THE JOURNAL OF
PHYSICAL
CHEMISTRY A

VOLUME 105, NUMBER 31, AUGUST 9, 2001

LETTERS

A Linear Chemical Cycle and Oscillations

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Received: March 29, 2001

We have found that for a simple first-order successive irreversible cyclic reaction, there exist oscillations in time for the concentrations of chemical species for a certain range in the number of reaction steps. If the steps are too small or too large, we do not obtain the oscillations, which has been thought to be the case previously.

In many fields of science, we have found it useful to introduce models based on chemical reactions including physical processes when we discuss macroscopic phenomenological dynamics where thermodynamics ceases to be applied. Chemical oscillations have attracted many scientists' interests recently in connection with nonlinear processes, typically represented by the BZ reaction.[1] For linear (first-order) chemical reactions, we have believed there is no room for finding an oscillation because they are essentially monotonically dissipative so that no restoring force would appear. However, in this letter we show that there exist chemical oscillations in successive cyclic reaction in Figure 1, where the final product is obtained through intermediate stages for which each reaction is first-order (linear). This is due to the fact that the restoring force can occur through the cycle when the number of intermediate stages, N, is appropriate, neither too small nor too large.

Rate equations for reactions in Figure 1 are given by

$$\frac{\mathrm{d}a_j(t)}{\mathrm{d}t} = -(k + k')a_j(t) + ka_{j-1}(t) + k'a_{j+1}(t)$$
$$j = 0, 1, 2,..., N - 1, \text{ with } a_{-1}(t) = a_{N-1}(t) \quad (1)$$

where $a_j(t)$ is the concentration of chemical species A_j at the site j and k and k' are the forward and backward rate coefficients, respectively, as indicated in Figure 1. Although the mathematical solutions for the rate equations (eq 1) have been expressed exactly in various previous studies,[2,3] we write them here for the sake of self-consistency. To this end, it is convenient to employ the generating function, $G(z,t)$, which is defined by the expression

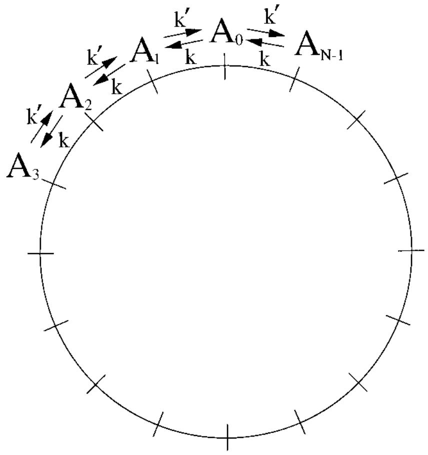

Figure 1. The present model of cyclic irreversible first-order chemical reactions.

$$G(z,t) = \sum_{j=0}^{N-1} z^j a_j(t) \quad (2)$$

On multiplying eq 1 with z^j, summing up and using the cyclic

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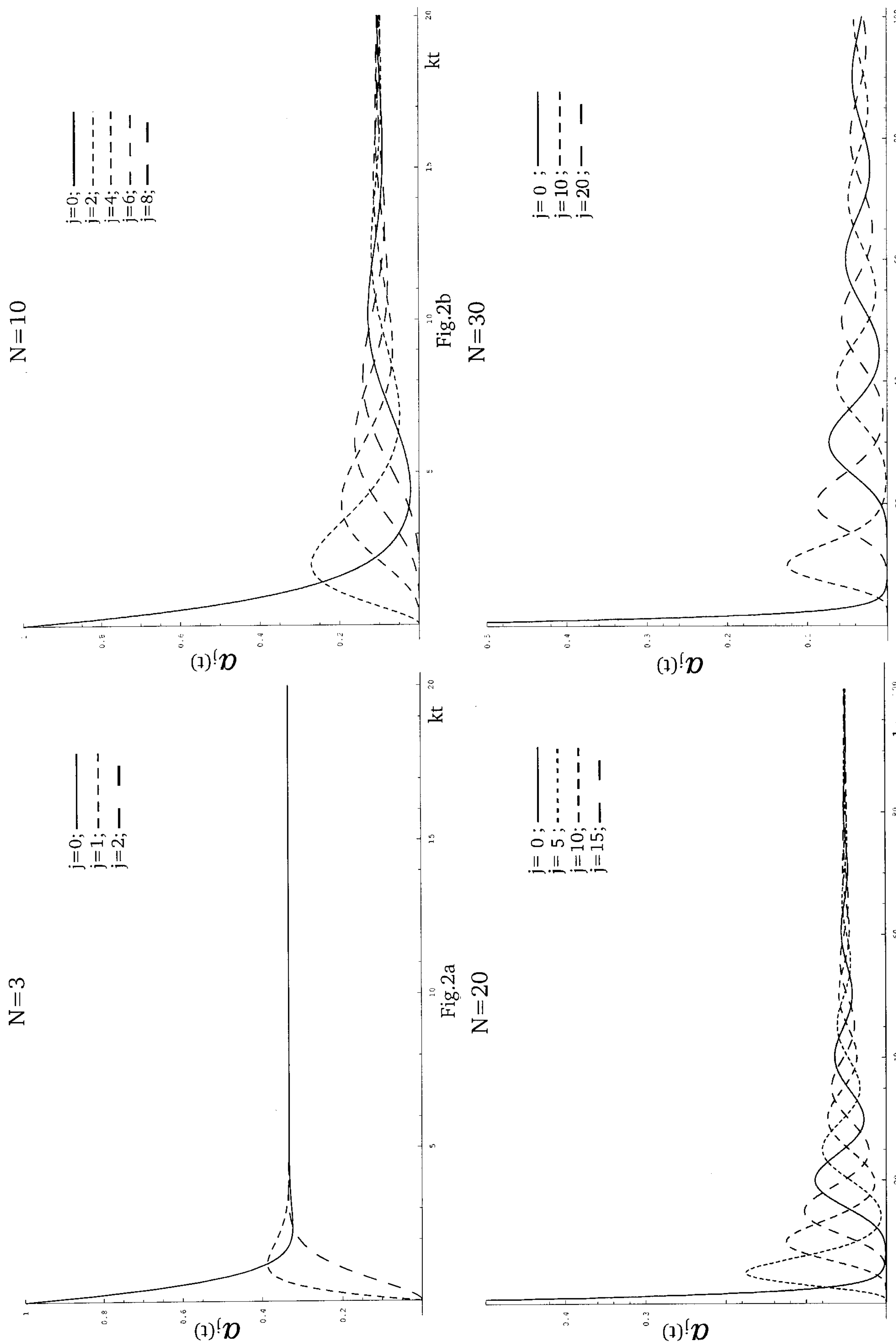

Figure 2. Plots of $a_j(t)$ vs *kt* for small values of *N*.

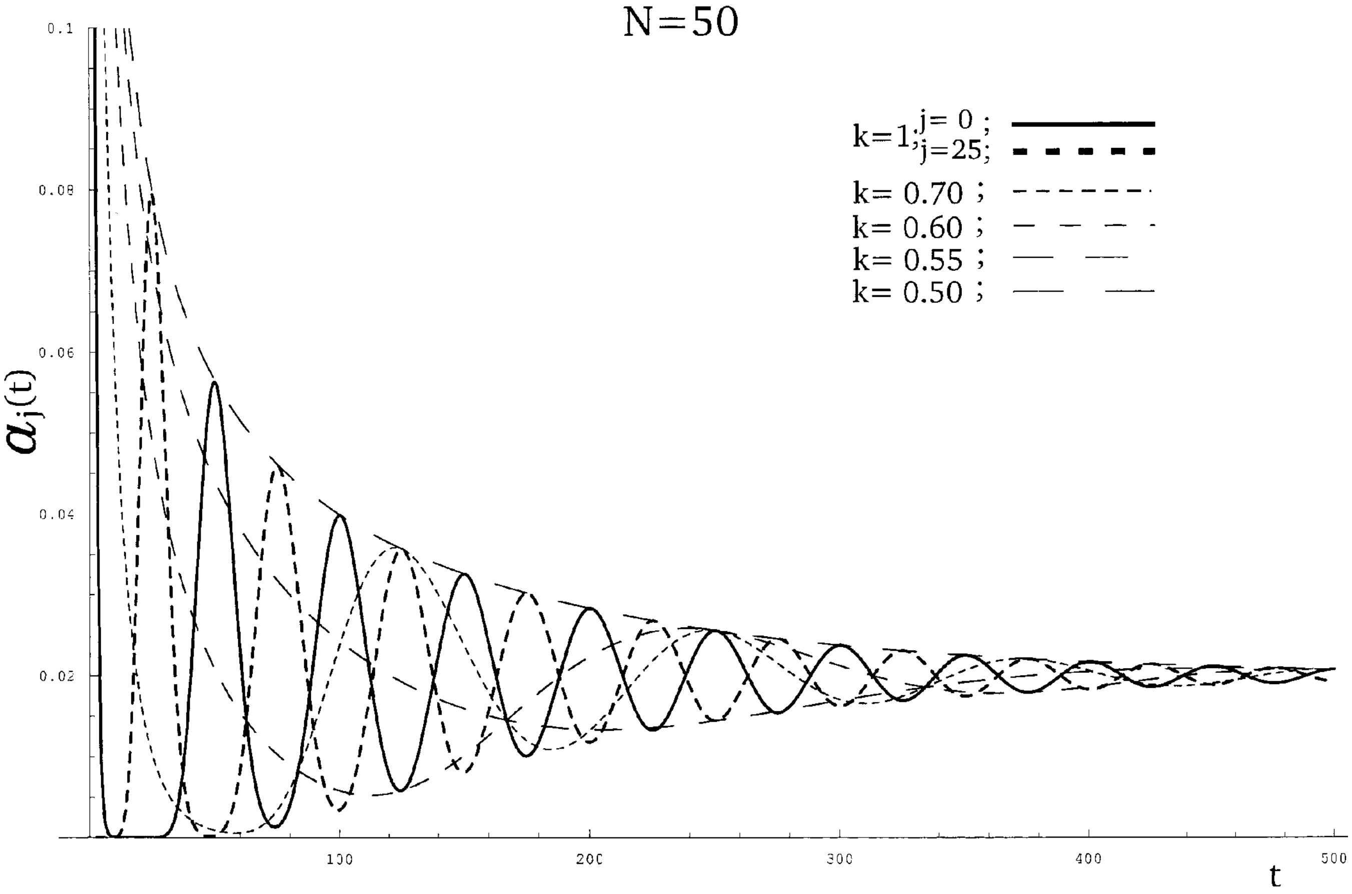

Figure 3. Plots of $a_j(t)$ vs t for $N = 50$, which leads to pronounced oscillations for $k' = 0$ where $j = 0$ and $j = 25$ are shown. When the value of k' increases, the oscillations tend to decay and finally vanish for $k = k' = 0.5$. Here we have assumed $k + k' = 1$.

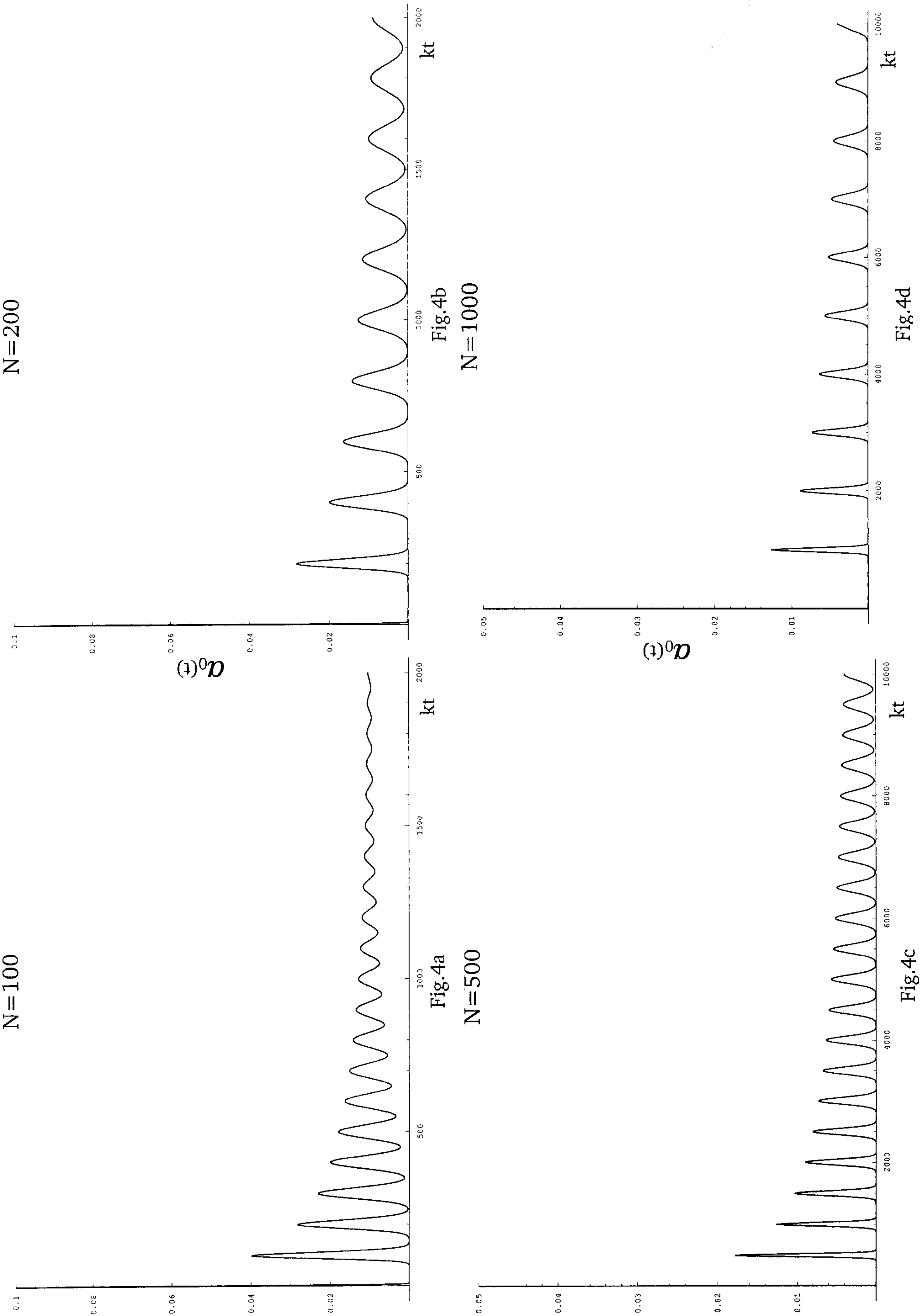

Figure 4. Plots of $a_j(t)$ vs kt for large values of N.

condition, we find that

$$\frac{\partial G(z,t)}{\partial t} = -\,(k + k' - kz - k'z^{-1})G(z,t) + (z^N - 1)[k'z^{-1}a_0(t) - ka_{N-1}(t)] \quad (3)$$

Particularly when $z^N = 1$, namely $z = e^{i2\pi m/N}$, where $m = 0, 1, 2, ..., N - 1$, we can ignore the second term on the right-hand side of eq 3 so that we can write

$$G(m,t) = \sum_{j=0}^{N-1} e^{i2\pi mj/N} a_j(t) = G(m,0) \exp[-\,(k + k' - ke^{i2\pi m/N} - k'e^{-i2\pi m/N})t] \quad (4)$$

where $G(m,0)$ should be determined by the initial values for $a_j(0)$. At this stage, we note the relation

$$\sum_{m=0}^{N-1} e^{i2\pi mM/N} = \begin{cases} N & \text{for } M = 0, \pm N, \pm 2N, ... \\ 0 & \text{otherwise} \end{cases} \quad (5)$$

On using this relation and summing up with respect to m after multiplying eq 4 with $e^{-i2\pi mL/N}$, we find that

$$a_L(t) = \frac{1}{N}\sum_{m=0}^{N-1} e^{-i2\pi mL/N} G(m,0) \exp[-\,(k + k' - ke^{i2\pi m/N} - k'e^{-i2\pi m/N})t] \qquad L = 0, 1, 2, ..., N - 1 \quad (6)$$

This is a general expression for $a_L(t)$, but here for the sake of simplicity, we shall confine ourselves to the particular case of $a_0(0) = 1$ and $a_j(0) = 0$ for $j = 1, 2, 3, ..., N - 1$, where $G(m,0) = 1$ so that

$$a_L(t) = (k/k')^{L/2} \sum_{n=-\infty}^{\infty} (k/k')^{nN/2} I_{L+nN}(2t\sqrt{kk'})$$

in which $I_n(z)$ is the modified Bessel function.

In Figures 2−4, we have plotted $a_j(t)$ in eq 6 after putting $L = j$. In Figure 2, we have shown how oscillations may begin with small values of N for the case of $k' = 0$. For $N = 50$, the oscillation is strongly pronounced for the case of $k = 1$ and $k' = 0$, which can be seen from Figure 3, where $k + k' = 1$ has been assumed. Moreover, we see that the larger k' is, the weaker the oscillation becomes where the presence of the reverse reaction hinders it. As N becomes still larger, it tends to vanish, a behavior seen in Figure 4 in the case of $k' = 0$, where it should be noted that scales in abscissas and ordinates are different. The oscillations arise from the cyclic boundary condition for the reaction so that they would be dependent upon N. For reversible reactions with the cyclic boundary, the oscillation becomes weak due to the fact that each site plays a role of a sink which absorbs reactants or products so that it no longer releases it to the cycle of the reaction. Further studies on this chemical reaction will be published elsewhere. Since the present chemical reactions are so fundamental for considering elemental steps including physical processes, we hope the oscillations will be confirmed experimentally.

References and Notes

(1) Gray, P.; Scott, S. K. *Chemical Oscillations and Instabilities - Non-linear Chemical Kinetics*; Clarendon Press: Oxford, 1990.

(2) van Kampen, N. G. *Stochastic Processes in Physics and Chemistry*, North-Holland: Amsterdam, 1981.

(3) Karlin, S. *A First Course in Stochastic Processes*; Academic Press: New York, 1966.