The Chlorate–Nitrous Acid–Iodine–Iodide Oscillating Reaction
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ABSTRACT: This work presents a new oscillating reaction based on chlorate and observed in a CSTR at room temperature. This can be the first member of a new family of oscillating reactions. In addition, it is also the first oscillating reaction to use nitrous acid as a reactant. Four different behaviors were observed: simple oscillations, mixed mode oscillations, bursts, and quasiperiodicity. The period of oscillations is very short, which is around 1 s. Together with the fact that it also shows fast bursts, it opens the possibility that it can be used to simulate fast biological events, like the neuron’s communications signals.

1. INTRODUCTION
An oscillating reaction is a very special behavior, which can be found in nature and in the laboratory. Since its first observation in laboratory,1–5 it has been considered a simpler version of similar phenomena observed in the life world.6,7 Despite the fact that this area can be now considered mature and the research should focus more on applications,7,8 the discovery of a new oscillation reaction is still a remarkable event. The first two oscillating reactions observed in laboratory, the Bray–Liebhafsky reaction, BL (iodate–hydrogen peroxide reaction),1,2 and the Belousov–Zhabotinsky reaction, BZ (bromate–malonic acid–Ce(IV) reaction),3,4 were discovered accidentally, and many reactions discovered later were the result of changes in the composition of the BZ reaction, where the structure “bromate–organic substrate–metallic catalyst” was maintained.9 Some oscillating reactions arose after the coupling of two other oscillating reactions, such as the Briggs–Rausher reaction, which is a junction of the BL and the BZ oscillating reactions.3 Boissonade and De Kepper10 proposed a systematic method to find new oscillating reactions, and the first one discovered by this method was the arsenite–iodate–chlorite reaction11 and then substitutions of arsenite and/or iodate by other species allowed the discovery of a large number oscillating reactions.

Oscillating reactions can be classified in several different ways. They can be pH oscillators,12–14 oscillators that produce periodic luminescence,15 some reactions can be affected by light16,17 or oxygen,18 and many other aspects can be considered as a criterion. Among several possibilities, the classification by the oxidant component is one of the most common, and in this case, the biggest group is the bromate-driven oscillating reactions,19,20 which is based on modifications of the BZ reaction3,4 by changing the original malonic acid by other organic21–23 or inorganic compounds24 or by changing (or eliminating) the original metal-ion catalyst.6

Another big family of oscillating reactions is based on chloride.25,26 Although the BL reaction1,2 was the first oscillating reaction to be discovered, the family of oscillating reactions based on iodate has a few examples.7 Because chlorine, bromine, and iodine can present many different oxidation states, this favors the buildup of complex reaction networks, containing autocatalytic and a feedback sequence of reactions, which favor the emergence of the oscillating behavior. Although there are some oscillating reactions that do not have any halogen species,27 most of them contain halogen species. Despite this, until now, no oscillating reaction based on chloride was observed.

In this work, we present the results for a new oscillating reaction, which is based on chlorate and without any organic compound or metal catalyst. It is also the first oscillating reaction to use nitrous acid as a reactant. It was a planned discovery, inspired by the discovery of the chlorate–nitrous acid–iodine clock reaction.28 Considering that this clock reaction presents the autocatalysis necessary to produce oscillations, we managed the experiments to find the conditions that should favor emergence of the oscillating behavior. First, we set up a continuous stirred tank reactor (CSTR), but oscillations were observed only when iodide was

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included as a reactant. The experimental details can be found in the Materials and Methods Section, but it is worth to say that we were not able to determine the exact experimental route to get the oscillations. To observe oscillations, in some cases, it was necessary to observe the system for a long time, until the oscillations show up. The traditional procedure (starting from one stationary state and changing gradually the flow rate) did not lead, immediately, to the observation of bistability or a jump to an oscillation state or a gradual appearance of oscillations. Despite this difficulty, we observed simple oscillations, mixed mode oscillations, bursts, and quasiperiodicity behaviors. The simple oscillations present a period of oscillation, at room temperature, around 1 s, which is significantly smaller than most of the oscillating reactions. Similar high frequency oscillations were observed in the BZ system but only at higher temperatures.29,30

The observation of this oscillating reaction, which is based on chlorate, opens the possibility that other oscillating reactions containing this oxidation species can be discovered in the future, starting a new family of oscillating reactions based on chlorate. The high frequency of the oscillations shown by this nonlinear chemical system and the fact that it also shows fast bursts open the possibility that it can be used to simulate fast biological events, like the neurons communications signals, as has been suggested previously.31,32 Despite the fact that nerve impulses have an electrical nature and propagates over the cell’s membrane, the analogy with the nonlinear behavior of autocatalytic chemical systems can be very useful and has been recognized before.33

2. RESULTS AND DISCUSSION

Figure 1 shows different behaviors for the chlorate–nitrous acid–iodine–iodate system at a flow rate, \( k_f \) equal to 3.3 \( \times 10^{-3} \) s\(^{-1} \), with different stirring rates. The zero time in each figure is arbitrary, as the behaviors presented in these figures were observed after a variable time of observation.

As can be seen in Figure 1b,c, simple mode oscillations, with a period of oscillation equal to 1.2 s, were observed at 60 rpm, and 1\(^1\) mixed mode oscillations appeared when applying a slightly lower stirring rate (46 rpm). When applying a higher stirring rate, the oscillations disappear, as shown in Figure 1a.

The result presented in Figure 1a cannot be seen as a surprise. The disappearance of oscillations at a higher stirring rate has been observed by several authors in batch and in flow regimes for different chemical systems. Dutt and Müller34 have shown that the stirring rate is a control parameter that can make the bromate–gallic acid–ferroin system jump from the oscillatory behavior to the steady state, in a CSTR, when increased. For the chlorite–iodide system, in a CSTR, the disappearance of oscillations by increasing the stirring rate is well documented,35,36 and it was demonstrated that the maximum stirring rate in this system is dependent on the initial concentration of the reagents, pH, and \( k_f \). For the BZ system, several authors have reported the suppression of oscillations at a high stirring rate, especially when the reactor is open to the atmosphere.37

The explanation for the stirring rate effect on oscillating reactions has been the object of a long debate. In systems open to the air, the exchange of oxygen between the solution and atmosphere has been considered initially as the reason, mainly in the BZ system, which is known to be sensible to oxygen.38 However, systems under an inert atmosphere also showed sensitivity to the stirring rate.39,40 The presence of macroscopic heterogeneous regions produced by spontaneous nucleation-induced fluctuations, associated with micromixing theory, has also been considered the reason for stirring effects.36,41 In our case, as the system does not have any organic substrate like the BZ system, we consider that the main reason for the stirring effect is the nucleation-induced fluctuations, which are necessary for the oscillations to occur and which are reduced at a higher stirring rate.35

Figure 2 shows the results at a smaller \([\text{ClO}_3^-]_0\) higher flow rate, and different stirring rates. In this case, using a stirring rate equal to 60 rpm, simple mode oscillations were observed with a period of oscillation, approximately, 1 s. Moreover, as shown in Figure 2b, increasing the stirring rate to 82 rpm produced a sequence of bursts, with each one containing six oscillations of increasing and decreasing intensity. These results show that this system can present a rich set of different dynamic behaviors on a very narrow range of the stirring rate.

A change in the oscillating frequency, amplitude, and shape as a function of the stirring rate is known for the BZ system in batch.39,40 A change in the pattern of oscillation has also been reported in this system in batch41 and in CSTR.34 In the chlorite–iodide system, the pattern of oscillation can also be modified by changing the stirring rate, as shown by Menzinger and Giraudi.35 It means that the different oscillation patterns shown in Figures 1b,c and 2, which are obtained by changing the stirring rate, is not a new fact. However, as far as we know, there is no report of the observation of mixed mode
oscillations or bursts, which has been obtained by changing the stirring rate.

The effect of the flow rate was studied using the same concentrations employed in Figure 2 and a stirring rate equal to 60 rpm. As shown in Figure 3, when decreasing the flow rate to $3.33 \times 10^{-3}$ s$^{-1}$, two different oscillatory patterns were observed: simple mode oscillations and $1^1$ mixed mode oscillations. This is a very special situation because without any change of the experimental conditions, while observing the system during some time, the pattern changes from simple mode oscillation to $1^1$ mixed mode oscillations, back and forth. A clearer view of this behavior can be seen in Figure S1, at the same flow rate and chlorate concentration used in Figure 1b.

Increasing the flow rate to $4.17 \times 10^{-3}$ and $5.00 \times 10^{-3}$ s$^{-1}$, this same alternation of behavior was observed, as shown in Figures 4 and 5, respectively. However, at these higher flow rates, three different oscillatory patterns were observed: simple mode oscillations, $1^1$ mixed mode oscillations, and bursts. The simple mode oscillation pattern shown in Figure 4a is shown before in Figure 2a, but in Figure 4a, we present the results at additional wavelengths. Figure 4b indicates that this system also presents a quasiperiodic behavior, which is overlapped with $1^1$ mixed mode oscillations and simple oscillations. Quasiperiodicity was also observed at the same conditions of Figure 1b, as shown in Figure S2.

It is worth to say that the observation of different patterns of oscillation at the same experimental conditions pushed us to check the stability of the syringe pump and the stirring rate. While it was easy to be sure that the syringe pump was stable and reliable, it was more difficult to be sure that the stirring rate did not suffer from small variations and this can be the reason we observed more than one oscillation pattern at the same experimental conditions. This idea is supported by the results shown in Figures 1 and 2, which indicates that the oscillation patterns shown by this system is quite sensible to the stirring rate. However, it is also possible that the experimental conditions are such that the system is very close to a frontier of conditions that establish different behaviors and the unavoidable concentration fluctuations inside the reactor can be the reason for the change of behavior.
Absorbances at 288 and 358 nm are mainly related with the triiodide concentration and at 460 nm with the iodine concentration. These species are in fast equilibrium by the reaction indicated by eq 1 ($K = 721$, $I = 1.0 \text{ mol L}^{-1}$).42 As the triiodide molar absorptivity ($\lambda_{\text{max}} = 288 \text{ nm}, \varepsilon = 40,000 \text{ M}^{-1} \text{ cm}^{-1}; \lambda_{\text{max}} = 351 \text{ nm}, \varepsilon = 27,000 \text{ M}^{-1} \text{ cm}^{-1}$)42 is much higher than that for iodine ($\lambda_{\text{max}} = 460 \text{ nm}, \varepsilon = 740 \text{ M}^{-1} \text{ cm}^{-1}$),43 the oscillations were most easily observed at 288 or 358 nm and mixed mode oscillations and bursts were observed only at these wavelengths.

$$I_2 + I^- \rightleftharpoons I_3^- \quad (1)$$

As can be seen in Figures 4a and 5a, the oscillations at 288 and 358 nm are in phase, confirming that both belong to the same species, which we assign to the triiodide. Figure 4a shows that the oscillations at 460 nm are synchronized with the oscillations at 288 and 358 nm but in opposite directions. This can be explained considering that the total iodine concentration ([$I_2$] + [$I_3^-$]) is almost constant, and the oscillations are indeed in the iodide concentration. When iodide is formed, the iodine is converted to triiodide and the absorbances at 288 and 358 nm increase and the absorbance at 460 nm decreases. When iodide is consumed, iodine is set free and the absorbances change in the opposite direction.

As the starting point for the discovery of this oscillating reaction was the chlorate--nitrous acid--iodine--iodide system,28 it is reasonable to consider that the mechanism for the chlorate--nitrous acid--iodine--iodide oscillation reaction is based on the same reactions. In this mechanism,28 the reaction between chlorate and nitrous acid produces chlorite, which is immediately converted to HClO$_2$. This species starts a sequence of reactions with iodide, HOI, and HIO$_2$ that includes an autocatalytic sequence on HOI and HOCl (reaction 7, which is the sum of reactions 4, 5, and 6), which should be responsible for the nonlinear dynamics shown by this oscillating reaction.

$$\text{ClO}_3^- + \text{HNO}_2 \rightarrow \text{ClO}_2^- + \text{NO}_2^- + \text{H}^+ \quad (2)$$

$$\text{HClO}_2 \rightleftharpoons \text{ClO}_2^- + \text{H}^+ \quad (3)$$

$$\text{HClO}_2 + I^- + \text{H}^+ \rightarrow \text{HOC}_2 + \text{HOI} \quad (4)$$

$$\text{HClO}_2 + \text{HOI} \rightarrow \text{HIO}_2 + \text{HOC}_2 \quad (5)$$

$$\text{HOCI} + I^- \rightarrow \text{Cl}^- + \text{HOI} \quad (6)$$

$$2 \text{HClO}_2 + \text{HOC}_2 + 2 I^- + \text{HOI} + \text{H}^+ \rightarrow 2 \text{HOC}_2 + 2 \text{HOI} + \text{HIO}_2 + \text{Cl}^- \quad (7)$$

In a more recent work from our group,44 it was shown that the reaction between HClO$_2$ and HOCl can form the radical ClO$_2^*$, which reacts with nitrous acid to form the radical NO$_2^*$ that regenerates some nitrous acid, as shown by reactions 8 to 11 below. Considering that radical reactions are usually fast, this can be one of the reasons why we observed high frequency oscillations at room temperature. In addition, this oscillating reaction uses iodide as a reactant, differently from the chlorate--iodine--nitrous acid clock reaction. As this ion is easily oxidized and its concentration is, approximately, 30 times greater than iodine concentration, this can be an
additional reason to speed up the kinetic of this nonlinear system to produce high frequency oscillations.

\[
\text{HClO}_2 + \text{HCl} \rightarrow \text{ClO}_2\text{ClO} + \text{H}_2\text{O} \tag{8}
\]

\[
\text{ClO}_2\text{ClO} + \text{HClO}_2 \rightarrow 2 \text{Cl}_2^+ + \text{Cl}^- + \text{H}^+ \tag{9}
\]

\[
\text{ClO}_2^+ + \text{HNO}_2 \rightleftharpoons \text{HClO}_2 + \text{NO}_2^- \tag{10}
\]

\[
2 \text{NO}_2^- + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{NO}_3^- + \text{H}^+ \tag{11}
\]

### 3. CONCLUSIONS

We present the first chlorate-based oscillating reaction, which can be the first member of a new family of chlorate-based oscillating reactions. In addition, it is the first oscillating reaction that uses nitrous acid as a reactant. This system was investigated in the flow regime (CSTR) and has shown different dynamic behaviors, such as simple oscillations, mixed mode oscillations, bursts, and quasiperiodicity, with some of them at the same experimental conditions. It was also observed that the stirring rate can be very determinant to the dynamic pattern observed. These results indicate that this system has the potential to produce several different dynamic behaviors.

The very short oscillation period, close to 1 s, puts this system between the fastest chemical oscillating reactions and as a good candidate to simulate and to help understand the very fast chemical concentration pulses observed in biological systems. In addition, as the complex oscillations that we report for the title system do not last a long time and also changes, spontaneously, to another pattern of oscillation, this behavior is more similar to some biological events like neurons spontaneously, to another pattern of oscillation, this behavior is more similar to some biological events like neurons sequences of burst of pulses, and make this system attractive for mimetic studies of some biological systems.

### 4. MATERIALS AND METHODS

All reagents were of analytical grade and were used as received: NaClO₃ (Vetec), NaI (Isolar), I₂ resublimed (Control Tec), NaNO₂ (Carlo Herba), and HClO₄ (Vetec). All solutions were made using water previously distilled and deionized. The concentration of perchloric acid was determined by titration made using water previously distilled and deionized. The iodine system at the same experimental conditions. It was also observed that the stirring rate can be very determinant to the dynamic pattern observed. These results indicate that this system has the potential to produce several different dynamic behaviors.

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The reagents' solutions were divided in three syringes: (A) NaClO₃ and NaI; (B) NaNO₂; and (C) I₂ and HClO₄. Solutions A and C were prepared every day before use, and solution B was prepared every week. All solutions were stored out of light. The nitrite ion was converted to HNO₂ by the reaction with HClO₄, and the [H⁺] indicated in the experiments is equal to [HClO₄]₀ − [NaNO₂]₀. The initial concentrations of the reagents indicated in the experiments are the concentrations after mixing equal volumes of solutions A, B, and C inside the reactor and considering that no reaction occurred between them.

All experiments followed the same experimental protocol. Initially, the reactor was empty and a high flow rate (k₀ = 0.040 s⁻¹) was used to fill it. After the reactor was full, the flow rate was decreased to the intended flow rate.

The noise level for the experimental setup can be inferred by the trace observed in Figure 1a, when the system is in a non-oscillatory state. It is an important concern that some kind of noise can be mistaken with regular oscillations or with a complex pattern of oscillations. As can be seen by comparison of all figures with Figure 1a, the amplitude of the observed oscillations is much higher than the noise observed in Figure 1a.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c00933.

Additional figures showing the alternation of behavior and quasiperiodicity for the chlorate-nitrous acid-iodine-iodide system at the same conditions of Figure 1b (PDF)

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