Communication

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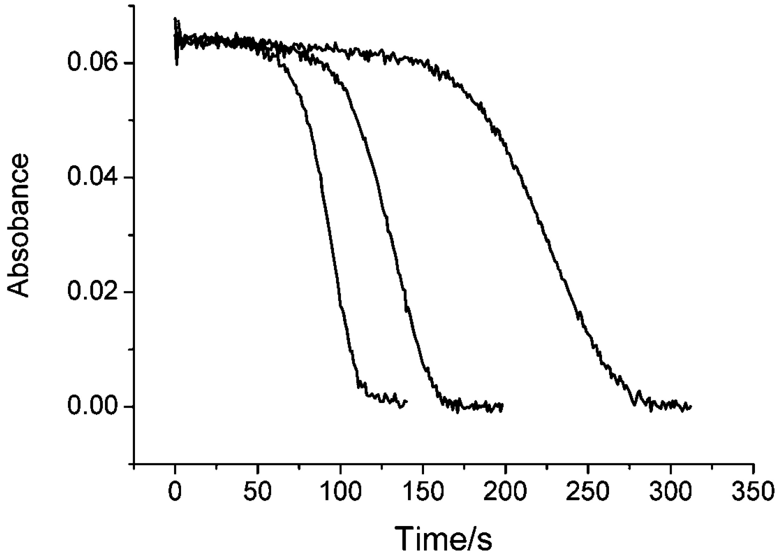

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The Chlorate−Iodine Clock Reaction

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Clock reactions are a special class of chemical phenomena characterized by an abrupt change in the concentration of some chemical species after an induction period. One of the best known of these is the Landolt clock reaction between sulfite and excess of iodate.[1] In the presence of starch, after the sulfite is exhausted, a sudden formation of a blue color occurs, due to the lack of sulfite to reduce the formed iodine to iodide. Substituting arsenite for sulfite produces another very well-known clock reaction,[2] which works by the same principle (i.e., after the arsenite is exhausted the iodine appears).

The sudden formation of iodine is not a simple question of stoichiometry. In the case of the Landolt reaction, the clock behavior is a consequence of autocatalysis by iodide and H^+, both formed in the reaction between iodine and sulfite.[3] The iodate−arsenite reaction has been shown to have a cubic autocatalysis.[4] This points to the importance of clock reactions as these can be the core of other nonlinear phenomena such as oscillations and chaos, which depend on autocatalysis in their mechanisms.[5]

The iodate−bisulfite reaction in the presence of $HgCl_2$ (the Old Nassau reaction)[6] exhibits clock behavior as do the iodate−(aminoimino)methanesulfinic acid[7] and the periodate−dithionate reactions.[8] Bromate undergoes clock reactions with iodide,[9] iodine,[10] bromite in the presence of phenol,[11] sulfite,[12] thiourea,[13] *N*-acetylcysteine,[14] guanylthiourea,[15] and (aminoimino)methanesulfinic acid,[16] and bromite shows clock behavior with iodide.[17] Clock reactions involving oxychlorides include chlorite reactions with iodide,[18] bromide,[19] iodine,[20] thiourea,[21] and hydroxymethanesulfinic acid,[22] and chlorine dioxide reactions with iodide[23] and thiocyanate.[24] Clock reactions not involving oxyhalide are the Ce(IV)−dithionate,[8] formaldehyde−sufite/bisulfate,[25] arsenite−thiosulfate,[26] arsenate−thiosulfate,[26] and Fe(III)/*p*-phenylenediamine−thiosulfate reactions.[27] Several of the above systems can also show oscillations in batch or in CSTR as, for example, the ClO_2-I^- system.[23]

As far as we know, no clock behavior is known for systems based on chlorate. There are reports on propagating wave fronts (an autocatalytic phenomenum) in systems containing chlorate and sulfur species such as sulfite,[28] tetrathionate, and dithionate.[29] However, there are no reports of clock behavior for these systems. Therefore, it remains unknown if clock behavior for these systems necessarily occurs.

In this communication, we report the first clock reaction involving chlorate, namely the chlorate−iodine reaction. This reaction was discovered while we were investigating the kinetics of the chlorate−iodide reaction, which will be described in a future article. This study has not yet been completed, but the discovered clock reaction is worth reporting now because it opens the possibility that oscillating reactions can be built employing chlorate.

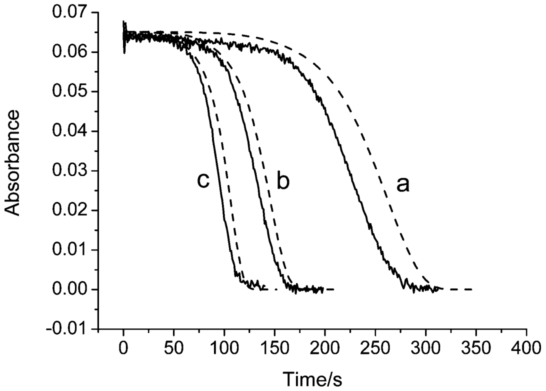

Figure 1. Effect of chlorate. $[I_2] = 8.8 \times 10^{-5}$ M; $[H^+] = 0.948$ M; $[ClO_3^-] = 0.0083$ M (a), 0.0167 M (b), 0.025 M (c). Continuous line: experimental; dash: model simulation.

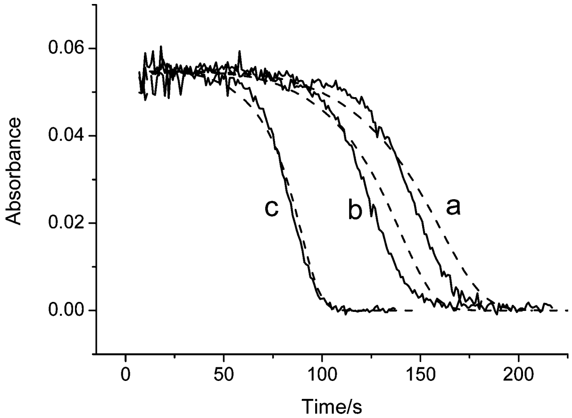

Figure 2. Effect of H^+. $[I_2] = 7.4 \times 10^{-5}$ M; $[ClO_3^-] = 0.033$ M; $[H^+] = 0.237$ M (a), 0.356 M (b), 0.948 M (c). Continuous line: experimental; dash: model simulation.

The reaction was followed at the maximum of the I_2 absorption spectra, 460 nm ($\epsilon = 740$ M^{-1} cm^{-1}).[20] Aqueous solutions of $NaClO_3$, iodine, and $HClO_4$ were sequentially added to a thermostatable and magnetically stirred quartz cuvette at 25 ± 0.1 °C inside an HP 8452A diode array spectrophotometer. Reagents were of the best quality available and were used without purification.

Figure 1 shows the effect of changing the initial concentration of chlorate. As can be seen, an increase in the concentration decreases the induction time. The effect of changing $[H^+]_0$ is similar, as can be seen in Figure 2. However, changing the initial iodine concentration does not show a significant change in the "clock time", as can be seen in Figure 3.

To explain the clock reaction behavior, we use the LLKE mechanism[30] proposed for the chlorine dioxide/chlorite−iodide reaction and the following reactions:

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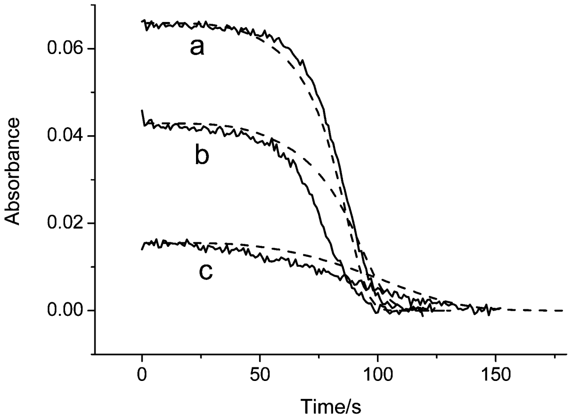

Figure 3. Effect of iodine. $[H^+] = 0.948$ M; $[ClO_3^-] = 0.033$ M; $[I_2] = 8.9 \times 10^{-5}$ M (a), 5.8×10^{-5} M (b), 2.1×10^{-5} M (c). Continuous line: experimental; dash: model simulation.

$$ClO_3^- + I^- + 2H^+ \rightarrow HOI + HClO_2 \ (k = 0.1\ M^{-3}\ s^{-1}) \quad (1)$$

$$ClO_3^- + HOI + 2H^+ \rightarrow HIO_2 + HClO_2 + H^+ \ (k = 18.5\ M^{-3}\ s^{-1}) \quad (2)$$

$$ClO_3^- + HIO_2 \rightarrow IO_3^- + HClO_2 \ (k = 7\ M^{-1}\ s^{-1}) \quad (3)$$

$$ClO_3^- + H_2OI^+ \rightarrow HClO_2 + HIO_2 \ (k = 0.28\ M^{-1}\ s^{-1}) \quad (4)$$

Submitting the full mechanism to a numerical integration using a semi-implicit Runge−Kutta method,[31] we obtained very good agreement with the experimental changes in absorbance at 460 nm, using $\epsilon = 740$[20] and 975 $M^{-1}\ cm^{-1}$,[32] for I_2 and I_3^-, respectively (see Figures 1−3).

On the basis of these numerical integration results, we can describe the chlorate−iodine clock reaction as being produced by the attack of iodide (produced by the iodine hydrolysis) on chlorate, which forms HOI. This species reacts with chlorate, forming HIO_2, which also reacts with chlorate. This produces an autocatalytic consumption of chlorate. The reaction with iodide creates a product (HOI), which reacts with chlorate, forming a product (HIO_2), which also reacts with chlorate. The induction period is the time taken to form the necessary amounts of HOI and HIO_2 to trigger the autocatalytic sequence, which produces the observed clock behavior. Reaction 4, as does reaction 2, produces HIO_2, but involves a different order in H^+ that helps to correctly simulate the effect of changing the initial H^+ concentration. The rate constants for reactions 1−4 were adjusted to obtain the correct simulation because there are no values for these reactions in the literature.

Because clock reactions are at the core of many oscillation systems, studies are being continued in our laboratory to find the first oscillating reaction using chlorate as a main reagent. If this is attained, it can lead to a new family of oscillation reactions based on chlorate.

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