J. Phys. Chem. A **2008,** *112,* 12007–12012010 **12007**

Temperature-Induced Route to Chaos in the $H_2O_2-HSO_3^--S_2O_3^{2-}$ Flow Reaction System

Gyula Rábai,* Tibor G. Szántó, and Klára Kovács

Institute of Physical Chemistry, University of Debrecen, P.O. Box 7, H-4010 Debrecen, Hungary

Received: June 23, 2008; Revised Manuscript Received: October 1, 2008

Low-frequency, high-amplitude pH-oscillations observed experimentally in the $H_2O_2-HSO_3^--S_2O_3^{2-}$ flow reaction system at 21.0 °C undergo period-doubling cascades to chemical chaos upon decreasing the temperature to 19.0 °C in small steps. Period-4 oscillations are observed at 20.0 °C and can be calculated on the basis of a simple model. A reverse transition from chaos to high-frequency limit cycle oscillations is also observable in the reaction system upon decreasing further the temperature step by step to 15.0 °C. Period-2 oscillations are measured at 18.0 °C. Such a temperature-change-induced transition between periodic and chaotic oscillatory states can be understood by taking into account the different effects of temperature on the rates of composite reactions in the oscillatory system. Small differences in the activation energies of the composite reactions are responsible for the observed transitions. Temperature-change-induced period doubling is suggested as a simple tool for determining whether an experimentally observed random behavior in chemical systems is of deterministic origin or due to experimental noise.

Introduction

Aside from the chaotic dynamical behavior reported by Olsen and Degn[1] on the horseradish peroxidase reaction as early as 1977, the first experimental observations of chemical chaos were confined to the bromate oscillators.[2−5] Later several other homogeneous chemical reaction systems have also been shown to exhibit this peculiar phenomenon in aqueous solutions when they were run in a continuous-flow stirred tank reactor (CSTR).[6−9] Chaotic behavior has also been observed in the gas-phase reaction between oxygen and carbon monoxide.[10,11] After considerable controversy over whether true chaos existed in homogeneous chemical systems or if the observed phenomena are caused by random, unintentional perturbation of the experimental system, the question seems to be settled now. The above listed experimental examples, results of modeling, and theoretical considerations confirm that chaos is a genuine property of some chemical systems. However, even nowadays, not all the experimental observations of chaotic-like behavior are proved to be true chaos in chemical reactions. It is therefore desired to be able to distinguish between chaos of deterministic origin and random responses caused by small unintentional perturbations in experimental parameters. For example, one should demonstrate experimentally several states in a period-doubling or period-adding sequence before one can say that the observed behavior is true chaos. It is obviously important to find well-defined and easily controlled experimental constraints, variation of which allows us to see a route (for example, period-doubling sequence) leading to chaos in the studied system. In most cases, flow rate in the CSTR mode or some of the reagent concentrations are used successfully as a variable control parameter for this purpose. In a peculiar example, light illumination was also used as a control parameter to see a light-induced route to chaos from limited cycle oscillations in a photosensitive system.[12] Here we propose the use of temperature as a control parameter for bringing about the period-doubling route in a chaotic chemical system. The advantage of using temperature as a control parameter in studying chaotic chemical systems is obvious, because of the possibility to measure and control it very precisely in a simple way. Usually the behavior of oscillatory systems is very sensitive to the change in temperature. For example, different modes of oscillations as a function of temperature are observed in the chlorite−thiosulfate reaction in a CSTR.[6] A change in the temperature of only 4 °C (in the range of 22−26 °C) causes the system to go from large amplitude peaks through complex periods consisting of small and large peaks to simple small amplitude oscillations.

TABLE 1: Rate Laws and Rate Constants for Reaction *M1*−*M7* as Given in Ref 13

rate law	rate constants, k_i^a
$v_1 = k_1[H_2O_2][S_2O_3^{2-}]$	see Figure *3*
$v_2 = k_2[H_2O_2][HOS_2O_3^-]$	$k_2 = 0.010$
$v_3 = k_3[S_2O_3^{2-}][S_2O_3]$	$k_3 = 5.0$
$v_4 = k_4[H_2O]$	$k_4[H_2O] = 1.0 \times 10^{-3}$ M s^{-1}
$v_{-4} = k_{-4}[H^+][OH^-]$	$k_{-4} = 1.0 \times 10^{11}$
$v_5 = k_5[H_2O_2][HSO_3^-]$	$k_5 = 4.0$
$v_5' = k_5'[H_2O_2][HSO_3^-][H^+]$	$k_5' = 1.0 \times 10^7$ M^{-2} s^{-1}
$v_6 = k_6[HSO_3^-]$	$k_6 = 3.0 \times 10^3$ s^{-1}
$v_{-6} = k_{-6}[SO_3^{2-}][H^+]$	$k_{-6} = 5.0 \times 10^{10}$
$v_7 = k_7[HOS_2O_3^-][H^+]$	$k_7 = 1.0 \times 10^3$
$v_{-7} = k_{-7}[S_2O_3]$	$k_{-7} = 0.020$ s^{-1}

[a] In M^{-1} s^{-1} unless otherwise indicated.

It has recently been shown that simultaneous oxidations of HSO_3^- and $S_2O_3^{2-}$ with hydrogen peroxide in a CSTR exhibit both periodic and chaotic temporal pH-oscillations with large amplitude under optimized conditions.[13] The main composite processes of this system appear to be reactions 1−3.

$$H^+ + SO_3^{2-} \leftrightarrow HSO_3^- \tag{1}$$

$$H_2O_2 + HSO_3^- + H^+ \rightarrow SO_4^{2-} + H_2O + 2H^+ \tag{2}$$

$$H_2O_2 + 2S_2O_3^{2-} + 2H^+ \rightarrow S_4O_6^{2-} + 2H_2O \tag{3}$$

The autocatalytic formation of H^+ in reaction 2 provides the necessary positive feedback, while reaction 3 consumes H^+, serving as a negative feedback for this pH-regulated oscillator.

---

* Corresponding author. E-mail: rabaigy@tigris.klte.hu.

10.1021/jp805509b CCC: $40.75

Equilibrium 1 controls the accumulation of the free H^+, separating the positive and negative feedbacks from each other in time. A more detailed mechanism (reactions M1−M7) is also known that can account for both regular oscillations, period-2 (P2), period-3 (P3), and chaos in calculations.[13]

$$H_2O_2 + S_2O_3^{2-} \rightarrow HOS_2O_3^{-} + OH^{-} \tag{M1}$$

$$H_2O_2 + HOS_2O_3^{-} \rightarrow 2HSO_3^{-} + H^{+} \tag{M2}$$

$$S_2O_3^{2-} + S_2O_3 \rightarrow S_4O_6^{2-} \tag{M3}$$

$$H_2O \rightarrow H^{+} + OH^{-} \tag{M4}$$

$$H_2O_2 + HSO_3^{-} \rightarrow SO_4^{2-} + H_2O + H^{+} \tag{M5}$$

$$H_2O_2 + HSO_3^{-} \rightarrow SO_4^{2-} + H_2O + 2H^{+} \tag{M5′}$$

$$HSO_3^{-} \leftrightarrow H^{+} + SO_3^{2-} \tag{M6}$$

$$HOS_2O_3^{-} + H^{+} \leftrightarrow S_2O_3 + H_2O \tag{M7}$$

Here we have made just a small modification on the reported scheme and accepted all the rate laws and rate constant values (Table 1) reported in an earlier paper.[13] The only difference between the present scheme and the earlier one is that here the oxidation of HSO_3^- by H_2O_2 is written in two separate reactions (M5, M5′) and is taken into account with two simple rate laws (v_5, v_5'). In the earlier model, a complex rate law was used for this composite process.

It has been found experimentally and could be calculated on the basis of reactions M1−M7 that the period-doubling transition from limit cycle periodic oscillations to chaos could simply be achieved by changing the flow rate or one of the input reagent concentrations.[13]

The effect of temperature on the dynamical behavior in this chemical system is very complex.[14] On the one hand, in a wide range of the experimental conditions, both the amplitude and period length of these oscillations depend strongly on temperature. On the other hand, however, a narrow range of conditions can be found in which temperature compensation exists in this oscillatory system.[13] Temperature compensation means that the period length of oscillations is independent of temperature in a certain temperature range. An interesting question arises whether transition between oscillatory and chaotic states can be brought about in this system by changing the temperature step by step. In order to answer this question, we have carried out systematic experiments in CSTR configuration at different temperatures. We report here on the results of our experiments and model calculations.

Experimental Section

In our experiments, we used a water-jacketed, cylindrical-shaped, glass CSTR with a liquid volume of 20.0 cm^3. Temperature-controlled water was circulated in the jacket from a Haake DC10 thermostat. The reactor was equipped with a pH electrode and a thermistor to measure both the pH and the temperature inside the reactor. A Teflon-covered magnetic stirrer bar (1.5 cm long) was used to ensure uniform mixing at about 600 rpm. Two input solutions were prepared daily with deoxygenated distilled water: One solution contained $Na_2S_2O_3$, Na_2SO_3, and H_2SO_4 together ($pH_0 = 7.8$), while the other contained H_2O_2 ($pH_0 = 6.8$) alone. Both input solutions were kept from air to avoid any effect of O_2 and air-CO_2. The reactor was fed with the prethermostated input solutions by means of a peristaltic pump (Gilson). Excess liquid was removed with the same pump through inversely connected tubing. The temporal course of the reaction was followed by measuring the change in the pH. pH−time data were collected and analyzed by a computer. Because of the slow flow rate, a long time was needed for the CSTR to reach the characteristic state. For this reason, we started to collect pH−time data not earlier than after a 4-h run.

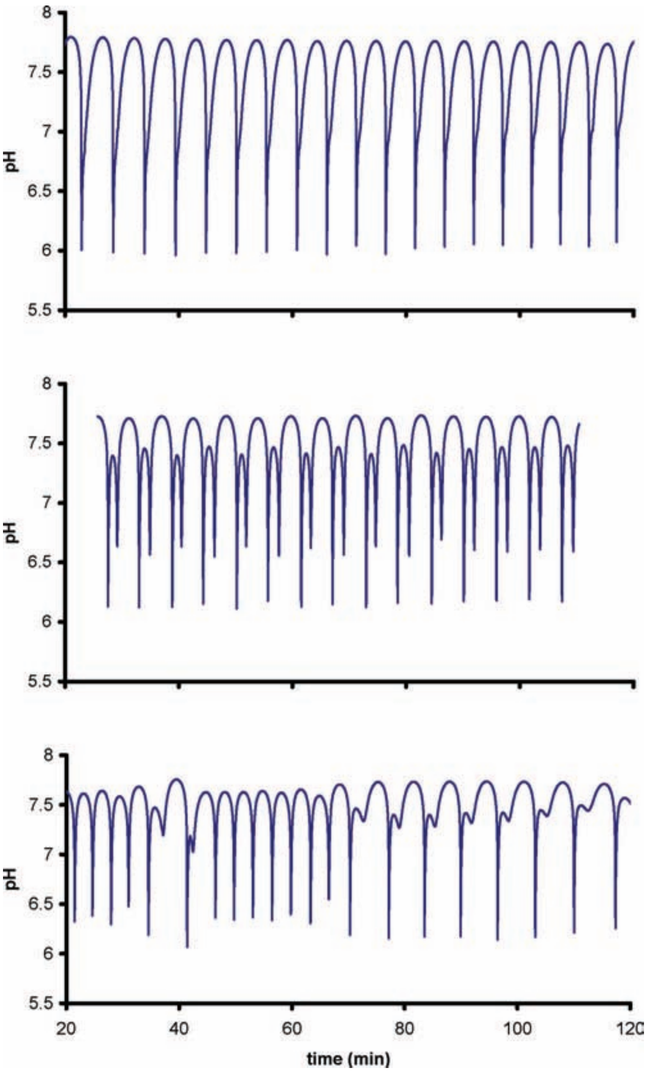

Figure 1. pH−time series measured in a CSTR at different temperatures. $[Na_2SO_3]_0 = 0.00250$ M, $[Na_2S_2O_3]_0 = 0.0040$ M, $[H_2SO_4]_0 = 3.50 \times 10^{-4}$ M, $[H_2O_2]_0 = 0.010$ M, $k_0 = 3.93 \times 10^{-4}$ s^{-1}. Observe the temperature-change-induced transition from low-frequency regular oscillations to chaos. $T = 21.0$ °C (top, regular P1 oscillations), 20.0 °C (middle, P4 oscillations with some transition to P2), 19.0 °C (bottom, chaos). Data collection started after a 4-h run in each case.

First, the experimental conditions for the oscillatory behavior were optimized to study the effect of temperature. Large-amplitude oscillations in the pH could be observed in a rather wide range of input concentrations. However, some critical concentration ratio had to be adjusted. It was necessary to use $[H_2O_2]_0$ in excess over the sum of sulfite and thiosulfate concentrations. It was also important to keep $[H^+]_0$ lower than $[S_2O_3^{2-}]_0$. The following input concentrations were found to be the most appropriate for the study the effect of temperature and were used in our further experiments: $[Na_2SO_3]_0 = 0.00250$ M, $[Na_2S_2O_3]_0 = 0.0040$ M, $[H_2SO_4]_0 = 3.50 \times 10^{-4}$ M, $[H_2O_2]_0 = 0.010$ M. The flow rate was $k_0 = 3.93 \times 10^{-4}$ s^{-1}.

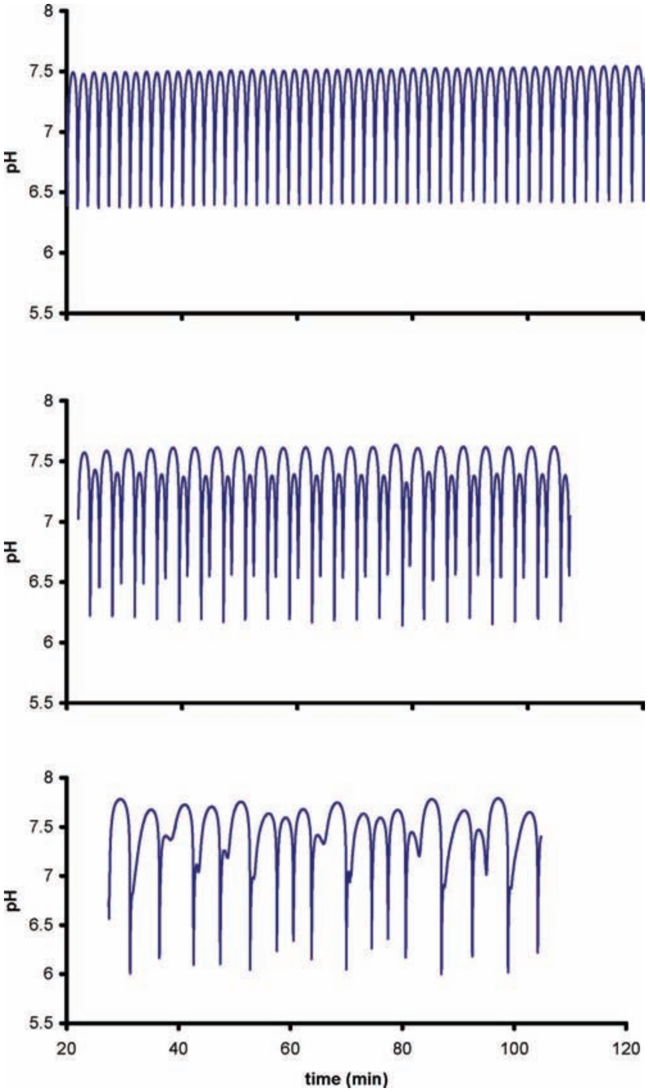

Figure 2. pH−time series at different temperatures from high-frequency regular oscillations to chaos in a CSTR. Experimental conditions are the same as in Figure 1, but $T = 15.0$ °C (top, regular oscillations), 18.0 °C (middle, P2 oscillations), and 19.0 °C (bottom, chaos). Data collection started in the CSTR after a 4-h run.

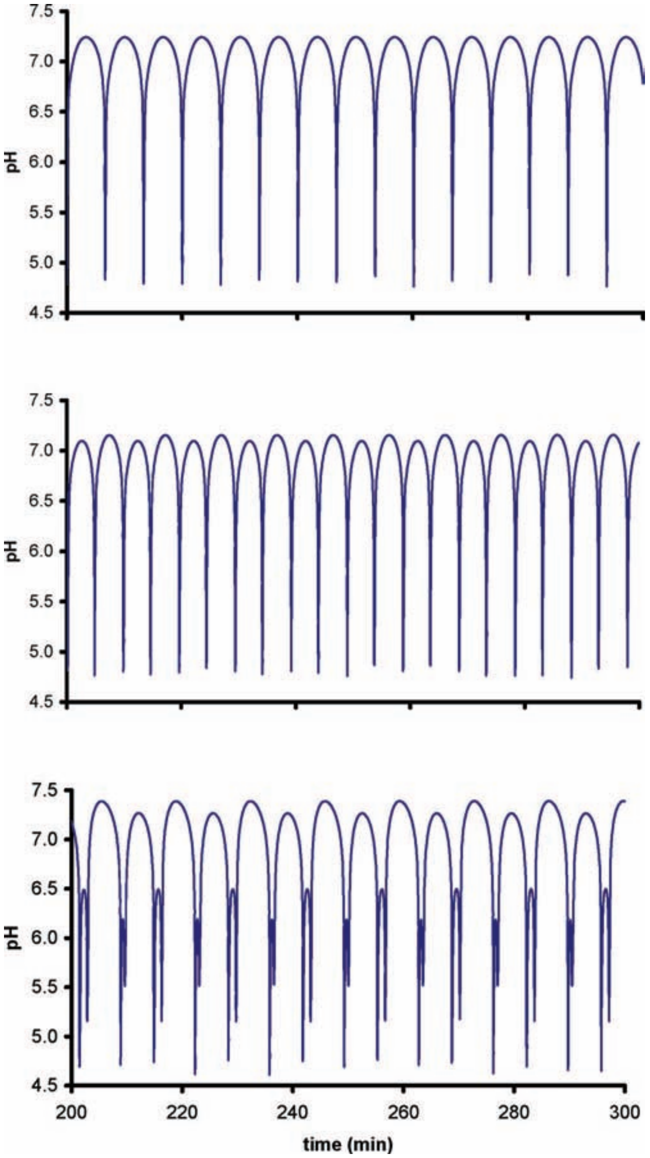

Figure 3. Calculated pH−time series. Calculations are based on reactions M1−M7 and rate constants shown in Table 1, but $k_1 = 0.015$ (top P1 oscillations), 0.0132 (middle, P2 oscillations), and 0.012 (bottom, P4 oscillations) $M^{-1}s^{-1}$.

Results and Discussion

Our systematic investigations have revealed that temperature-change-induced period-doubling route from simple low-frequency pH-oscillations to chemical chaos and a reverse transition from chaos to high-frequency oscillations are observable in this chemical system. Shown in Figure 1 are typical pH−time series measured at different temperatures. One can observe that the dynamical behavior appears to be very sensitive to any small changes in temperature. A change of several tenths of a degree may cause striking alteration in the behavior. Low-frequency, high-amplitude oscillations could be measured at $T = 21.0$ °C (top curve in Figure 1). The system exhibits period-2 oscillations at 20.4 °C (not shown in Figure 1), period-4 oscillations at 20.0 °C (middle curve in Figure 1), and chaotic behavior at 19.0 °C (bottom curve in Figure 1). Note that period-4 cannot be sustained for a long time.

Spontaneous transitions from P4 to P2 or chaos cannot be avoided during a run. Such a transition from P4 to P2 can be seen in Figure 1, where P4 type oscillations are seen in the early stage and then the pattern becomes P2. Later, P2 shifted back to P4. Such transitions were observed in our experiments many times, although special care was taken in order to keep experimental conditions constant.

Chaos can be approached from the other direction, as well. Shown in Figure 2 is a transition from high-frequency regular oscillation observed at 15.0 °C (top curve) through period-2 oscillations at 18.0 °C (middle curve) to chaotic series at 19.0 °C (bottom curve). Reproducibility of the observed transitions is rather good, but in repeated experiments some small shift can occur in the temperature range under which the described dynamical behavior and transitions can be found. Both input solutions and the reacting mixture should be kept from air-oxygen and carbon dioxide very carefully, because O_2 oxidizes HSO_3^- rather fast and CO_2 alters the pH of the reaction system.

The period-doubling route found in our experiments when we used temperature change as a control parameter confirms an earlier finding that this behavior is true chemical chaos. Some further analysis of the chaotic curves was carried out on the base of 18 000 measured time−pH pairs of data to obtain more evidence that the observed irregular oscillation is of deterministic origin and not due to some unnoticed random perturbation of the reactor. A well-defined cap-shaped next return map had been obtained when the pH of a maximum was delineated as a function of the pH of the previous maximum. Such a next return map and other data analysis also support that the chaos is of deterministic origin in this system.

We attempted to simulate the peculiar effect of temperature on the dynamical behavior of the system taking into account scheme M1−M7 and the rate constant values given in Table 1 according to the literature.[12,13] Obviously, increasing temperature increases the rate of all the composite reactions according to their activation energies. However, composite reactions cannot be studied separately, which means that their activation energies can only be estimated. Simulations show that the system behavior is very sensitive to the change in the rate constant of composite reaction M1 so that P1, P2, P3 periodic oscillations and chaos could be simulated if the rate of reaction M1 was changed step by step according to an estimated activation energy value of 56 kJ mol^{-1}, while all the other rates were kept constant.

Shown in Figure 3 are typical calculated pH−time series of different type. P1 oscillations could be calculated in a rather wide range of k_1 value (0.014−0.22 M^{-1} s^{-1}). P2 periods were calculated with $k_1 = 0.0132$ M^{-1} s^{-1}. The minima in the plot seemingly do not appear to be following a P2 sequence. However, this is due to the too few data points collected during calculations. In order to avoid too big data files, we have limited the program to collect the pH−time data in each second for plotting. In such a way, the very sharp pH-minima cannot be represented precisely. When 100 times more data points were collected in the simulation, the minima strictly followed the P2 sequence. However, in this later case, the data file was very big, which was difficult to handle. P4 oscillations were obtained with $k_1 = 0.012$ M^{-1} s^{-1}. However, we cannot obtain P8 oscillations in our calculations.

Similar transitions can be calculated by changing the rate of M2, while other rate constants were kept constant. At $k_2 = 0.010$ M^{-1} s^{-1} P1 oscillations, at $k_2 = 0.0112$ M^{-1} s^{-1} P2 oscillations, and $k_2 = 0.0117$ M^{-1} s^{-1} P4 oscillation could be calculated. Small changes in the values of rate constants of reactions M3−M7 do not affect significantly the characteristic of oscillations. It is interesting that an increase in the value of the rate constant of reaction M5′ increases the length of the period, which is just the opposite of the normal effect of the rate increase on period length. This peculiarity of the temperature effect on a composite reaction of an oscillatory system is the key to the temperature-compensation reported earlier.[13]

Finally, it is worth mentioning that such a unique temperature response found in our present study may open the way for controlling the chaotic behavior in chemical systems by small changes in controlled temperature. The slow response of the behavior to the temperature change might be a drawback for such a use. Further study is now under way in our laboratory.

Acknowledgment. Financial support was obtained from the Hungarian Science Foundation (OTKA 46325).

References and Notes

(1) Olsen, L.; Degn, H. *Nature (London)* **1977**, *267*, 177–8.

(2) Schmitz, R. A.; Graziani, K. R.; Hudson, J. L. *J. Phys. Chem.* **1977**, *67*, 3040–4.

(3) Vidal, C.; Roux, J. C.; Bachelart, S. C. R. *Acad. Sci. Paris, Ser. C* **1979**, *289*, 73–6.

(4) Vidal, C.; Roux, J. C.; BachelartS.; Rossi, A. *Ann. N.Y. Acad. Sci.* **1980**, *357*, 377–96.

(5) Turner, J. S.; Roux, J. C.; McCormick, W. D.; Swinney, H. L. *Phys. Lett. A* **1981**, *85*, 9–12.

(6) Orbán, M.; Epstein, I. R. *J. Phys. Chem.* **1982**, *86*, 3907–10.

(7) Maselko, J.; Alamgir, M.; Epstein, I. R. *Physica D* **1986**, *19*, 153–61.

(8) Alamgir, M.; Epstein, I. R. *Int. J. Chem. Kinet.* **1985**, *17*, 429–39.

(9) Rabai, G. *J. Phys. Chem. A* **1997**, *101*, 7085–89.

(10) Johnson, B. R.; Scott, S. K. *J. Chem. Soc. Faraday Trans.* **1990**, *86*, 3701–05.

(11) Johnson, B. R.; Griffiths, J. F.; Scott, S. K. *Chaos* **1991**, *1*, 387–95.

(12) Rabai, G.; Hanazaki, I. *J. Am. Chem. Soc.* **1997**, *119*, 1458–59.

(13) Rabai, G.; Hanazaki, I. *J. Phys. Chem. A* **1999**, *103*, 7268–73.

(14) Kovacs, K.; Rabai, G. *Phys. Chem. Chem. Phys.* **2002**, *4*, 5265–69.

JP805509B