Platinum as a Chlorine Dioxide/Chlorite Redox Electrode in ClO_2-Based Oscillating Reactions and a New Semibatch Oscillator: The ClO_2−Acetone System with I^- Inflow

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A systematic study of the potential response of platinum electrode to various redox species in ClO_2-based chemical oscillators proves that it is the Cl(+4)/Cl(+3) redox pair that determines the potential in these systems. According to the results reported here, the electrode potential can be predicted from known concentrations of the Cl(+4) and Cl(+3) species, or inversely, these concentrations can be estimated from the measured potential. Thus, at constant ClO_2 levels the platinum behaves as a "chlorite selective" electrode. To demonstrate the feasibility of this approach, potentiometric oscillations were recorded in two different ClO_2-based oscillating systems, and the experimental results were compared with potentiometric traces calculated by two alternative models.

Introduction

Chlorite- and chlorine dioxide-based chemical oscillators play an important role in "nonlinear chemistry" and are in the focus of current interest.[1−13] Recently a new ClO_2-based chemical oscillator, the ClO_2−I_2−acetone (CIA) system, was found in our laboratory.[1] Oscillations were observed in a novel semibatch reactor called a membrane-fed stirred tank reactor (MSTR), in which a constant iodine inflow permeating through a selective membrane generated potential oscillations of platinum and iodide selective electrodes. Model calculations based on a combination of the Citri−Epstein[4] and the Lengyel−Rábai−Epstein[6] (LRE) mechanisms resulted in a qualitative agreement with the observations: both the period and the duration of the calculated oscillations were rather close to the experimental values. However, the amplitudes of potential oscillations of a platinum electrode calculated from the concentrations of the I_2/I^- redox couple were different from those recorded in the experiments. In our previous work[1] no attempts were made to explain the absolute potential level of the electrodes, since it was realized that a careful calibration for the possible electroactive species was needed. These electrochemical investigations were postponed for a separate study, which is reported here. The results of these investigations prove that the potential of the platinum electrode in ClO_2-based chemical oscillators is determined not by the I_2/I^- redox couple but by the Cl(+4)/Cl(+3) redox pair. Under the applied experimental conditions, the contribution of other redox species (such as chloride, chlorine, hypochlorous acid, chlorate, iodide, iodine, hypoiodous acid, iodous acid, and iodate) to the measured electrode potential is negligible. Consequently, at a constant chlorine dioxide concentration the recorded potential oscillations can be interpreted as the result of changes in the concentration of chlorite exclusively. It will be shown that the agreement between experiments and modeling can be greatly improved by taking into account these new observations. The potential oscillations measured in the CIA system are compared with those calculated by two alternative models: (i) the LRE model,[6] and (ii) a detailed mechanism developed recently by Lengyel, Li, Kustin, and Epstein[14] (LLKE). Finally, we report on a new semibatch version of the CIA oscillator: the ClO_2−I^-−acetone system, in which (substituting for the iodine inflow through a selective membrane in the former system) a direct inflow of iodide is applied (maintained by a peristaltic pump). The experimentally observed potential oscillations of a platinum electrode in this new system are also compared with the results of simulations based on the LRE and the LLKE models.

Experimental Section

Chemicals. Gaseous chlorine dioxide and ClO_2 solutions were prepared by a textbook method[15] modified by Lengyel et al.[6,9] The concentration of the ClO_2 stock solution was determined with ascorbinometric titrations.[7] Solutions of chlorine dioxide were freshly prepared from the stock that was kept refrigerated. The stock solution was stable for several months.

$NaClO_3$, NaCl, $NaIO_3$, I_2, NaI, acetone, and sulfuric acid applied in the experiments were of reagent grade and used without further purification. $NaClO_2$ was purified by the method of Nagypál and Epstein.[16] HOCl was prepared by adding AgOH in excess to an alkaline mixture of NaOCl and NaCl. The precipitate was filtered, and the filtrate was acidified with sulfuric acid. The HOCl concentration was determined by adding NaI to the solution and performing an ascorbinometric titration of the iodine formed. Aqueous solution of chlorine was prepared by acidifying the NaOCl−NaCl mixture. The chlorine concentration was determined by the procedure described above for the HOCl solutions. HOI[17] and HIO_2[18] was prepared by the method of Noszticzius et al.[17,18]

In all experiments, before starting either the iodine or the iodide inflow, the reactor contained the same solution. The standard initial solution (50 mL) was prepared by mixing 43.7 mL of H_2O, 3.3 mL of 0.05 M H_2SO_4, 1 mL of 0.0065 M ClO_2, and 2 mL of acetone in this order; thus the initial concentrations were the following: $[ClO_2]_0 = 1.3 \times 10^{-4}$ M, $[H^+]_0 = 5.6 \times 10^{-3}$ M (calculated from the sulfuric acid concentration [H_2-

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$SO_4]_0 = 3.3 \times 10^{-3}$ M by taking into account its second dissociation constant[19] $K_d = 1.2 \times 10^{-2}$ M), and $[\text{acetone}]_0 = 5.5 \times 10^{-1}$ M.

Apparatus. The experimental setup was the same as used earlier by Marlovits et al.[1] In the MSTR experiments the same iodine permeator was applied, generating a constant iodine current of 2.5×10^{-8} M s^{-1}. In the new version of the CIA oscillator the iodide inflow was controlled by a peristaltic pump (Ismatec REGLO 4/8 with a tubing of 0.19 mm inner diameter) applying low flow rates (usually below 0.1 mL/min). The reactor was thermostated at 25 ± 0.2 °C.

Electrodes. The potential of a platinum-wire electrode was recorded with respect to a silver−silver chloride reference electrode placed in 1 M KCl solution. To avoid any contamination of the reacting mixture with chloride ions, a salt bridge filled with 0.005 M sulfuric acid was applied. It is important to note that those parts of the platinum electrode that are not in direct contact with the reaction mixture must be covered evenly with an insulating material. For this purpose a combination of a narrow Tygon tubing and silicon grease was applied. To maintain the original sensitivity of the electrodes, the renewal of the silicon grease layer (between the electrode wire and the covering Tygon tubing) is necessary after a few days. Otherwise, an electrolyte layer formed between the platinum surface and the Tygon tubing (and containing electroactive species in different concentrations than those in the reaction mixture) would spoil the potential measurements, resulting, for example, in smaller amplitude oscillations.

Signal Recording. To record the small changes in the potential of the platinum electrode, a variable offset circuit and a high input impedance amplifier (gain: 20×) were applied. The signal from the amplifier was measured and recorded by a PC486 personal computer equipped with a PC Labcard (Advantech PCL-711S). The collected data were analyzed by the LABTECH Acquire software package.

Results and Discussion

Calibration of the Platinum Electrode for the Cl(+4)/Cl-(+3) Redox Couple. In a complex system like the one studied here there is a large number of redox reactions that may determine or at least contribute to the potential of a platinum electrode. Regarding the main components of the ClO_2-based chemical oscillators, however, it was a rather natural choice to start the calibration of the platinum electrode with the ClO_2/ClO_2^- redox pair, as the one-electron reduction of chlorine dioxide gives chlorite ion:

$$ClO_2 + e^- \leftrightarrow ClO_2^- \qquad \text{(E1)}$$

First, the electrode potential was measured as a function of the total concentration of chlorite $[Cl(+3)]_T$ added to the standard reaction mixture. In an acidic solution, chlorite ion is partially protonated in an equilibrium reaction, giving chlorous acid. However, as the concentration of sulfuric acid is not varied in our experiments, the amount of chlorite ion is always a constant fraction of the total Cl(+3) concentration. Therefore, if a Nernst equation is valid for chlorite ion, it should be valid for $[Cl-(+3)]_T$ as well. Figure 1a shows that in a wide range of concentrations the slope of the plot E vs log $[Cl(+3)]_T$ is close to the theoretical value (59 mV/decade) according to the following Nernst equation:

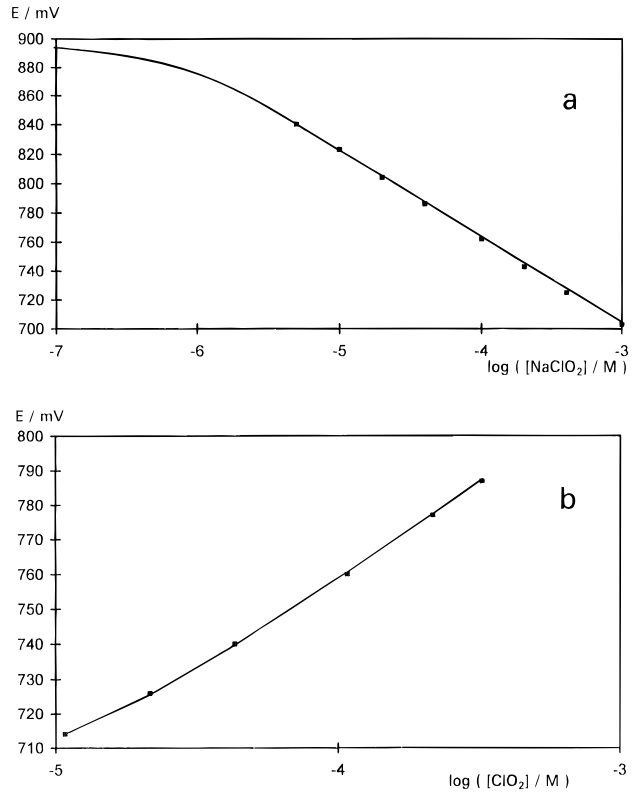

Figure 1. (a) Platinum electrode potential (measured against a Ag/AgCl reference electrode) vs logarithm of the total chlorite concentration added to the solution. Concentrations of other species are $[ClO_2] = 1.3 \times 10^{-4}$ M, $[H_2SO_4] = 3.3 \times 10^{-3}$ M, and [acetone] = 0.55 M. Squares show the measured data. Solid curve is calculated according to eq 2. The total chlorite concentration was calculated assuming equilibrium in the chlorine dioxide−acetone reaction.[20] (b) Platinum electrode vs logarithm of the chlorine dioxide concentration. Other concentrations are $[NaClO_2] = 10^{-4}$ M, $[H_2SO_4] = 3.3 \times 10^{-3}$ M, and [acetone] = 0.55 M. Squares are measured data. Solid curve is calculated according to eq 2 assuming that the initial concentration of ClO_2 (contaminating the chlorite solution) is 8×10^{-6} M.

$$E = E_0^* + 0.059 \log\left(\frac{[ClO_2]}{[ClO_2^-]}\right) = E_0^* + 0.059 \log\left(\frac{[ClO_2]}{a[Cl(+3)]_T}\right) = E_0 + 0.059 \log\left(\frac{[ClO_2]}{[Cl(+3)]_T}\right)(\text{V}) \qquad \text{(1a)}$$

where

$$a = \frac{[ClO_2^-]}{[Cl(+3)]_T} \quad \text{and} \quad E_0 = E_0^* - 0.059 \log a\ (\text{V}) \qquad \text{(1b)}$$

Obviously, there must be deviations from the Nernst formula at low (total) chlorite concentrations since eq 1a predicts an infinite potential for zero chlorite level. In the experiments, however, at very low chlorite concentrations the measured electrode potential becomes independent of the chlorite added to the solution. This indicates that at high potentials a minute amount of chlorite is generated in some redox processes at least on the surface of the electrode, and at low chlorite concentrations this surface chlorite acts as the potential-determining species. This behavior of the electrode can be taken into account by adding a small correction term ϵ to the total chlorite concentration. Therefore, throughout this paper the platinum electrode

potential is calculated by the following equation (for the sake of simplicity in the following platinum electrode potentials denote potentials measured against the Ag/AgCl reference electrode applied in our experiments):

$$E = E_0 + 0.059 \log\left(\frac{[\mathrm{Cl}(+4)]}{[\mathrm{Cl}(+3)]_T + \epsilon}\right) (\mathrm{V}) \qquad (2)$$

where $\epsilon = 1.6 \times 10^{-7}$ M according to our measurements in an aqueous solution containing $[ClO_2]_0 = 1.3 \times 10^{-4}$ M and $[H_2SO_4] = 3.3 \times 10^{-3}$ M. Note that these concentrations are the same as in the standard initial solution but without acetone. Surprisingly, a bit lower potential was measured in the complete standard mixture containing acetone as well. This is due to the fact that acetone can reduce a small fraction of chlorine dioxide to chlorite in a slow, reversible reaction (see later) resulting in a lower, equilibrium potential of the system. To include the effect of any "background" chlorite produced this way and to modify the calibration curve for the presence of acetone, the total chlorite concentration was calculated as follows:[20]

$$[\mathrm{Cl}(+3)]_T = [\mathrm{Cl}(+3)]_A + [\mathrm{Cl}(+3)]_P \qquad (3)$$

where $[Cl(+3)]_A$ is the concentration of the added chlorite and $[Cl(+3)]_P$ is the chlorite produced in the ClO_2−acetone equilibrium reaction. In most cases $[Cl(+3)]_P$ is insignificant compared to $[Cl(+3)]_A$ and can be neglected. In this concentration range the electrode shows a regular Nernstian behavior with a slope of 59 mV/decade (Figure 1a). $E_0 = 0.758$ V was determined from the potential values measured in this Nernstian region. (For example if $[Cl(+3)]_T + \epsilon \approx [Cl(+3)]_A = [Cl(+4)] = 1.3 \times 10^{-4}$ M, then $E = E_0$.)

At low $[Cl(+3)]_A$ concentrations the electrode potential becomes independent of the added chlorite. In the presence of acetone the constant potential value was 0.895 V. This means that an equilibrium concentration of $[Cl(+3)]_P = 4.6 \times 10^{-7}$ M is produced in the absence of added chlorite. The equilibrium constant K of the ClO_2−acetone reaction was determined[21] from this value of $[Cl(+3)]_P$.

To double-check whether the platinum electrode indeed responds to the ClO_2/ClO_2^- redox pair, the electrode potential was measured also as a function of the ClO_2 concentration at a constant but low chlorite concentration ($[NaClO_2] = 10^{-4}$ M). Again, the same sulfuric acid and acetone concentrations were applied as in the standard reaction mixture. The resulted calibration curve with the theoretically expected slope (59 mV/decade) is shown in Figure 1b. The small, positive deviation from the Nernstian response at low chlorine dioxide concentrations is due to ClO_2 traces in the applied chlorite solution.

Response of the Platinum Electrode to Other Chlorine-Containing Species. It was shown in the previous section that a platinum electrode gives a true Nernstian response to the Cl(+4)/Cl(+3) redox couple, and consequently, small variations in the Cl(+3) concentration can be detected at constant ClO_2 concentration. Next, the effect of chlorate (one of the components of the Cl(+5)/Cl(+4) redox couple) was studied. It has been found, however, that adding chlorate to our standard reaction mixture resulted in no significant changes in the platinum electrode potential, even if the chlorate concentration was as high as 0.005 M. That is, the exchange current of the Cl(5+)/Cl(4+) redox couple is too low to contribute to the electrode potential.

There are three other chlorine-containing species that may affect the platinum potential: HOCl, Cl_2, and Cl^-. The electrode does give a response to hypochlorous acid and to elementary chlorine whenever their concentrations exceed 10^{-6} M. In the concentration range 10^{-6}−10^{-5} M, the response of the platinum electrode to HOCl and Cl_2 was found identical within experimental error. This is not surprising since at low concentrations the added Cl_2 hydrolyses to HOCl and Cl^- nearly quantitatively. Thus in dilute solutions the effect of elementary Cl_2 on the electrode potential is negligible compared to that of HOCl. Adding 10^{-5} M HOCl to our standard solution resulted in a sudden potential jump of 10 mV followed by a gradual decrease. According to Peintler et al.,[23] HOCl can react with chlorite, giving chlorine dioxide. That is, HOCl affects the electrode potential by reacting with the chlorite generated in the chlorine dioxide−acetone reaction. As in the oscillating reaction, the maxima of HOCl concentrations are around (2−3) × 10^{-6} M; even the indirect contribution of HOCl to the potential oscillations must be minute.

Somewhat unexpectedly the platinum electrode placed into our standard reaction mixture was rather insensitive to chloride. For example, by increasing the concentration of Cl^- to 10^{-4} M the potential decreased by only 5 mV. Moreover, to achieve another 5 mV drop, the chloride concentration had to be increased up to 2×10^{-3} M. According to these observations, the effect of chloride on the potential of a platinum electrode in the CIA oscillators can be neglected.

The conclusion is that of the great variety of chlorine-containing redox species in the CIA system it is exclusively the ClO_2/ClO_2^- redox pair that determines the electrode potential.

Response of the Platinum Electrode to Iodine-Containing Redox Species. When iodate was added (even at rather high concentrations) to our standard mixture, the platinum electrode practically gave no response. For example, a 10^{-4} M stepwise increase in the iodate concentration resulted only in 1 mV peaks in the potential.

Injection of hypoiodous acid into the standard reaction mixture first caused a small increase in the potential (about 5 mV when a 10^{-5} M concentration jump was applied), which then was followed by a rapid relaxation (in about 20 s) back to the original potential. The effect of HOI can be explained in the same way as that of HOCl since they both decrease the chlorite concentration. The subsequent decrease in the potential can be related to the iodination of acetone, which rapidly consumes the added HOI. As the calculated maxima of HOI concentrations in the oscillatory CIA systems are only on the order of 10^{-7} M, hypoiodous acid is certainly not able to contribute to the potential oscillations.

The response of the platinum electrode to iodous acid was very similar to that caused by HOI. Most probably it is entirely due to the hypoiodous acid contamination of the HIO_2 solution.[18] The conclusion is that iodous acid is not a potential-determining species in the CIA systems.

Injection of iodine and iodide into our standard reaction mixture resulted in a sharp potential drop ("negative peak") followed within a few seconds by a fast rise to a potential value close to but somewhat lower than the original one. Nevertheless, we believe that iodide or iodine does not play a direct role in the observed potential changes. The negative peak and the subsequent increase in the potential can be explained by the effect of chlorite, which is formed in the reactions initiated by the injected iodine species. Note in Table 1 that in the ClO_2−I^- direct reaction one iodide produces one chlorite, which also explains the following observation: when 10^{-5} M iodide was added to the standard initial mixture, the measured potential drop was the same (about 80 mV) as that observed by adding 10^{-5} M chlorite. While the initial potential drop is the same

for either iodide or chlorite, the subsequent potential traces are different. For chlorite the potential stays at the lower level, but for iodide it relaxes back close to its original value. This latter potential increase is due to a reaction between chlorite and HOI. Hypoiodous acid is the hydrolytic product of iodine formed in the direct reaction between chlorine dioxide and the added iodide. However, the chlorite (also produced in the direct reaction) will not be completely removed by its reaction with HOI, since iodine, its source, is partially lost in the iodination reaction with acetone. Thus the small deviation from the original potential is due to some unreacted chlorite remaining in the solution. When a small amount of iodine is now injected into this solution, the potential increases (and not decreases), indicating that the unreacted chlorite is being removed. All these experiments suggest that iodide and iodine affect the potential only indirectly by generating or consuming chlorite.

The Effect of Acetone on the Initial Potential Level. It has been observed during the preparation of the standard reaction mixture that acetone, which is not an electroactive species, has a small effect on the electrode potential: adding acetone to the acidic solution of chlorine dioxide initiated a slow potential drift toward a new value about 35 mV below the original one. As reasoned earlier, this potential decrease might be due to an increase in the concentration of chlorite, which could be formed by the following equilibrium reaction between chlorine dioxide and acetone:

$$ClO_2 + HR \leftrightarrow H^+ + ClO_2^- + R \qquad \text{(ER)}$$

where HR = acetone and R = organic radical. The value of the equilibrium constant has been estimated by applying the following formula:[21]

$$K = \frac{[ClO_2^-][H^+][R]}{[ClO_2][HR]} = \alpha 1.66 \times 10^{-11}\ \text{M} \qquad (4)$$

It is somewhat disturbing that the value of K is model dependent, as $\alpha = 1$ in the LRE model (in which the protonation of chlorite ion is neglected) while $\alpha = 0.738$ according to the LLKE model for our experimental conditions. There is no conflict between the predictions of the two different models when a theoretical calibration curve is calculated because it is the total chlorite concentration that determines the electrode potential and the equilibrium concentration of the total chlorite is the same in both models:

$$[Cl(+3)]_T = \frac{K}{\alpha}\frac{[ClO_2][HR]}{[H^+][R]} = 1.66 \times 10^{-11}\ \text{M}\ \frac{[ClO_2][HR]}{[H^+][R]} \qquad (5)$$

The forward and backward rate constants of reaction ER, $k_{ER}^+ = 9.6 \times 10^{-5}\ M^{-1}\ s^{-1}$ and $k_{ER}^- = 5.8 \times 10^6/\alpha\ M^{-2}\ s^{-1}$, respectively, have been estimated[22] from the initial slope of the measured potential drift. Again, it might be a bit confusing that the value of rate constant k_{ER}^- is model dependent. However, as in the rate law for the backward reaction, the concentration of chlorite appears as $[ClO_2^-] = \alpha[Cl(3+)]_T$, and the two α's cancel out, resulting in the same rate equation in both models.

To start the iodine or iodide inflow at a stable potential level after the addition of acetone, a waiting period of 5 min was applied in all experiments. The equilibrium potential after this waiting period was 895 ± 10 mV.

The CIA System with Iodine Inflow: Experiments and Modeling. First we repeated the experiment of Marlovits et al.,[1] but now more precautions were taken in measuring the electrode potential. The electrolyte in the reference electrode, the salt bridge, and the silicon grease inside the flexible Tygon tubing were refreshed every day. As mentioned above, a waiting period of 5 min was also applied after mixing up the initial solution. With this procedure we were able to get better reproducible results.

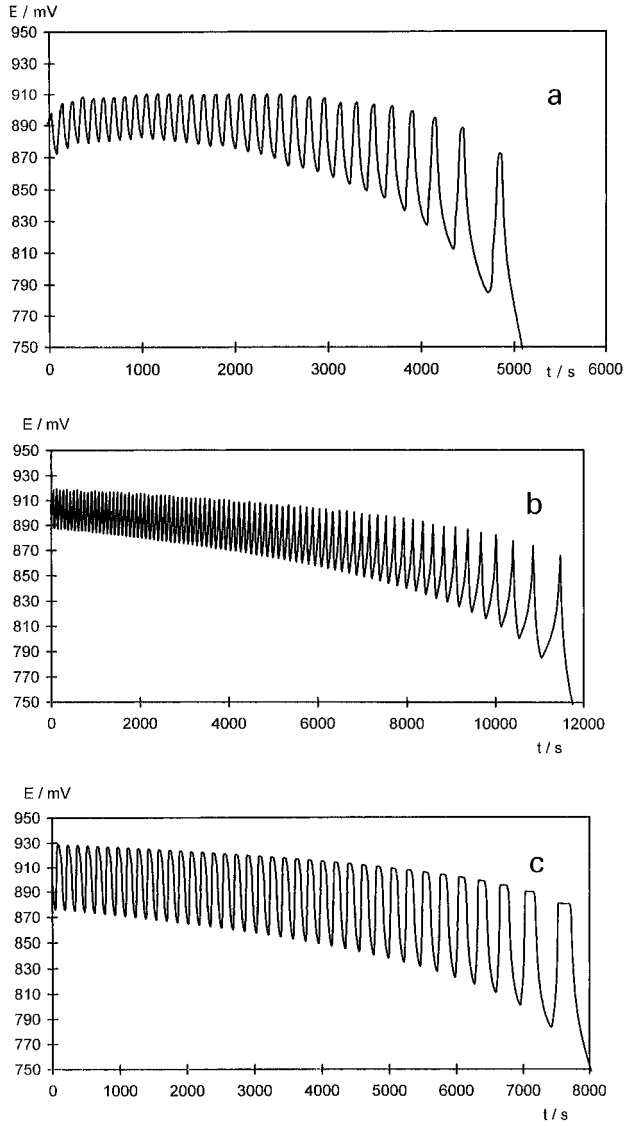

Figure 2. (a) Experimental potential oscillations of the platinum electrode in a semibatch CIA system with iodine inflow. Initial concentrations: $[ClO_2]_0 = 1.3 \times 10^{-4}$ M, $[H_2SO_4] = 3.3 \times 10^{-3}$ M, and [acetone] = 0.55 M. Iodine inflow rate: 2.5×10^{-8} M s^{-1}. (b) Potential oscillations calculated by the LRE model. (c) Potential oscillations calculated by the LLKE model.

Figure 2a shows the potential oscillations observed in an MSTR experiment applying the same iodine permeator as Marlovits et al.[1]

The potential oscillations predicted by simulations based on the LRE and the LLKE models (Table 1) are shown, respectively, in Figure 2b,c. To avoid any confusion, we emphasize here again the following: in the simple LRE model only one type of Cl(+3) species, the chlorite ion, is considered ($\alpha = 1$); thus the electrode potential was calculated by applying eq 2 and assuming that $[Cl(+3)]_T = [ClO_2^-]$.

The agreement between the observed and calculated potential vs time curves is qualitatively good. The characteristics (period, duration, number of maxima, and the average amplitude) of the measured and calculated potential oscillations are listed in Table 2.

TABLE 1: Reactions and Rate Laws of the Modified LRE and LLKE Models[a]

LRE Model[6] [b]

no.	reaction	rate law
R1	$ClO_2 + I^- \rightarrow ClO_2^- + {}^1/_2I_2$	$6 \times 10^3[ClO_2][I^-]$
R2	$ClO_2^- + 4I^- + \{4H^+\} \rightarrow 2I_2 + Cl^- + \{2H_2O\}$	$2.65 \times 10^{-3}\,[ClO_2^-][I_2][I^-]/\{u+[I^-]^2\}$
R3	$\{HR\} + I_2 \rightarrow \{IR\} + I^- + \{H^+\}$	$3.8 \times 10^{-1}\,[I_2]$
R4	$\{HR\} + ClO_2 \leftrightarrow R + ClO_2^- + \{H^+\}$	$5.2 \times 10^{-5}[ClO_2] - 3.2 \times 10^4[R][ClO_2^-]$

LLKE Model[14] [c]

no.	reaction	rate law
M1	$ClO_2 + I^- \rightarrow ClO_2^- + {}^1/_2I_2$	$6 \times 10^3[ClO_2][I^-]$
M2	$I_2 + \{H_2O\} \leftrightarrow HOI + I^- + \{H^+\}$	$1.98 \times 10^{-3}\,[I_2]/[H^+] - 3.67 \times 10^9\,[HOI][I^-] + 5.52 \times 10^{-2}\,[I_2] - 3.48 \times 10^9\,[H_2OI^+][I^-]$
M3	$HClO_2 + I^- + \{H^+\} \rightarrow HOI + HOCl$	$7.8[HClO_2][I^-]$
M4	$HClO_2 + HOI \rightarrow HIO_2 + HOCl$	$6.9 \times 10^7[HClO_2][HOI]$
M5	$HClO_2 + HIO_2 \rightarrow \{IO_3^-\} + HOCl + \{H^+\}$	$1.0 \times 10^6[HClO_2][HIO_2]$
M6	$HOCl + I^- \rightarrow HOI + \{Cl^-\}$	$4.3 \times 10^8[HOCl][I^-]$
M7	$HOCl + HIO_2 \rightarrow \{IO_3^-\} + \{Cl^-\} + \{2H^+\}$	$1.5 \times 10^3[HOCl][HIO_2]$
M8	$HIO_2 + I^- + \{H^+\} \leftrightarrow 2HOI$	$1.0 \times 10^9[HIO_2][I^-][H^+] - 22[HOI]^2$
M9	$2HIO_2 \rightarrow \{IO_3^-\} + HOI + \{H^+\}$	$25[HIO_2]$
M10	$HIO_2 + H_2OI^+ \rightarrow \{IO_3^-\} + I^- + \{3H^+\}$	$110[HIO_2][H_2OI^+]$
M11	$\{HR\} + ClO_2 \leftrightarrow R + ClO_2^- + \{H^+\}$	$5.2 \times 10^{-5}[ClO_2] - 4.1 \times 10^4[R][ClO_2^-]$

no.	equilibrium	K
M12	$HClO_2 \leftrightarrow ClO_2^- + \{H^+\}$	2.0×10^{-2}
M13	$H_2OI^+ \leftrightarrow HOI + \{H^+\}$	3.4×10^{-2}
M14	$I_2 + I^- \leftrightarrow I_3^-$	7.4×10^2

Reactions Added to Both Models

no.	reaction	rate law	
C1	$\{HR\} + I_2 \rightarrow \{IR\} + I^- + \{H^+\}$	$3.8 \times 10^{-1}[I_2]$	
C2	$\{\ \} \rightarrow I_2$	exptl and model calc in Figure 2	2.5×10^{-8}
C3	$\{\ \} \rightarrow I^-$	exptl and model calc in Figure 3	3.3×10^{-8}

[a] To model the CIA reaction with I_2 or I^- inflow, the iodination of acetone (C1) was added to the given models and the zeroth-order reactions of iodine or iodide inflow, (C2) or (C3), were included. An equilibrium reaction (R4) or (M11) between ClO_2 and acetone was also included. The rate constants of their backward reactions are model dependent because of the different variables (see text for explanation). The concentrations of all components in bracelets { } were assumed to be time independent constant (pool of chemicals approximation). [b] Variables: $[I^-]$, $[I_2]$, $[ClO_2]$, $[ClO_2^-]$, and [R]. [c] Variables: $[I^-]$, $[I_2]$, $[I(+1)]_T$, $[HIO_2]$, $[ClO_2]$, $[Cl(+3)]_T$, [HOCl], and [R]. Based on these equilibriums for our experimental conditions $[ClO_2^-] = \alpha[Cl(+3)]_T = 0.783[Cl(+3)]_T$, $[HOI] = 0.858[I(+1)]_T$, and $[I_3^-] \approx 0$.

TABLE 2: Measured and Calculated Potential Oscillations of the Platinum Electrode in a CIA System with Iodine Inflow (2.5×10^{-8} M s^{-1})

	Figure	period[a] (s)	duration[b] (s)	no.[c]	amplitude[d] (mV)
experiment	2a	115	4860	31	28
LRE model	2b	80	11 470	84	35
LLKE model	2c	148	7480	38	55

[a] Average period of oscillations during the first 1000 s of the reaction. [b] Time of the last maximum. [c] Total number of the potential maxima (excluding the extremum at $t = 0$). [d] Averaged over the first 1000 s of the reaction.

A detailed comparison of the observed and simulated behaviors is beyond the scope of the present paper. Our current interest is limited to the amplitude and the absolute level of the potential oscillations. It is seen from Figure 2a-c that both models result in potential values rather close to the experimental ones. We note that the value of u suggested by LRE[6] ($u = 10^{-14}$) had to be modified; otherwise no oscillations could have been calculated at the given conditions. Decreasing u to 10^{-16} resulted in only small-amplitude oscillations following a long induction period. For the present calculations $u = 10^{-18}$ was applied. Further decrease of u to 10^{-20} had no significant effect on the calculated behavior. Since fitting of calculated curves to experimental ones was not our original aim, we did not try to find the optimal value for parameter u.

A New Semibatch Oscillator: The ClO_2−Acetone System with Iodide Inflow. Having been successful in simulating the behavior of the CIA system, we tried to find another chlorine dioxide-based semibatch oscillator by which our explanation for the origin of potential oscillations could be further tested. As the only role of acetone in the CIA system with iodine inflow is to convert iodine to iodide, and since Lengyel et al.[9] observed oscillations in the chlorine dioxide−iodide reaction in a continuously fed stirred tank reactor (CSTR), we hoped to find oscillations in a semibatch configuration as well. First we flowed iodide into a semibatch reactor containing only the acidic solution of ClO_2. It seems, however, that the accumulation of iodine in the absence of acetone prevents oscillations.[26] On the other hand, when iodide is flowed into our standard initial mixture containing acetone, too, oscillations are easily produced. A typical example for potential oscillations in such a system and the related model calculations are shown in parts a and b,c of Figure 3, respectively.

In Table 3 the characteristics of the measured and calculated potential oscillations are compared.

The dynamical behavior of the new semibatch oscillator with iodide inflow is rather similar to the CIA reaction with iodine inflow. Even the deviations of the experimental results from the model predictions are similar in character. An important difference between the two CIA oscillators is that while the rate of the iodine inflow is fixed (by the applied membrane), the iodide inflow can be easily controlled. This allowed us to run experiments at different flow rates and then to compare the measured and calculated amplitude and period of the potential oscillations as a function of iodide inflow.

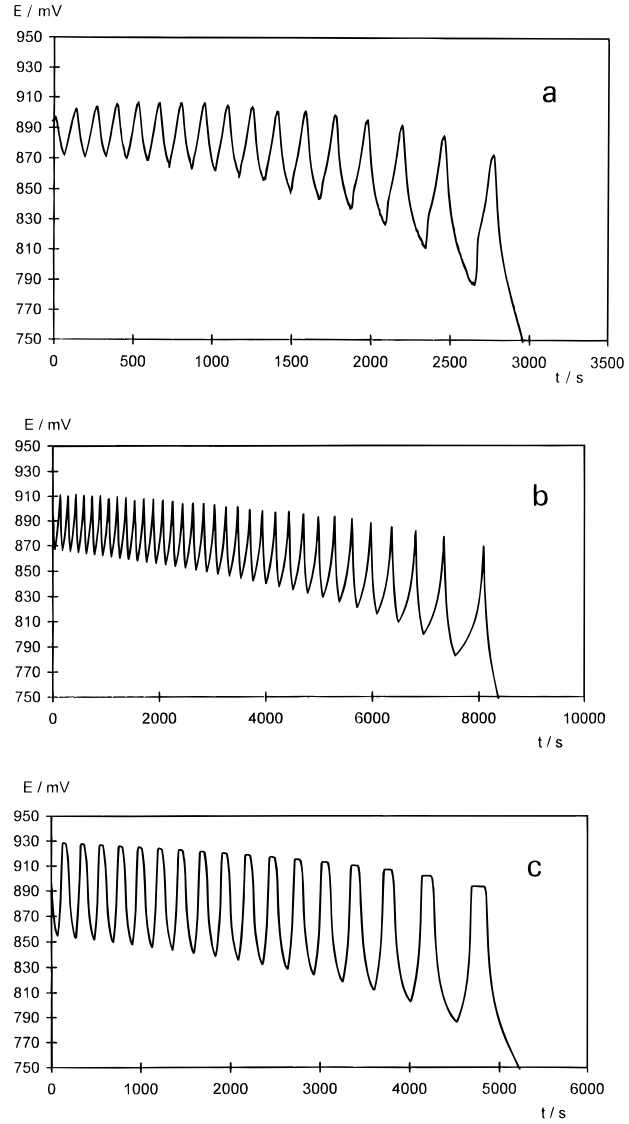

Figure 3. (a) Experimental potential oscillations of the platinum electrode in a semibatch CIA system with iodide inflow. Initial concentrations: $[ClO_2]_0 = 1.3 \times 10^{-4}$ M, $[H_2SO_4] = 3.3 \times 10^{-3}$ M, and [acetone] = 0.55 M. Iodide inflow rate: 3.3×10^{-8} M s^{-1}. (b) Potential oscillations calculated by the LRE model. (c) Potential oscillations calculated by the LLKE model.

TABLE 3: Measured and Calculated Potential Oscillations of the Platinum Electrode in a CIA System with Iodide Inflow (3.3×10^{-8} M s^{-1})

	Figure	period[a] (s)	duration[b] (s)	no.[c]	amplitude[d] (mV)
experiment	3a	125	2720	16	37
LRE model	3b	153	8090	33	48
LLKE model	3c	211	4670	17	77

[a] Average period of oscillations during the first 1000 s of the reaction. [b] Time of the last maximum. [c] Total number of the potential maxima (excluding the extremum at $t = 0$). [d] Averaged over the first 1000 s of the reaction.

Figure 4 illustrates that our interpretation for the electrode potential variations can also be applied for the new CIA oscillator. Also note in Figure 4a that both the LRE and LLKE models predict the amplitudes of the potential oscillations rather well. An interesting feature of this new oscillator is its high sensitivity to iodide inflow. It is our hope that based on this observation a new, sensitive and highly selective analytical method can be developed for monitoring low iodide levels.

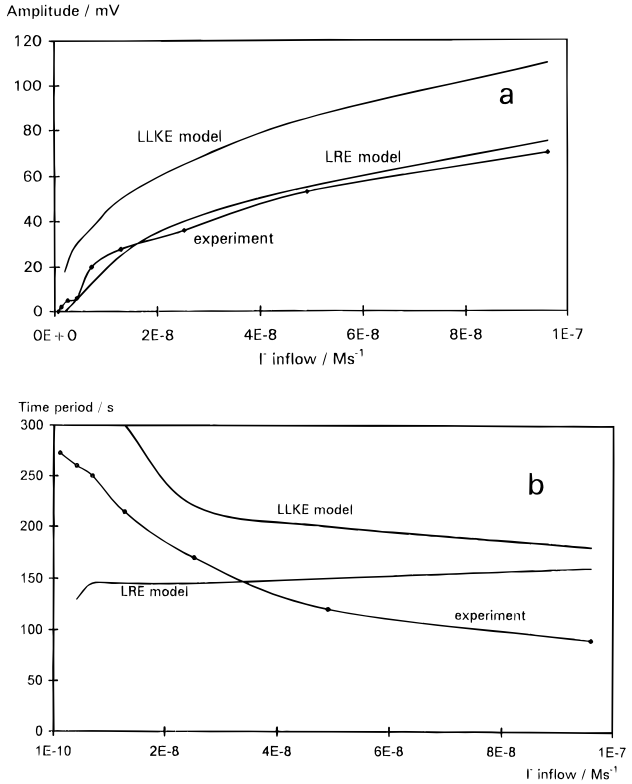

Figure 4. (a) Amplitude and (b) period of the potential oscillations in the new CIA system as a function of the iodide inflow concentration. The symbols show the experimentally obtained values. The amplitude and period were calculated at the same inflow rate values as in the experiments, and the curves shown in the figure were fitted to these points. The experimentally determined Hopf bifurcation[25] point is at 6.45×10^{-10} M s^{-1}. The calculation for the amplitude curve by the LLKE model was interrupted at 2×10^{-9} M s^{-1} because the calculated period became unrealistically large (more than 10^4 s), as shown in the other figure.

Conclusions

(i) Chlorite is an intermediate of crucial importance in ClO_2-based chemical systems. Thus it is highly desirable to be able to measure the chlorite concentration in a sensitive and selective way. According to our observations, in chlorine dioxide-containing systems platinum is basically a Cl(+4)/Cl(+3) redox electrode. Consequently, in ClO_2-based chemical oscillators, where changes in the ClO_2 level are relatively small, platinum can be applied as a sensitive "chlorite selective electrode".

(ii) As Rábai and Epstein[24] pointed out, semibatch reactors with selective inflow of one or few components of an oscillating system are well suited for studying chemical mechanisms with dynamical methods.[25] The new ClO_2-based semibatch oscillator reported here has a control parameter, the iodide inflow, which is easier to vary than the iodine inflow in the previous CIA system. Thus it is also easier to map the dynamical behavior of this new oscillator as a function of the inflow parameter and to compare the experimental results with the theoretical predictions in order to check mechanistic details and rate constants of the different models.

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(20) Calculation of the total chlorite concentration for the calibration curve:

$$[\mathrm{Cl}(+3)]_T = [\mathrm{Cl}(+3)]_A + [\mathrm{Cl}(+3)]_P = \frac{1}{2}\left\{[\mathrm{Cl}(+3)]_A + \sqrt{[\mathrm{Cl}(+3)]_A^{\,2} + 4\frac{K[\mathrm{ClO_2}][\mathrm{HR}]}{\alpha\,[\mathrm{H^+}]}}\right\}$$

where K is the equilibrium constant of the chlorine dioxide−acetone reaction[21] and [HR] is the acetone concentration.

(21) The value of K was determined from the equilibrium concentration of the total chlorite $[\mathrm{Cl}(+3)]_P = 4.6 \times 10^{-7}$ M produced from acetone in the absence of any added chlorite. The following formula and data were applied:

$$K = \frac{[\mathrm{ClO_2^-}][\mathrm{H^+}][\mathrm{R}]}{[\mathrm{ClO_2}][\mathrm{HR}]} = \frac{\alpha[\mathrm{Cl}(+3)]_P(5.6 \times 10^{-3})[\mathrm{Cl}(+3)]_P}{(1.3 \times 10^{-4})0.55} = \alpha 1.66 \times 10^{-11}\ \mathrm{M}$$

$\alpha = 1$ in the LRE model, while $\alpha = 0.738$ according to the LLKE model for our experimental conditions.

(22) The rate constant k_{ER}^+ was estimated from the initial slope $(dE/dt)_0$ of the electrode potential decrease caused by the addition of the acetone to the reaction mixture. Based on the following two equations

$$\left(\frac{dE}{dt}\right)_0 = -\frac{0.026}{\epsilon}\left(\frac{d[\mathrm{Cl}(+3)]_T}{dt}\right)_0 \text{ (V/s)}$$

and

$$\left(\frac{d[\mathrm{Cl}(+3)]_T}{dt}\right)_0 = k_{ER}^+[\mathrm{HR}][\mathrm{ClO_2}]$$

the value of k_{ER}^+ can be calculated as

$$k_{ER}^+ = -\frac{(dE/dt)_0}{0.026}\frac{\epsilon}{[\mathrm{HR}][\mathrm{ClO_2}]} = 9.5 \times 10^{-5}\ \mathrm{M^{-1}\ s^{-1}}$$

as the measured initial slope was

$$(dE/dt)_0 = -1.1 \pm 0.1\ \mathrm{mV/s}$$

The value of k_{ER}^- was calculated from k_{ER}^+ and the equilibrium constant K:

$$k_{ER}^- = \frac{k_{ER}^+}{K} = \frac{9.5 \times 10^{-5}}{\alpha 1.66 \times 10^{-11}} = \frac{5.7 \times 10^6}{\alpha}\ \mathrm{M^{-2}\ s^{-1}}$$

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(25) In ideal open systems like in CSTRs all kinds of attractors (also periodic and chaotic ones) may occur in the far-from-equilibrium situation established by the flow, and varying parameters may reveal bifurcations of these attractors. On the other hand, in batch or in semibatch reactors the only possible real asymptotic state is the final point attractor. (In semibatch reactors that state is reached at infinite time and at infinite large volume.) However, if the advance toward the real steady state is slow, one may introduce the concept of pseudosteady states: the pseudoattractor is given by the early behavior of the system, but its characteristics are slowly drifting because of the evolution toward equilibrium. This way we can speak about the bifurcations of these pseudoattractors and reveal them performing separate experiments by varying initial concentrations in batch or varying inflow concentrations in semibatch.

(26) One of our referees is aware of some unpublished results according to which oscillations can be obtained also in the absence of acetone when diluted iodide solution is flowed into ClO_2 solution at low concentration of H^+. A systematic search to find the right conditions is in progress.

(27) In Palmer, D. A.; van Eldik, R. *Inorg. Chem.* **1986**, *23*, 928, the rate of iodine hydrolysis is much higher, which is certainly more realistic than the rate law given in the LLKE model (reaction M2). Besides, we are aware of the result of I. Fábián and G. Gordon (submitted to *Inorg. Chem.*) concerning the reaction between ClO_2 and iodide (R1, M1) that gives a 3 times slower rate. As the main scope of this work was to explain the platinum oscillations, such modifications in the rate constants that require a systematic screening of all steps are postponed for a separate study.