Clock Reactions

Conference Paper · December 2010

CITATIONS
0

READS
1,972

1 author:

Guy Schmitz
Université Libre de Bruxelles
84 PUBLICATIONS **818** CITATIONS

SEE PROFILE

Clock reactions

Guy Schmitz

Faculty of Applied Sciences, Université Libre de Bruxelles, CP165/63, Av. F. Roosevelt 50, 1050 Brussels, Belgium. E-mail: gschmitz@ulb.ac.be

ABSTRACT

Clock behaviours, resulting from transitions between different dynamical states, are observed in many different chemical systems. Some examples are discussed and compared: the Landolt reaction, the oxidation of Ce(III) by bromate, the reduction of iodate by hydrogen peroxide and the oxidation of iodine by hydrogen peroxide in the absence of iodate. In the last case, the bell rings when a stable steady state suddenly disappears.

CLASSICAL IODINE CLOCK REACTIONS

The hydrogen peroxide-iodide reaction is a simple example of classical clock reaction. When a solution containing potassium iodide, sodium thiosulfate and starch is added to an acidic solution of hydrogen peroxide the reactions are:

$$H_2O_2 + 3\ I^- + 2\ H^+ \rightarrow I_3^- + 2\ H_2O \qquad (1)$$

$$I_3^- + 2\ S_2O_3^{=} \rightarrow 3\ I^- + S_4O_6^{=} \qquad (2)$$

At the beginning, the very fast reaction (2) consumes the triiodide ions as fast as they are produced by reaction (1) and the solution remains colorless. If the initial thiosulfate concentration $[S_2O_3^{=}]_o$ is less than two times the hydrogen peroxide concentration $[H_2O_2]_o$, the thiosulfate ends up being totally consumed. The triiodide ions are no longer consumed by reaction (2) and the blue color of their complex with starch appears. The induction time depends on the ratio $[S_2O_3^{=}]_o/[H_2O_2]_o$ and on the rate of reaction (1). Increasing the initial concentrations of H_2O_2, I^- or H^+ decreases the induction time.

This example illustrates a first kind of clock reactions. The induction period ends up when a reactant has been totally consumed. This is also the case of the most famous clock reaction, the Landolt reaction [1-4]. In a mixture of a potassium iodate solution and a slightly acidic solution of sodium bisulfite the first reaction is (3).

$$2\ IO_3^- + 5\ HSO_3^- \rightarrow I_2 + 5\ SO_4^{=} + 3\ H^+ + H_2O \qquad (3)$$

The produced iodine reacts very quickly with bisulfite ions.

$$I_2 + HSO_3^- + H_2O \rightarrow 2\ I^- + SO_4^{=} + 3\ H^+ \qquad (4)$$

After a while, so produced iodide reacts with iodate following the classical Dushman reaction (5).

$$IO_3^- + 5\ I^- + 6\ H^+ \rightarrow 3\ I_2 + 3\ H_2O \qquad (5)$$

As long as bisulfite remains in the solution, the iodine is reduced by reaction (4) and the net reaction is (6).

$$IO_3^- + 3\ HSO_3^- \rightarrow I^- + 3\ SO_4^{=} + 3\ H^+ \qquad (6)$$

Thus, the concentration of the iodide ions increases and, consequently, the rate of reaction (5) increases. Reaction (6) is autocatalytic. Moreover, in non-buffered solution, the acidity increases so that the reaction is doubly catalytic or super catalytic. The rate of iodine formation is the largest at the end of the induction period making the Landolt reaction particularly spectacular. When all the bisulfite has reacted, the iodine appearance, or its blue complex with starch, is not progressive as in the other iodine clock reactions but very abrupt. Beautiful demonstrations can be found on the internet but the detailed mechanisms of these reactions are still not completely understood.

THE BROMATE-CEROUS REACTION

Instead of being controlled by the disappearance of some reactant, the induction time of a clock reaction can be controlled by the appearance of some intermediate compound. This is the case of the bromate-cerous reaction. The global reaction is (7) that is the inorganic part of the oscillating Belousov-Zhabotinskii reaction [5, 6]. Figure 1 shows an example of Ce(IV) production versus time.

$$BrO_3^- + 4\ Ce(III) + 5\ H^+ \rightarrow HOBr + 4\ Ce(IV) + 2\ H_2O \qquad (7)$$

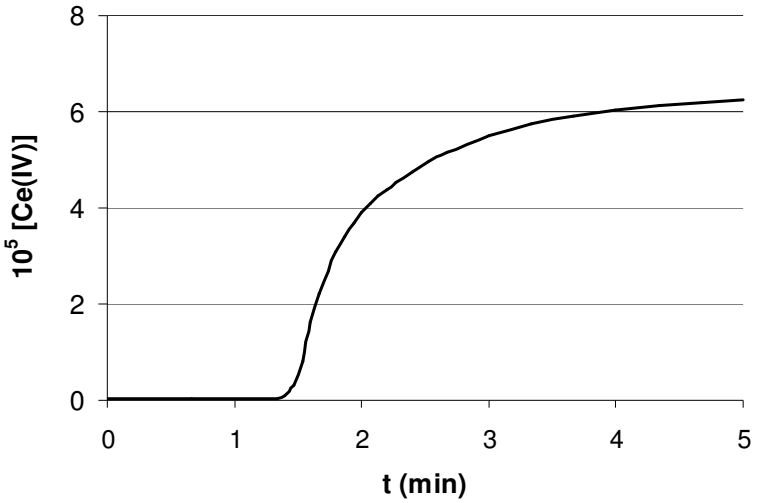

Figure 1. Time evolution of the Ce(IV) concentration. Initial concentrations: $[BrO_3^-]_o = 5\times10^{-2}$, $[Ce(III)]o = 1.68\times10^{-4}$, $[H_2SO_4] = 0.5$ M.

Different mechanisms were proposed to explain this behavior. The Field, Körös and Noyes (FKN) mechanism [7] includes the following steps.

$$BrO_3^- + Br^- + 2\ H^+ \rightleftharpoons HOBr + HBrO_2 \quad (8)$$
$$HBrO_2 + Br^- + H^+ \rightarrow 2\ HOBr \quad (9)$$
$$HOBr + Br^- + H^+ \rightleftharpoons Br_2 + H_2O \quad (10)$$
$$BrO_3^- + H^+ + HBrO_2 \rightleftharpoons 2\ BrO_2^\bullet + H_2O \quad (11)$$
$$BrO_2^\bullet + Ce(III) + H^+ \rightleftharpoons HBrO_2 + Ce(IV) \quad (12)$$
$$2\ HBrO_2 \rightleftharpoons HOBr + BrO_3^- + H^+ \quad (13)$$
$$BrO_2^\bullet + Ce(IV) + H_2O \rightleftharpoons BrO_3^- + Ce(III) + 2\ H^+ \quad (14)$$

The sum 2×(11) + 4×(12) + (13) gives the global reaction (7). Bromate does not react directly with Ce(III) but with $HBrO_2$ giving $BrO_2^\bullet$ radicals in reaction (11) and these radicals oxidize Ce(III) in reaction (12). Thus, the rate of reaction (7) remains very small until some $HBrO_2$ has accumulated in the solution. The initial production of $HBrO_2$ is explained by the traces of bromide ions always present in bromate solutions giving reaction (8). One $HBrO_2$ giving two $BrO_2^\bullet$ radicals in reaction (11) and these two radicals giving two $HBrO_2$ in reaction (12), the reaction is autocatalytic. At the end of the induction period, the rate of Ce(III) oxidation increases exponentially.

The KKN mechanism is widely accepted because it allows reproducing by numerical simulations a wide variety of experimental results especially the Belousov-Zhabotinskii oscillations and the oscillations of the bromate-cerous reaction in a CSTR [8-11]. However, the set of rate constants used for these simulations has changed with time and it is far from evident that all the successful simulations supporting this model could be obtained using a single set of rate constants. Very recently, the group of Belgrade has presented a new experimental study of the Belousov-Zhabotinskii oscillations and has shown that the FNK mechanism should be modified [12-13]. The inorganic part of the proposed model does not include reaction (14) and splits reaction (9) introducing Br_2O as an important intermediate compound in the organic part of the model.

$$HBrO_2 + Br^- + H^+ \rightarrow Br_2O + H_2O \quad (9')$$
$$Br_2O + H_2O \rightleftharpoons 2\ HOBr \quad (9")$$

Reaction (8) is neither elementary [14] and must be split into

$$BrO_3^- + Br^- + 2\ H^+ \rightleftharpoons Br_2O_2 + H_2O \quad (8')$$
$$Br_2O_2 + H_2O \rightleftharpoons HOBr + HBrO_2 \quad (8")$$

These reactions suggest an analogy with the well-known chlorine system. We have proposed [15] that $BrO_2^\bullet$ is produced in a reaction similar to the reaction producing $ClO_2^\bullet$ [16, 17] and that reaction (11) should be replaced with reaction (15).

$$HBrO_2 + Br_2O_2 \rightleftharpoons 2\ BrO_2^\bullet + Br^- + H^+ \quad (15)$$

Reaction (15) leads also to an autocatalytic increase of the $HBrO_2$ and here too further kinetic studies are necessary.

INDUCTION PERIOD OF THE BRAY-LIEBHAFSKY REACTION

The oscillating Bray-Liebhafsky (BL) reaction [18] is the decomposition (D) of hydrogen peroxide catalyzed by iodate in acidic solutions.

$$2\ H_2O_2 \xrightarrow{IO_3^-,\ H^+} 2\ H_2O + O_2 \qquad (D)$$

Reaction (D) is the result of two reactions where hydrogen peroxide acts as a reducing (R) and as an oxidizing (O) agent. The sum of reactions (R) and (O) gives reaction (D).

$$2\ IO_3^- + 2\ H^+ + 5\ H_2O_2 \rightarrow I_2 + 5\ O_2 + 6\ H_2O \qquad (R)$$
$$I_2 + 5\ H_2O_2 \rightarrow 2\ IO_3^- + 2\ H^+ + 4\ H_2O \qquad (O)$$

When the rates of these two reactions are equal, the decomposition of hydrogen peroxide is monotonous. However, under some conditions, the reactions (R) and (O) dominate alternately resulting in a cascading consumption of hydrogen peroxide and an oscillatory evolution of the intermediates [5, 19-22]. The concentration of one of them, the iodide ions, can be followed easily using a selective ions electrode, whereas another one, the iodine, can be followed spectrophotometrically. Figure 2 gives an example of measured time evolution of iodide and iodine species [23].

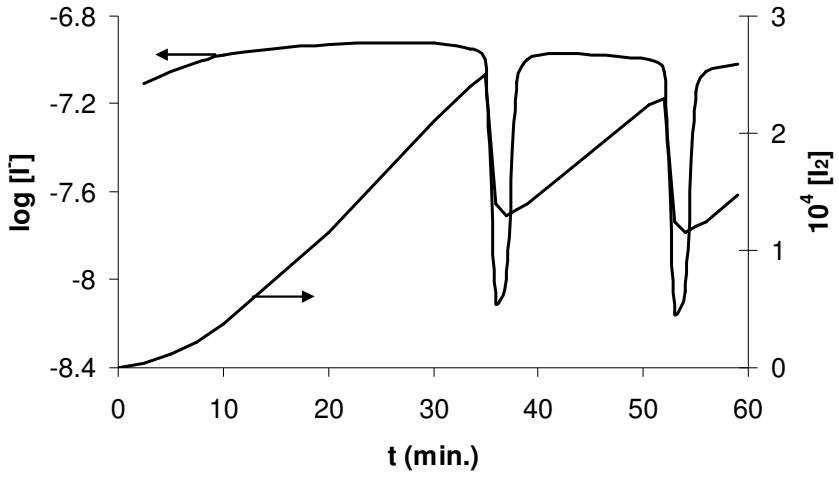

Figure 2. Time evolution of the iodide ions (left hand scale) and of the iodine (right hand scale) concentrations. T = 60°C, $[HClO_4]_o$ = 0.0625 M, $[NaIO_3]_o$ = 0.10 M, $[H_2O_2]_o$ = 0.050 M.

If we look only at the time evolution of the iodide ions concentration, we could conclude that the reaction begins with an induction period. However, if we look also at the time evolution of the iodine concentration we see that it should rather be called a pre-oscillatory period. It is similar to the following periods of increasing concentration of iodine and is longer only because the initial iodine concentration is zero. Comprehensive studies of this period were presented by S. Anić and Lj. Kolar-Anić [20(c, g, j, l, m)].

INDUCTION PERIOD OF THE IODINE OXYDATION BY HYDROGEN PEROXIDE

In acidic solutions of iodine and hydrogen peroxide containing no iodate, the iodine concentration can remain nearly unchanged for long. Figure 3 shows an example of characteristic time evolution.

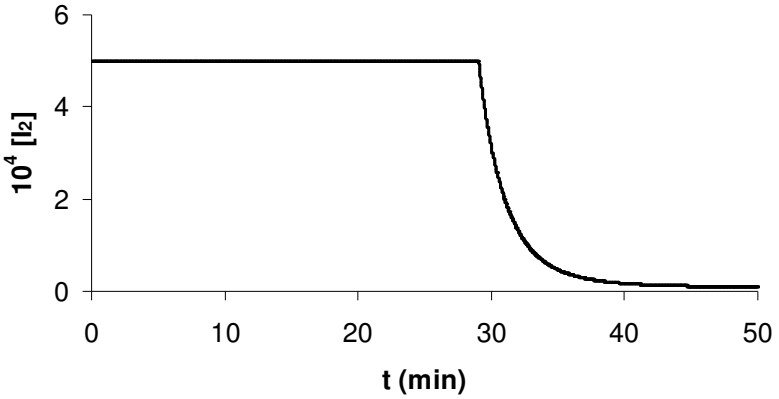

Figure 3. Time evolution of the iodine concentration in a solution containing no iodate initially. $[HClO_4]_o = 0.07$ mol/l, $[H_2O_2]_o = 0.05$ mol/l, $[I_2]_o = 5\times10^{-4}$ mol/l. Curve calculated with the model discussed in reference 24.

An induction period is observed because there is no direct reaction between iodine and hydrogen peroxide. The writing of reaction (O) is misleading and the compound actually oxidized by hydrogen peroxide is IOH produced by the iodine hydrolysis (16).

$$I_2 + H_2O \rightleftharpoons IOH + I^- + H^+ \qquad (16)$$

Reaction (O) can start only if the IOH concentration is above a critical level [24] and, taking the equilibrium (16) into account, this means that it can start only if there are reactions removing the iodide ions sufficiently quickly. During the BL reaction, the removal of the iodide ions is provided by reactions of iodate. On the other hand, the model we have proposed to explain the BL oscillations foresees that a mixture of iodine and hydrogen peroxide without iodate reaches a different stable steady state were the only global reaction is slow hydrogen peroxide decomposition. The iodine oxidation by hydrogen peroxide should never start. To explain that it finally starts, we must consider another reaction. Oxygen produced by the hydrogen peroxide decomposition can oxidize the iodide ions.

$$I^- + H^+ + \tfrac{1}{2}\, O_2 \rightarrow IOH \qquad (17)$$

The direct reaction between iodide and oxygen is too slow and reaction (17) is the result of complex processes involving probably radicals. Its mechanism remains unclear but adding it to the model with an empirical rate law $r_{17} = k_{17}\,[I^-][H^+][O_2]$ explains the experimental results [24]. When the oxygen concentration reaches a critical level the mentioned stable steady state disappears and reaction (O) starts. This is a new kind of clock reaction: the bell rings when a steady state disappears.

CONCLUSION

In the classical clock reactions, the clock time is controlled by the disappearance of some reactant, like sulfite in the Landolt reaction, but there are other kinds of clock behaviors. Some examples are summarized in this paper. In the bromate-cerous reaction, the clock time is controlled by the autocatalytic increase of the concentration of an intermediate compound, $HBrO_2$. In the BL reaction, the induction period observed if we measure only the iodide ions concentration appears differently if we measure also the iodine concentration and should rather be named pre-oscillatory period. In the iodine oxidation by hydrogen peroxide a new kind of clock behavior is observed: the clock belles when another reaction destroys the stable steady state of the hydrogen peroxide decomposition. Beyond there differences, all clock reactions involve transitions between different dynamical states. The experimental curves can be analyzed identifying time intervals with identical combination of first and second derivative signs of the time concentrations profiles and this trend analysis can give useful information about the involved dynamical state transitions [25].

REFERENCES

1. H. Landolt, Ber. Dtsch. Chem. Ges., **19**, 1317 (1886).
2. V. Gaspar and K. Showalter, J. Amer. Chem. Soc., **109**, 4869 (1987).
3. E. Edblom, L. Gyorgyi, M. Orban and I. Epstein, J. Amer. Chem. Soc., **109**, 4876 (1987).
4. A. Horvath, J. Phys. Chem. A, **112**, 3935 (2008).
5. *Oscillations and Traveling Waves in Chemical Systems*, R.J. Field and M. Burger, ed., Wiley, New York (1985).
6. S.K. Scott, *Oscillations, Waves and Chaos in Chemical Kinetics,* Oxford University Press (1994).
7. R.J. Field, E. Körös and R.M. Noyes, J. Amer. Chem. Soc., **94**, 8649 (1972).
8. W. Geiseler, Ber. Bunsenges. Phys. Chem. **86**, 721 (1982).
9. K. Bar-Eli and W. Geiseler, J. Phys. Chem. **87**, 3769 (1983).
10. L. Gyorgy and R.J. Field, J. Phys. Chem. **96**, 1220 (1992).
11. A.K. Dutt and M. Menzinger, J. Chem. Phys. **110**, 7591 (1999).
12. S. Blagojević, S. Anić, Ž. Čupić, N. Pejić and Lj. Kolar-Anić, Phys. Chem. Chem. Phys., **10**, 6658 (2008).
13. S. Blagojević, S. Anić, Ž. Čupić, N. Pejić and Lj. Kolar-Anić, Russian J. Phys. Chem. A, **83**, 1496 (2009).
14. G. Schmitz, Int. J. Chem. Kinet., **39**, 17 (2007).
15. G. Schmitz, Can. J. Chem., **54**, 2628 (1976).
16. G. Gordon, R. Kieffer and D. Rosenblatt, Prog. Inorg. Chem., **15**, 201 (1972).
17. R. Kieffer and G. Gordon, Inorg. Chem., **7**, 235 and 239 (1968).
18. (a) W. C. Bray, J. Am. Chem. Soc., **43**, 1262 (1921); W. C. Bray and H. A. Liebhafsky, J. Am. Chem. Soc., **53**, 38 (1931).
19. G. Schmitz, J. Chim. Phys., **84**, 957 (1987).
20. (a) S. Anić, D. Mitić and Lj. Kolar-Anić, J. Serb. Chem. Soc., **50,** 53 (1985); (b) S. Anić, D. Mitić, D. Veselinović and Lj. Kolar-Anić, J. Serb. Chem. Soc., **50**, 529 (1985); (c) S. Anić and Lj. Kolar-Anić, Ber. Bunsenges. Phys. Chem., 90, 539 (1986); (d) S. Anić and Lj. Kolar-Anić, Ber. Bunsenges. Phys. Chem., **90**, 1084 (1986); (e) S. Anić and Lj. Kolar-Anić, Ber. Bunsenges. Phys. Chem., **91**, 1010 (1987); (f) S. Anić, D. Mitić and M. Ćurčija, J. Serb. Chem. Soc., **52**, 575 (1987); (g) S. Anić and Lj. Kolar-Anić, J. Chem.

Soc., Faraday Trans. 1, **84**, 3413 (1988); (h) S. Anić, D. Stanisavljev, G. K. Belovljev and Lj. Kolar-Anić, Ber. Bunsenges. Phys. Chem., **93**, 488 (1989); (i) Lj. Kolar-Anić, D. Misljenović, D. Stanisavljev and S. Anić, J. Phys. Chem., **94**, 8144 (1990); (j) Lj. Kolar-Anić, D. Stanisavljev, G. Krnajski Belovljev, Ph. Peeters and S. Anić, Computers Chem., **14**, 345 (1990); (k) S. Anić and Lj. Kolar-Anić, J. Serb. Chem. Soc., **61**, 885 (1996); (l) S. Anić, Lj. Kolar-Anić and E. Körös, React. Kinet. Catal. Lett., **61**, 111 (1997); (m) S. Anić, D. Stanisavljev, Ž. Čupić, M. Radenković, V. Vukojević and Lj. Kolar-Anić, Science of Sintering, **30**, 49 (1998).

21. G. Schmitz, Lj. Kolar-Anić, S. Anić and Ž. Čupić, J. Phys. Chem. A, **112**, 13452 (2008).
22. Lj. Kolar-Anić, Ž. Čupić, G. Schmitz and S. Anić, Chem. Engineering Sci., **65**, 3718 (2010).
23. G. Schmitz, Thesis, Université Libre de Bruxelles, 1983.
24. G. Schmitz, Phys. Chem. Chem. Phys., **12**, 6605 (2010).
25. Ž. Čupić, D. Lončarević, A. Ivanovic, P. Banković and S. Petrović, Computers Chem. Eng., **32**, 1293 (2008) and references therein.