

the same nature as that of ammonia with only a slightly stronger bond formed as a result of the substituent methyl group.

2. Preferential dehydrogenation is observed relative to C-N bond cleavage. Approximately ~70% of the irreversibly adsorbed methylamine dehydrogenates completely to surface cyano, μ_3 - η^2 -CN, with $\nu(\text{CN}) = 1660 \text{ cm}^{-1}$.

3. Activation of C-H bonds is more facile than that of N-H bonds, as judged by the isolation of η^1 -(C)-HCNH₂ and μ -CNH₂ intermediates.

4. No desorption products other than reversibly adsorbed methylamine are observed to retain the CN bond, and the surface cyano is stable to 450 K at which point it begins to decompose to carbon and nitrogen adatoms.

5. A mechanism for amine disproportionation and amination of aliphatic alcohols is proposed that involves the secondary aminocarbene, η^1 -(C)-HCNH₂, stable on this surface under these ultrahigh vacuum conditions between 300 and 330 K.

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Registry No. CH₃NH₂, 74-89-5; Bu, 7440-18-8; H₂CNH₂, 10507-29-6; CH, 3315-37-5; H, 12385-13-6; N₂, 7727-37-9; C, 7440-44-0; HCNH₂, 35430-17-2; CNH₂, 84654-89-7; NH₃, 7664-41-7; NH, 13774-92-0.

Long-Lived Oscillations in the Chlorite-Iodide-Malonic Acid Reaction in Batch

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Abstract: The title reaction is the subject of current interest because the first experimental Turing patterns were observed recently in this system. Here we report the first observation of oscillations that are long-lived (over 1 h) in this system in a batch reactor; even after cessation the oscillations can be restarted several times by adding ClO₂ to the exhausted system. These low-frequency low-amplitude (LL) oscillations were detected with both platinum and iodide-selective electrodes in the chlorite-iodide-malonic acid (original CIMA) reaction and in the closely related chlorine dioxide-iodide-malonic acid (minimal CIMA) system. The LL oscillations follow after the already known high-frequency oscillations, sometimes separated by a second induction period. LL oscillations can appear without any induction period if appropriate concentrations of chlorine dioxide, iodomalonic acid, and chloride (CIMA-Cl system) are established in a dilute sulfuric acid medium. In this case neither iodine, iodide, nor malonic acid is needed. Some suggestions are made regarding the mechanism of these newly discovered oscillations.

Introduction

The oscillatory chlorite-iodide-malonic acid (CIMA) system and the closely related chlorine dioxide-iodine-malonic acid oscillator (the "minimal" CIMA system) are presently the focus of much interest.¹⁻³ The CIMA reaction shows exceptionally rich, dynamical behavior in continuously fed stirred tank reactors⁴ and is one of the few simple chemical systems, besides the popular Belousov-Zhabotinsky (BZ) reaction,⁵⁻⁷ that are capable of producing batch oscillations⁸ and traveling chemical waves.^{8,9} The principal reason for the renewed interest, however, is the recent discovery, using different types of continuously fed unstirred reactors (CFURs), of the long sought Turing patterns^{10,11} in some CIMA systems.¹²⁻¹⁵ Experiments in these newly developed, open spatial reactors—the gel ring,¹⁶ the disk,¹⁷ and the membrane^{18,19} reactors—exhibited interesting wave behavior¹⁹⁻²¹ in the BZ reaction but did not produce stationary Turing structures. A particular reason for the current interest in Turing structures is that they may play a fundamental role in biological pattern formation¹¹ and morphogenesis. Thus, the first experimental evidence for a Turing bifurcation in a relatively simple chemical system is an important development and focuses interest on the mechanism of the CIMA reaction. Here we report a new type of oscillatory behavior of the CIMA system in batch. These observations suggest some additional features of the mechanism.

The fundamental features of the mechanism were clarified recently by Lengyel, Rábai, and Epstein.^{1,2} They discovered that,

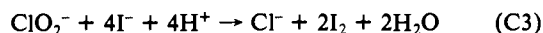
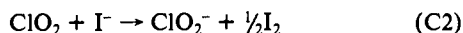
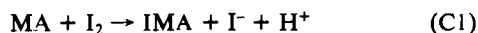
during the induction period of the CIMA reaction, the chlorite-iodide-malonic acid system was transformed to an oscillatory

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chlorine dioxide-iodine-malonic acid system. They found that the latter system produces oscillations immediately, that is, without any induction period. Other intermediates produced in the induction period of the original CIMA system (e.g., iodate) were not crucial in initiating the oscillation. On the basis of the above observations, they developed a simple and elegant mechanism for the oscillatory chlorine dioxide-iodine-malonic acid reaction, consisting of the following three composite reactions:



Here MA denotes malonic acid and IMA stands for iodomalonic acid. Processes C1 and C2 provide a slow inflow of I^- and ClO_2^- ions. In the oscillating system, a gradual accumulation of I^- and ClO_2^- is interrupted periodically by their sudden depletion due to the periodic acceleration of process C3. C3 is a so-called self-inhibited or substrate-inhibited reaction: its rate increases with decreasing I^- concentration. (The empirical rate law contains the I^- concentration in the denominator.²) Thus, the process accelerates while it consumes the I^- ions. Model calculations using experimental rate laws for processes C1-C3 gave excellent agreement with the experimental findings.

Lengyel et al.² made their experimental observations with a UV-visible spectrophotometer following the absorbance at 280 nm. (The main absorbing species at this wavelength is triiodide ion.) Using an identical apparatus at the same wavelength, we confirmed their results. The high-frequency spectrophotometric batch oscillations (with a period of the order of 10 s) lasted for 6-8 min, depending on the initial concentrations, in agreement with the behavior reported by Lengyel et al. Using iodide-selective and platinum electrodes, however, we were also able to find in certain cases a subsequent oscillatory regime lasting for more than 1 h. These long-lived oscillations, which were not detected by the spectrophotometer, were characterized by a relatively low amplitude (1-2 mV for the iodide electrode and 10-20 mV for the platinum electrode) and by a lower frequency (typical periods were of the order of minutes). The transition from the high- to the low-frequency oscillations can be continuous, but under certain conditions, a second induction period was observed. No elementary iodine was detected spectroscopically during these long-lived low-frequency oscillations, which were found in both the original CIMA and the minimal CIMA system.

For appropriate initial concentrations of chlorine dioxide, iodomalonic acid, and somewhat unexpectedly, *chloride* ion (CIMA-Cl system), the low-amplitude low-frequency oscillations appear immediately, without any induction period. After the cessation of oscillations, they can be restarted several times simply by adding chlorine dioxide to the system.

Experimental Section

Materials. NaClO_2 (Kodak) was purified by the method of Nagypál and Epstein.²² ClO_2 and ClO_2^- solutions were prepared by the method²³ used by Lengyel et al.² The concentrations of NaClO_2 and ClO_2^- stock solutions were determined with iodometric titrations. Aliquots of the stock solutions were added to 0.05 M sulfuric acid containing a large excess of NaI. The triiodide formed in this way was titrated with ascorbic acid. HOI was produced by a modification of a method of Noszticzus et al.²⁴ NaIO_3 (50 mg) and 127 mg of I_2 were dissolved in 25 mL of concentrated sulfuric acid. The hypiodous acid concentration of the dark brown solution was 4×10^{-2} M. The HOI concentration was

determined by injecting a 0.1-mL aliquot into 100 mL of 0.1 M H_2SO_4 and titrating it with a 10^{-3} M NaI solution in the presence of an iodide-selective electrode. Malonic acid was first recrystallized from acetone²⁵ and then from acetone-chloroform.²⁶ Iodomalonic acid stock solution was prepared with a titration procedure according to the following recipe: 3 mL of 1 M malonic acid, 1.6 mL of 5 M H_2SO_4 , and 5 mL of 0.2 M NaIO_3 were measured into a 30-mL beaker equipped with a magnetic stirrer. The mixture was titrated with 5 mL of 0.4 M NaI solution added dropwise from a buret. An excess of iodide was indicated by the dark color of iodine beyond the equivalence point. Then 1-2 drops of iodate and malonic acid were added because elementary iodine catalyzes the decomposition of iodomalonic acid. The color of the iodine-free iodomalonic acid solution is slightly green. The solution was diluted immediately with ice cold distilled water to a final volume of 250 mL and was stored at 5 °C. Final concentrations of the stock solution: $[\text{IMA}] = 1.2 \times 10^{-2}$ M, $[\text{H}_2\text{SO}_4] = 2 \times 10^{-2}$ M, $[\text{NaHSO}_4] = 1.2 \times 10^{-2}$ M. The stock solution was stable for several days in a refrigerator. At room temperature the autocatalytic decomposition of the iodomalonic acid occurs within 1-2 h. All other chemicals were of reagent grade and were used as received.

Apparatus. The batch reactor was a 100-mL quartz crucible (height, 50 mm; diameter at the top, 60 mm; diameter at the bottom, 30 mm) stirred by a 14-mm-long, 8-mm-diameter magnetic stirring bar at 800 rpm. The total volume of the reaction mixture was 50 mL. Most of the experiments were carried out in a reactor open to the laboratory atmosphere, except for a few in which a N_2 atmosphere was used to show that the CIMA system is not sensitive to oxygen. In the electrochemical measurements, a bright platinum electrode (Corning 476060) and a AgI iodide-selective electrode were used. The AgI electrode was prepared by dipping a 0.25-mm-diameter silver wire into a AgI melt, in a way analogous to the AgBr electrode preparation.²⁷ The double-junction Ag/AgCl (Sensorex) electrode was connected to the system via a salt bridge containing 5 mM sulfuric acid and closed by a Vycor porous glass disk. This precaution was made to avoid absorption of I_2 and ClO_2 in some plastic parts of the reference electrode and to diminish drift in the diffusion potential. Electrode potentials were amplified with high input impedance amplifiers and were recorded on a personal computer equipped with a 12-bit analog-to-digital converter board (Metra Byte Dash-8) using a Labtech Notebook program. The sampling rate was 4 Hz, and a moving average of four samples was stored on the computer. All experiments were carried out in a laboratory thermostated to 22 °C. Spectrophotometric measurements were made on 3-mL samples transferred from the batch reactor into a 1-cm quartz cuvette. The measurements were made with a HP 8452A UV-vis diode array spectrophotometer at 280 nm. The spectrophotometric cell was stirred at 600 rpm using an 8-mm-long, 1.5-mm-diameter magnetic stirring bar.

Procedure. The original CIMA reaction was started by adding NaClO_2 to the system as the last component. Samples for spectrophotometric measurements were withdrawn with a glass pipet after a 20-s mixing period following the addition of NaClO_2 . The minimal CIMA oscillator was started by adding malonic acid to the system that already contained all the other components. In the case of the CIMA-Cl system, the last two components were chlorine dioxide and then chloride.

Results

The original aim of our investigation was to obtain more information about the iodide level in the batch CIMA systems. That level is important because the starch-triiodide complex formation is able to slow down the diffusional transport of the iodide ions²⁸ only if the iodide concentration is relatively low compared to the concentration of the binding sites. At high iodide levels, the binding sites can be saturated and no slowing down will occur. On the other hand, if the iodide concentration is very low, then unidentified binding sites, present even in the pure gel matrix of a Turing experiment, can be important. For example, Turing patterns were observed in our laboratory²⁹ in a highly cross-linked pure acrylamide gel, without using any triiodide binding indicator. Thus, we decided to follow the oscillations by means of iodide-

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Table I. Initial Concentrations of the Components^a

name of the system	NaClO ₂	ClO ₂	I ⁻	I ₂	IMA	MA	Cl ⁻	Figure
original CIMA	5.0	-	4.57	-	-	1	-	1
	6.2	-	4.57	-	-	1	-	2
	8.8	-	4.57	-	-	1	-	5a
minimal CIMA	-	0.21	-	0.5	-	1	-	3
	-	0.25	-	0.5	-	1	-	4
	-	0.29	-	0.5	-	1	-	5b
CIMA-Cl	-	0.13	-	-	1	-	6	6a
	-	~0.13 ^b	-	-	~1 ^b	-	~6 ^b	6b

^aThe concentrations are given in millimoles/liter. All experiments were performed in a 5 mM sulfuric acid medium. Besides the sulfuric acid, the CIMA-Cl system contained 1 mM NaHSO₄. ^bApproximate concentrations after adding 0.12 mL of 0.056 M ClO₂ solution to the exhausted CIMA-Cl system of Figure 6a (final volume: 50.1 mL).

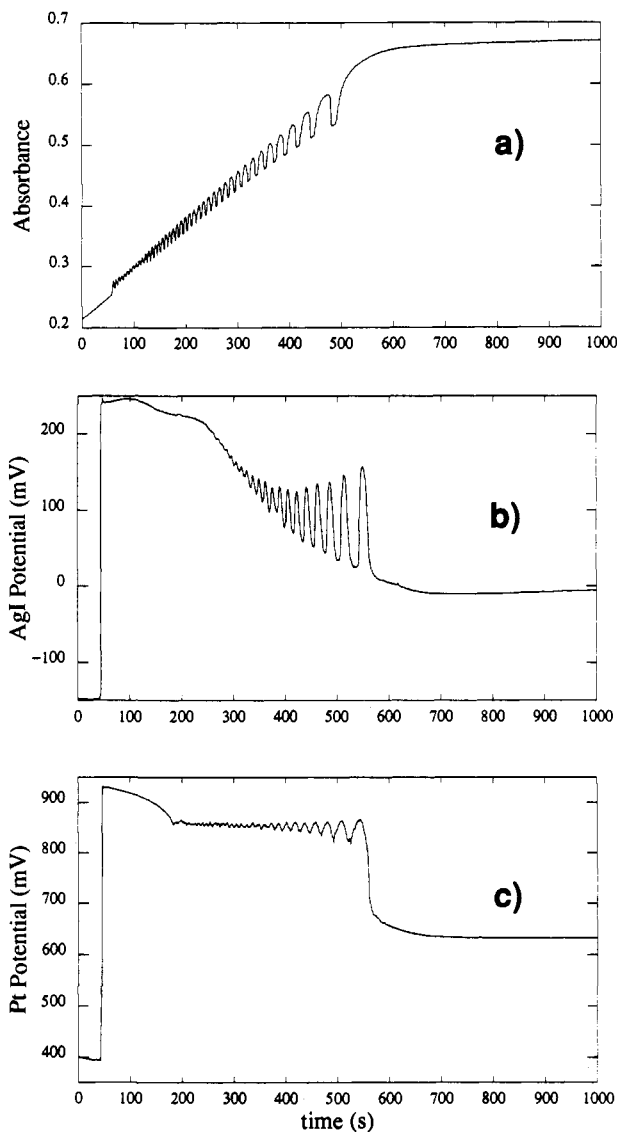


Figure 1. High-frequency oscillations in the original CIMA system with a relatively low initial NaClO₂ concentration (see Table I for concentration data). The sudden jump of the electrode potentials marks the injection of NaClO₂, which starts the reaction. The electrode potentials were recorded simultaneously in the same experiment. The light absorbance measurement started with an 80-s delay because it was performed separately on a 3-mL sample transferred from the batch reactor to the spectrophotometer. The absorbance was measured at 280 nm.

selective and platinum electrodes, to get information about the iodide level and the iodide/iodine ratio. The initial conditions for our batch experiments are given in Table I.

High-Amplitude High-Frequency and Low-Amplitude Low-Frequency (LL) Oscillations in the Original CIMA System. First, we studied the original CIMA system at different initial NaClO₂ concentrations. Two characteristically different kinds of behavior were found, as shown in Figures 1 and 2. At low-chlorite con-

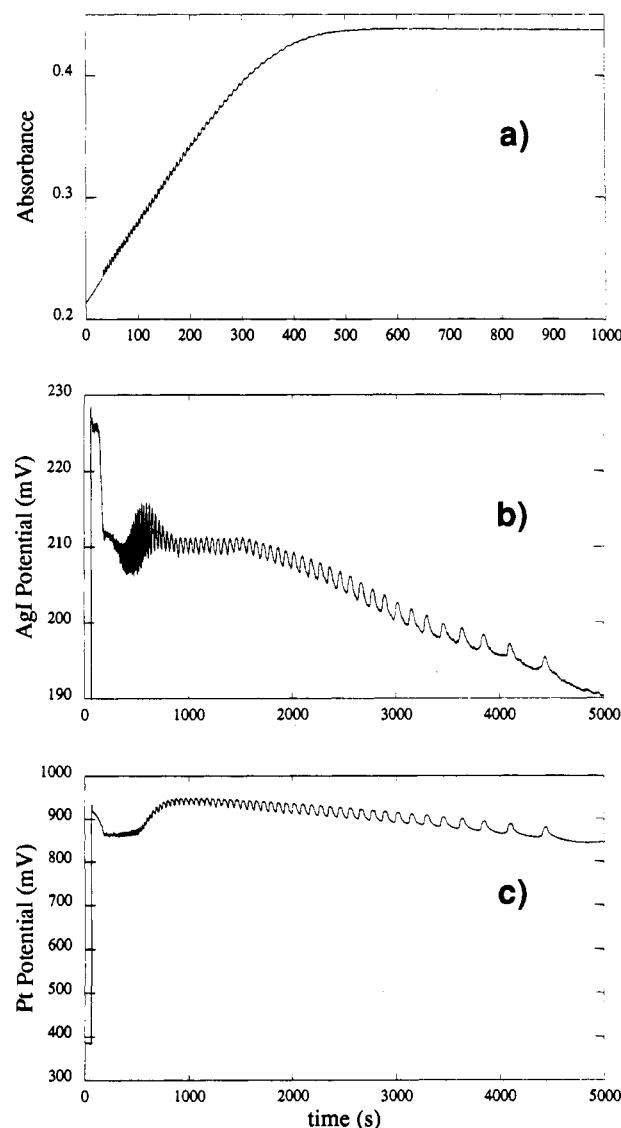


Figure 2. High-frequency and low-amplitude low-frequency (LL) oscillations in the original CIMA system with a medium NaClO₂ concentration (see Table I for concentration data). The experiment was conducted in a way similar to that described in the caption of Figure 1. Observe the shorter time scale of the spectrophotometric oscillations and the lower amplitude of all oscillations compared to those in Figure 1. The typical LL oscillations started after the Pt potential had reached its maximum. A part of the initial AgI potential jump is not shown in order to make the small-amplitude AgI electrode potential oscillations more visible in the figure.

centrations we reproduced the high-frequency high-amplitude oscillations reported by Lengyel, Rábai, and Epstein¹ (Figure 1). At higher chlorite concentrations, however, the system behaved differently (Figure 2). Here, after the cessation of the usual high-frequency oscillations, a much longer regime of low-frequency low-amplitude (LL) oscillations appeared. Besides the low am-

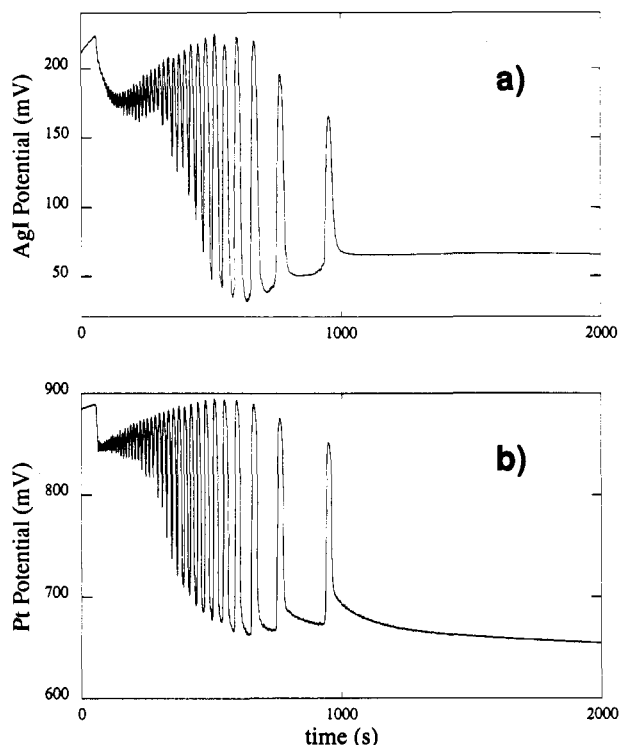


Figure 3. High-frequency AgI and Pt potentials in the minimal CIMA system at a low initial ClO_2 concentration. The initial concentrations are given in Table I. The experiment was started by adding malonic acid to the system as the last component. This event is marked by the sudden drop of the potential, and oscillations start immediately. Observe the short duration of the oscillatory regime (~ 1000 s) and the high amplitude of some oscillations (~ 150 – 200 mV).

plitude and frequency, these new oscillations are characterized by relatively high electrode potentials. While exact iodide levels cannot be calculated from these high potentials, an upper limit can be estimated. For example, the calibration of the ion-selective electrode in a 5×10^{-5} M sulfuric acid, 10^{-4} M I_2 medium gives an electrode potential of +7 mV for 10^{-3} M I^- and +240 mV for 10^{-5} M HOI. Thus, the high iodide electrode potentials measured during the oscillations (190–210 mV) are corrosion potentials^{24,30} due mostly to iodine species in the +1 oxidation state (HOI and ICl). These species react rapidly with the AgI substrate of the electrode, generating Ag^+ ions there and establishing a corrosion potential.^{24,30} The maximum iodide level can be estimated as 10^{-8} M or less. This is not the case with the conventional high-amplitude oscillations (Figure 1b), for which the maximum I^- concentration, especially after the cessation of the oscillations, can reach 10^{-5} M or more. Since there are several redox couples present simultaneously in the reaction mixture, the interpretation of the platinum electrode potential is more difficult. During the low-frequency oscillations, however, there is time enough for the different redox couples to establish an equilibrium among themselves, especially because the amplitude of the oscillations is also small. Thus, in the LL regime the measured electrode potential reflects the potential of the iodine/iodide redox couple as well as other redox couples. In the regime of the high-amplitude high-frequency oscillations the assumption of a redox equilibrium is less obvious. Nevertheless, in this regime the iodine concentration is relatively high; therefore it is reasonable to assume that the I_2/I^- redox couple is the potential-determining one. Calibration of the platinum electrode in 5×10^{-3} M H_2SO_4 gave 650 mV in a solution containing 10^{-5} M I^- and 10^{-4} M I_2 , and 870 mV in a solution containing 10^{-5} M HOI and 10^{-4} M I_2 . An estimation of the iodide concentration based on the platinum electrode potential during the small-amplitude oscillations (around 900 mV) again gives a 10^{-8} M maximum. In the case of the high-amplitude

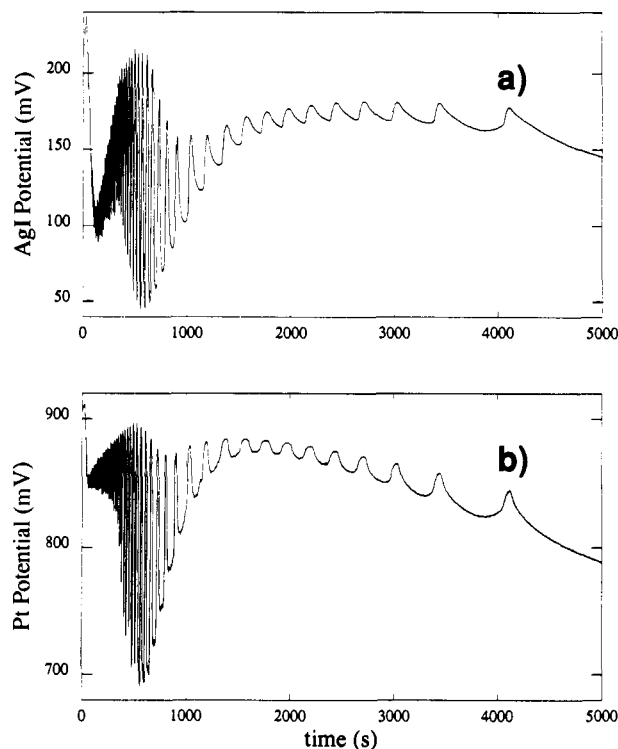


Figure 4. High-frequency and low-frequency low-amplitude oscillations in the minimal CIMA system at a medium initial ClO_2 concentration. The initial conditions are given in Table I. The reaction was started by adding malonic acid as the last component of the system. This event is marked by the sudden potential drop in the Pt potential. Oscillations start immediately. Observe the long period of the LL oscillations.

oscillations the potential is considerably lower and even drops below 650 mV after the cessation of the oscillations (Figure 1c). Thus, there is agreement between the iodide levels indicated by the two different electrodes.

The most striking difference between the different modes of oscillations, however, is in their optical density records (Figures 1a and 2a). The LL oscillations were almost undetectable in the spectrophotometer records, while the usual oscillations were easily detected. These differences suggest differences in the mechanisms giving rise to the two types of oscillations.

LL Oscillations in the Minimal CIMA System. After the discovery of this new kind of oscillation in the original CIMA system, the next step was to search for them in the minimal CIMA oscillator (Figures 3 and 4). At low ClO_2 concentrations, the oscillations in the minimal CIMA system (Figure 3) are qualitatively similar to the oscillations in the original CIMA system measured at low NaClO_2 concentrations (Figure 1). The only difference is that the amplitudes of the Pt potential oscillations are higher here. (Compare Figure 1c and Figure 3b.) By increasing the initial ClO_2 concentration, as Figure 4 shows, one can find LL oscillations in the minimal CIMA system as well. There are some differences, however, in the behavior of the original and the minimal CIMA systems. First, the LL oscillations are more difficult to find in this system, because they appear only for a narrow range of initial ClO_2 concentrations. Second, there are few (10 or fewer) LL oscillations, due to its even lower frequency. Third, the initial high-frequency oscillations have a higher maximum amplitude (about 150 mV) than in the original CIMA system. (See Figure 2b,c.)

Induction Period for the LL Oscillations. If the initial NaClO_2 concentration in the original CIMA or the initial ClO_2 concentration in the minimal CIMA system is too high, then the LL oscillations appear only after a certain induction period. (See Figure 5.) If the dynamical behaviors of the original and the minimal CIMA systems are compared, the same similarities and differences discussed in the previous paragraph can be observed. The presence of a second induction period separating the normal high-frequency and the LL oscillations suggests again that they

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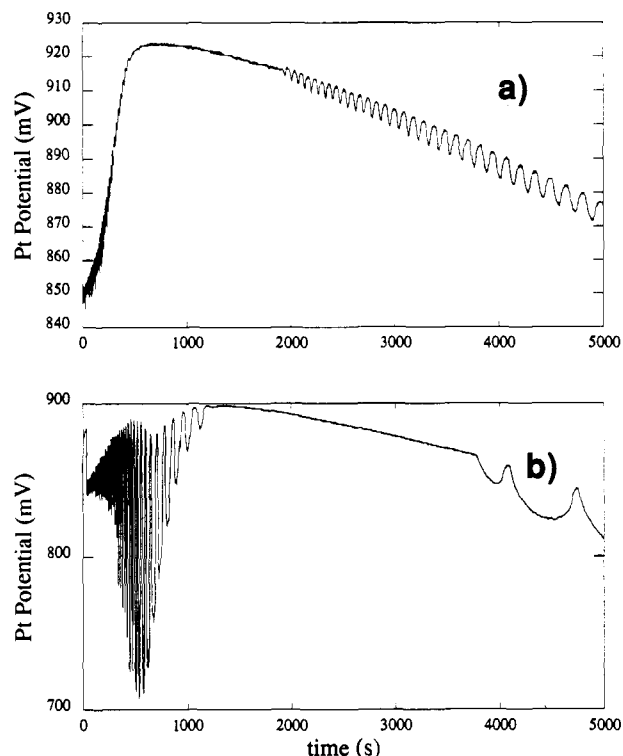


Figure 5. Platinum potential time series illustrating an induction period that separates the high-frequency and the LL oscillations: (a) in the original CIMA system with high initial NaClO_2 concentration; (b) in the minimal CIMA system with high initial ClO_2 concentration. The initial potential jump and the first induction period before the high-frequency oscillations are omitted from Figure 5a. Initial conditions are given in Table I for both figures.

are of a different nature, at least in some respects. It is clear that the onset of LL oscillations requires conditions which are different from the ones necessary for the normal oscillations.

Conditions Necessary for the LL Oscillations: The CIMA-Cl System. Our discovery that the LL oscillations in the original CIMA system can be reinitiated after their cessation simply by adding NaClO_2 or ClO_2 to the system again was a crucial observation. (Not shown as a figure.) There was a significant difference between the effect of NaClO_2 and ClO_2 , however. While NaClO_2 reinitiated the LL oscillations only after an induction period, ClO_2 reestablished them immediately. From this observation it was logical to assume that an exhausted CIMA system contains all the essential components necessary for the LL oscillations except ClO_2 . The next step was to perform experiments to determine the chemical identity of these essential components. Our first guess was that iodomalonic acid as an iodine source, together with malonic acid and ClO_2 , can form an oscillating system similarly to iodine, malonic acid, and ClO_2 in the minimal CIMA system. In spite of our best efforts, however, we were not able to observe oscillations using many different concentration combinations of ClO_2 , iodomalonic acid, and malonic acid in a 0.005 M sulfuric acid medium. We then tried adding iodate to the system since, according to Lengyel et al.,² IO_3^- is also a product of the reaction. Again, no oscillations were observed. Tartronic and glyoxylic acids, possible oxidation products of malonic acid, were also tried without success. Adding chloride ion to the system was a last resort because it is usually regarded to be an inert end product. Nevertheless, when a sodium chloride solution was added to a system already containing iodomalonic acid and chlorine dioxide, the LL oscillations appeared without any induction period (Figure 6a). Also, after the LL oscillations had ceased, they could be reinitiated by adding ClO_2 again (Figure 6b). The presence of malonic acid is not necessary, but no LL oscillations were observed without iodomalonic acid or chloride ions. The importance of chloride ions was also emphasized by another observation. If chloride ions were added initially to a minimal CIMA

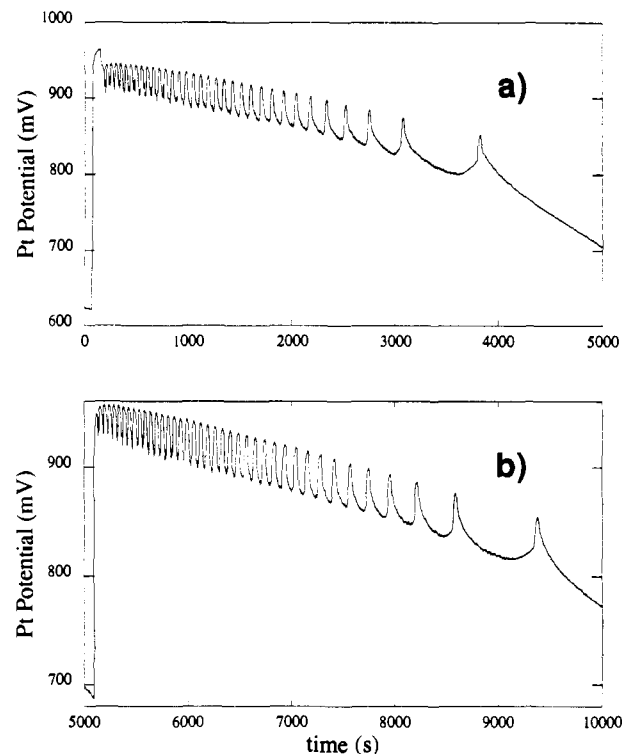


Figure 6. (a) Low-frequency low-amplitude oscillations in the CIMA-Cl system. See Table I for initial conditions. The addition of ClO_2 is marked by a jump in the electrode potential above 900 mV. After a short waiting period (about 60 s), chloride was added to the system, which led to a sudden drop of the potential and to the appearance of LL oscillations without an induction period. (b) Adding ClO_2 to the exhausted CIMA-Cl system of Figure 6a reinitiates oscillations immediately. Addition of ClO_2 is marked by the sudden jump of the platinum potential. The reinitiation can be done several times.

system, then the subsequent LL oscillations appeared with the same frequency as in the original CIMA system. Thus, the original CIMA system produced more LL oscillations only because it contained a large amount of chloride after the induction period. In the induction period most of the initial chlorite ($\sim 6 \times 10^{-3}$) was transformed to chloride ions. In the case of the minimal CIMA system the relatively low initial chlorine dioxide concentration ($\sim 2 \times 10^{-4}$ M) produced much less chloride by the end of the high-frequency oscillations. Thus, the conditions were less favorable for LL oscillations in the minimal CIMA system without the added chloride, and this is why there are fewer of them in Figure 4 compared to Figure 2. That difference disappears if an appropriate amount of chloride ($\sim 6 \times 10^{-3}$ M) is added to the system initially.

Experiments in a Controlled Atmosphere. There was no difference in the LL oscillations if the experiments were performed in high-purity N_2 or in the laboratory atmosphere. Applying a strong ($\sim 1\text{--}2$ L/min) N_2 or air flow above the reaction mixture, however, shortened somewhat the oscillatory regime by the physical removal of ClO_2 . On the other hand, closing the top of our reactor by a rubber stopper lengthened the oscillatory regime. Unfortunately, the ClO_2 absorbed in the rubber stopper caused some problems in this case, and construction problems prevented us from making a closed "all glass" reactor without any absorbing parts. Thus, we decided to keep the top of the reactor open to the laboratory atmosphere. This method gave good reproducibility for the length of the oscillatory regime.

Discussion

Some CIMA systems are capable of a new type of oscillation that can last 5000 s or even more. The principal components producing these low-frequency low-amplitude (LL) oscillations are chlorine dioxide, iodomalonic acid, and chloride ion (CIMA-Cl system). It is interesting to observe the sequence of events in the original CIMA system (Figure 2). First, the original CIMA

system is transformed to the minimal CIMA system and high-frequency oscillations appear. Then, in a subsequent step, products that are inert or play a secondary role in the high-frequency oscillations initiate the LL oscillations. Note that two of the input reactants in the CIMA-Cl system, IMA and Cl⁻, appeared as "inert products" of the minimal CIMA system.

Experiments are in progress in our laboratories to address the following questions:

i. What is the mechanism of the LL oscillations in the CIMA-Cl system? Here, the reversibility of the malonic acid iodination³¹ (dissociation of iodomalonic acid to malonic acid and hypoiodous acid) and the reaction of hypoiodous acid with chlorine ion to form ICl^{32,33} may play an important role.

ii. Do the reactions and principal components of the LL oscillations play an important role in the Turing experiments? Since the residence times in the gel of a Turing experiment are relatively long (1000 s or more), accumulation of reaction products such as chloride ion and iodomalonic acid is unavoidable. This suggests that these components could contribute to the formation of Turing patterns.

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Gas-Phase Selectivities of Crown Ethers for Alkali Metal Ion Complexation

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Abstract: Gas-phase size selectivities of crown ethers have been investigated by application of the kinetic method. Ion complexes of crown ethers with two different alkali metals were generated by liquid secondary ion mass spectrometry. Upon gas-phase isolation and high-energy dissociation, these complexes predominantly produced crown ether/alkali metal adduct ions. The abundance ratios of product ions were correlated to the alkali metal ion selectivities of the crown ether. The concept of "maximum contact point" best described gas-phase selectivities because binding preferences were for a smaller metal diameter than what is predicted by the "best fit" concept. The following orders of selectivities were observed for alkali metal ions: 15-crown-5, Li⁺ >> Na⁺ > K⁺ > Cs⁺; 18-crown-6, Na⁺ ≥ K⁺ > Li⁺ > Rb⁺ > Cs⁺; and 21-crown-7, K⁺ > Na⁺ ≥ Rb⁺ > Li⁺ > Cs⁺. Theoretical studies agree with the present selectivity of 18-crown-6 for sodium ion in the absence of solvation effects. Also, steric and/or pseudo-solvation effects on gas-phase selectivities were evaluated. Complexes of crown ether dimers with two different alkali metal ions were examined, and 18-crown-6 showed a binding preference for potassium over sodium ion.

Introduction

The principles of understanding many biological phenomena, such as enzyme binding and signal transmission across cell membranes, are based on molecular recognition and host-guest binding interactions.¹ The selective binding involved in host-guest complexation requires an optimum or "preorganized" structure for each substrate prior to possible electrostatic or hydrogen-bonding interactions.² These processes are highly influenced by solvation effects.³ Macrocycles such as cage cryptands, which have isolated cavities,⁴ and substituted lipophilic crown ethers⁵ have been designed to study the factors of preorganization and solvation energy in recognition and complexation. However, controversy remains concerning the importance of solvent effects on host-guest selectivities. Gas-phase media provide an optimum environment to study the intrinsic behaviors of host-guest interactions.

Previously, alkali metal/crown ether binding in solution has been investigated by several experimental techniques including calorimetric titration,⁶ potentiometry with ion-selective electrodes,⁷ NMR spectroscopy,⁸ and ultrasonic absorption kinetic methods.⁹ These studies provide a comparison when the solvation energy and ion-pairing effects dominate selectivities. The investigation of

gas-phase encapsulation of alkali metals by crown ethers provides a systematic model for understanding the direct influence of the electronic properties of the enclosing cavity on selective electrostatic interactions. Recent theoretical studies of solvation effects¹⁰ and solvent-induced preorganization¹¹ of ligands have been reported

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