oscillators are composed of reducing and oxidizing reagents which include atoms with multiple oxidation states available. This suggests a possibility that a new oscillator could be made from reducing and oxidizing reagents suitably selected. Along these considerations, we have found a new halogen-free redox reaction which exhibits oscillatory behavior in a continuous flow stirred tank reactor (CSTR). Permanganate and nitrite ions were selected for the oxidizing and the reducing reagents, respectively, because manganese and nitrogen atoms have multiple oxidation states available. It was found that the addition of formic acid and methanol is needed to produce oscillations. Without them only vague and noisy oscillations with small amplitudes appear. The oscillations were monitored as changes in Pt-electrode potential. To our knowledge, the nitrite-permanganate oscillatory system is the first example of nitrogen-based oscillator. It exhibits not only complex periodic oscillations but also birhythmicity.[12,20,21)]

Experimental

All experiments were carried out in a thermally regulated CSTR with a reaction cell of 9.5 cm^3 volume. Each of stock solutions of $KMnO_4$ (10^{-4}—10^{-2} mol dm^{-3}), KNO_2(10^{-4}—10^{-2} mol dm^{-3}), HCOOH (1.05 mol dm^{-3}) or CH_3OH (1.24 mol dm^{-3}) was prepared by dissolving the highest-purity-grade chemicals (Wako Chemicals) in doubly distilled water. Four syringe pumps (Micro Feeder, Furue Science) were used to feed simultaneously the respective stock solutions into the CSTR at controlled flow rates. In all experiments, the flow rate was set to be equal for the four pumps. The solution in the CSTR was mixed well with a magnetic stirrer at a constant stirring rate. The redox potential of the solution was monitored on an electrometer (Takeda Riken, TR-8651) as a potential difference between a standard Ag/AgCl reference electrode (TOA Electonics) and a platinum electrode. The temperature of the CSTR was kept constant at 25.0±0.1 °C throughout the experiments.

Results and Discussion

The system shows a stable stationary state and an oscillatory state, depending on the feed rate of the reagent solutions. Figure 1 shows typical behavior of the system. In this figure, the reciprocal residence time k_0 is used instead of the feed rate. The value of k_0 was calculated from $k_0=4J/V$, where J is the flow rate of the stock solution and V is the volume of the cell. When k_0 is lower than 6×10^{-3} s^{-1}, the potential difference is low (ca. 250 mV vs. Ag/AgCl). In this case, manganese is mainly in its reduced form (Mn^{2+}) and the solution is colorless in the CSTR. On increasing k_0 beyond 6×10^{-4} s^{-1}, the system enters into an oscillatory region. The amplitude of the oscillations is shown with bars in Fig. 1. With an increase in k_0 from 6×10^{-4} s^{-1} to 2×10^{-3} s^{-1}, the amplitude and the period of oscillations become large. It should be noted that the minimum potential in each cycle is almost constant, but the maximum potential tends to increase gradually. On the contrary, when k_0 increases beyond 2×10^{-3} s^{-1}, the maximum potential is nearly unchanged and the minimum potential increases.

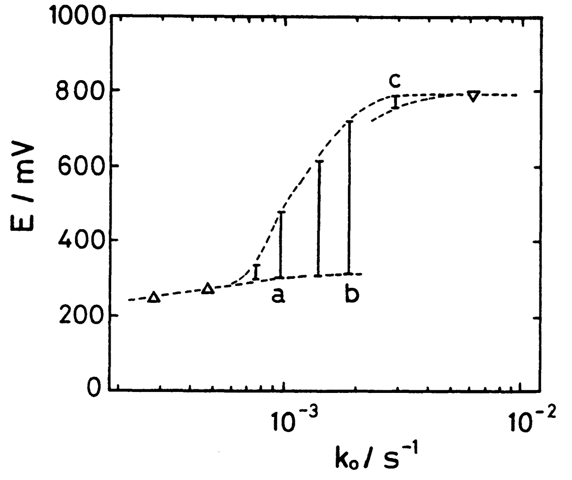

Fig. 1. Plots of the redox potential E vs. the reciprocal residence time k_0. Amplitudes of oscillations are shown with bars. The amplitude varies abruptly at about $k_0=2.3\times10^{-3}\,s^{-1}$. Fixed conditions; $[KMnO_4]_0=6.0\times10^{-4}$ mol·dm^{-3}, $[KNO_2]_0=1.0\times10^{-3}$ mol·dm^{-3}, $[HCOOH]_0=1.05$ mol·dm^{-3}, $[CH_3OH]_0=1.24$ mol·dm^{-3}, and the temperature in the CSTR is 25.0 °C. The notation $[A]_0$ is used to show the concentration of a reagent A in the stock solution hereafter.

Finally the system falls into a stable steady state with a high redox potential (ca. 800 mV) when k_0 reaches $5\times10^{-3}\,s^{-1}$. In this steady state the manganese is in the form of MnO_4^-.

Characteristics of these oscillations is strongly dependent of the experimental conditions such as concentrations of the reagent solutions and k_0. The period of oscillation ranges from 30 s to 15 min, and the amplitude changes from 50 mV to 450 mV. Typical oscillatory traces are shown in Fig. 2. At lower values of k_0, a simple oscillation with a short period is exhibited, as illustrated in Fig. 2(a). Figure 2(b) shows a complicated periodic oscillation consisting of small and large period oscillations. Interestingly, the small period oscillation diminishes as k_0 increases. For example, when $k_0=2\times10^{-3}\,s^{-1}$, a simple oscillation with a large period continues stably, as shown in right-hand part of Fig. 3. At higher values of k_0, the system exhibits a simple high-potential-based oscillation of small amplitude (Fig. 2(c)).

When $k_0=2.3\times10^{-3}\,s^{-1}$, the amplitude of oscillation changes drastically and the presence of birhythmicity is suggested in this region. Detailed experiments show that either of two oscillations having different amplitudes appears depending on the initial state. These results are shown in Fig. 3, where k_0 is $2.3\times10^{-3}\,s^{-1}$. The concentrations of the reagent solutions were the same with those of Fig. 1. Initially, the potential of the Pt electrode oscillates with a small amplitude. At the time denoted by an asterisk in the figure, all the pumps were stopped for a few seconds and then turned on again. The potential then began to oscillate with a

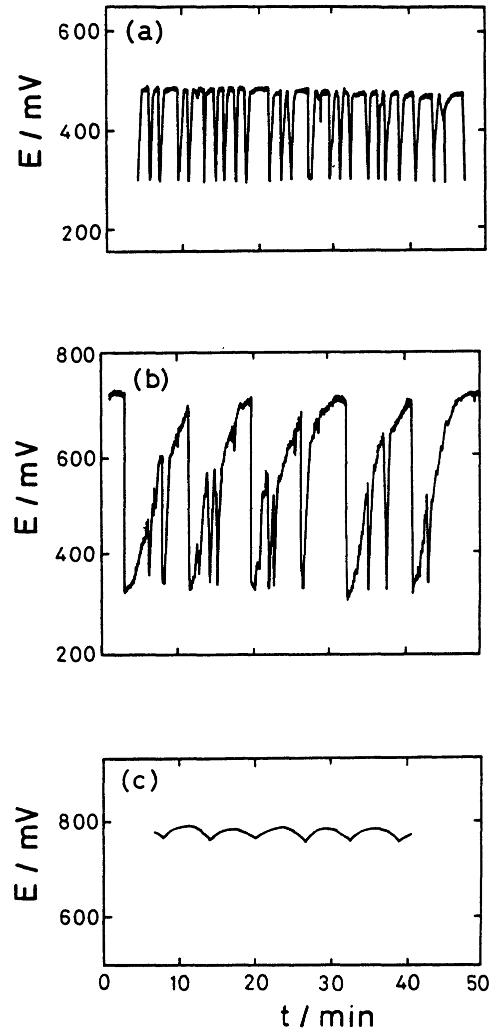

Fig. 2. Modes of oscillations vs. time t at **a**, **b**, and **c** marked in Fig. 1. The reciprocal residence time k_0; (a) $9.6\times10^{-4}\,s^{-1}$, (b) $1.7\times10^{-3}\,s^{-1}$, and (c) $2.9\times10^{-3}\,s^{-1}$.

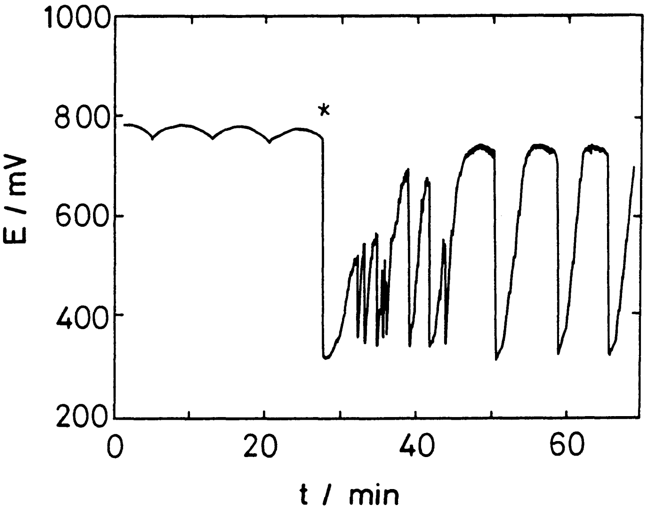

Fig. 3. Birhythmicity observed at $k_0=2.3\times10^{-3}\,s^{-1}$ in Fig. 1: All the pumps were stopped at (*) for a few second. Both two different oscillatory states are stable under the same conditions.

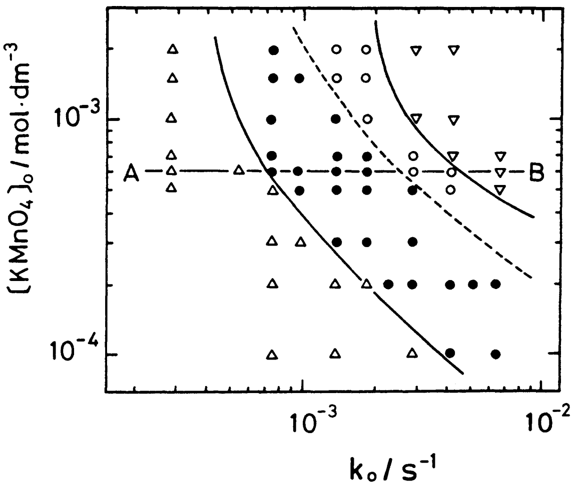

Fig. 4. Phase diagram in the reciprocal residence time k_0-$[KMnO_4]_0$ plane with $[KNO_2]_0=1.0\times10^{-3}$ mol·dm^{-3}, $[HCOOH]_0=1.05$ mol·dm^{-3}, $[CH_3OH]_0=1.24$ mol·dm^{-3}, and the temperature in the CSTR is 25.0 °C. Symbols; (△) lower potential steady state, (▽) higher potential steady state, (●) lower potential-based oscillations, (○) higher potential-based oscillations. Figure 1 shows the behavior of the system along the broken line A-B in this figure.

large amplitude, even though the conditions including the flow rate were exactly the same as before. Thus, this is birhythmicity.

Figure 4 shows a phase diagram of the system obtained by changing the concentration of the stock solution of potassium permanganate and k_0. The concentrations of other stock solutions were fixed. The phase diagram is divided into three regions; a region of oscillation and two regions of stable steady states. In the lower left-hand corner of Fig. 4, the system is in a reduced and stable steady state of lower potential. In the upper right-hand corner, it is in an oxidized and stable steady state of higher potential. Large amplitude oscillations are observed in the center of the oscillatory region. Lower potential-based oscillations are observed in the left part of the oscillatory region, and higher potential-based osillations appear in the right-hand region of the broken line in Fig. 4. In the region around the broken line, the system exhibits birhythmicity.

Without continuous supply of the reagent solutions, no oscillation takes place, probably because permanganate ions are reduced rapidly and an equilibrium state is attained immediately. By introducing constant flow of reactants, the system is kept far from equilibrium and a bifurcation takes place, producing oscillation.

Both manganese and nitrogen atoms have several oxidation states, and it is supposed that there exists a positive feedback mechanism between different oxidation states. According to the literature of inorganic chemistry,[22,23)] we could give an example of the key mechanism of the system by the following process of reactions. In the first stage of the process, permanganate ions are reduced to manganese dioxide by formic acid:

$$2MnO_4^- + 3HCOOH + 2H^+ \rightarrow 2MnO_2 + 3CO_2 + 4H_2O. \quad (R1)$$

The second step is the reduction of manganese dioxide by nitrite ions:

$$MnO_2 + NO_2^- + 2H^+ \rightarrow Mn^{2+} + NO_3^- + H_2O. \quad (R2)$$

At the third step the oxidation of manganous ions by permanganate ions is followed:

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2 + 4H^+. \quad (R3)$$

Then, 3(R2)+(R3) gives

$$3MnO_2 + 2MnO_4^- + 3NO_2^- + 2H^+ \rightarrow 5MnO_2 + 3NO_3^- + H_2O.$$

Therefore, three molucules of MnO_2 yield five molecules of MnO_2 in the process. This autocatalytic process may be the key mechanism of our system, because an autocatalytic reaction plays an essential role in chemical oscillation. Further studies are under way on the detailed mechanism and behavior of this chemical oscillator.

References

1) "Oscillations and Traveling Waves in Chemical Systems," ed by R. J. Field and M. Burger, Wiley, New York (1985).

2) P. De Kepper, I. R. Epstein, and K. Kustin, *J. Am. Chem. Soc.*, **103**, 6121 (1981).

3) G. A. Papsin, A. Hanna, and K. Showalter, *J. Phys. Chem.*, **85**, 2575 (1981).

4) M. Orban and I. R. Epstein, *J. Am. Chem. Soc.*, **104**, 5918 (1982).

5) J. L. Hudson, M. Hart, and D. Marinko, *J. Chem. Phys.*, **67**, 1601 (1979).

6) M. Orban and I. R. Epstein, *J. Phys. Chem.*, **86**, 3907 (1982).

7) J. L. Hudson and J. C. Markin, *J. Chem. Phys.*, **74**, 6171 (1981).

8) A. Hanna, A. Saul, and K. Showalter, *J. Am. Chem. Soc.*, **104**, 3838 (1982).

9) A. T. Winfree and S. H. Strogatz, *Nature(London)*, **311**, 611 (1984).

10) I. R. Epstein, *J. Phys. Chem.*, **88**, 187 (1984).

11) M. Alamgir, P. De Kepper, M. Orban, and I. R. Epstein, *J. Am. Chem. Soc.*, **105**, 2641 (1983).

12) M. Alamgir and I. R. Epstein, *J. Am. Chem. Soc.*, **105**, 2500 (1983).

13) J. H. Jensen, *J. Am. Chem. Soc.*, **105**, 2639 (1983).

14) M. Burger and R. J. Field, *Nature(London)*, **307**, 720 (1984).

15) M. Orban and I. R. Epstein, *J. Am. Chem. Soc.*, **107**, 2302 (1985).

16) A. Nagy and L. Treindl, *Nature(London)*, **320**, 344 (1986).

17) J. S. Reckley and K. Showalter, *J. Am. Chem. Soc.*, **103**, 7012 (1981).

18) N. Ganapathisubramanian, *J. Phys. Chem.*, **92**, 414 (1988).

19) L Treindl and A. Nagy, *Chem. Phys. Lett.*, **138**, 327 (1987).

20) J. C. Roux, *Physica,* **7D**, 57 (1983).

21) P. Lamba and J. L. Hudson, *Chem. Eng. Commun.*, **32**, 369 (1985).

22) W. M. Latimer, "Oxidation Potentials," 2nd ed., Prentice-Hall, N. J., (1952).

23) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed., Wiley, New York (1966).