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Mechanism of the oscillatory decomposition of the dithionite ion in a flow reactor

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A simple mechanism consisting of three protonation equilibria and seven redox reactions between sulfur species can describe the large amplitude-sustained temporal pH-oscillations observed during acid-induced decomposition of the dithionite ion in a continuous-flow stirred tank reactor (CSTR) in the temperature range 25–60 °C.

Dithionite ($S_2O_4^{2-}$) undergoes rather rapid disproportionation in aqueous, oxygen-free solution to form more stable HSO_3^- and $S_2O_3^{2-}$ ions:

$$2S_2O_4^{2-} + H_2O \rightarrow 2HSO_3^- + S_2O_3^{2-} \qquad (1)$$

Colloidal sulfur is transiently visible as an intermediate. Other stable sulfur species (SO_4^{2-}, $S_2O_6^{2-}$, H_2S) are also formed in traces. The rate of the above reaction is greatly affected by the pH, being slow in alkaline medium and rapid at low pH values. The reaction has autocatalytic kinetics: an early induction period is followed by a fast decomposition.[1–7] Moreover, the addition of the products of the reaction to fresh dithionite solution decreases the length of the induction period of the decomposition. HSO_3^- is thought to be the autocatalyst, but H^+ plays the similar role in an unbuffered solution. Under some conditions the rapid stage of the reaction may be interrupted, and the concentration of dithionite ion may level off at some value well above zero. The slowing up of the fast stage has been attributed to the removal of the catalyst by a chemical reaction.[4] It is known that such a kinetic cross effect (autocatalysis and the removal of the catalyst by a composite reaction with appropriate time delay, *i.e.* negative feedback) may result in periodic behavior in a reacting system being far from equilibrium. It has, indeed, been reported that, at elevated temperatures, the concentration of the dithionite ions and the pH show several small peaks in time in the early stages of the reaction, even in a system closed with respect to mass.[8] However, this observation has never been confirmed by other laboratories, though many laboratories have studied the kinetics of $S_2O_4^{2-}$ decomposition under different conditions using different methods.[1–7] Our own efforts repeatedly failed to reproduce pH or redox potential oscillations in a closed reactor when we studied the disproportionation of $S_2O_4^{2-}$ in the concentration range 0.001–0.05 M and in the temperature interval 20–60 °C excluding the air oxygen.[9] Only a minimum followed by a single maximum appeared on the pH–time curves obtained in a closed reactor. Similar traces could be observed in the redox potential, as well. Based on these results, it seems to be probable that the thermal decomposition of aqueous dithionite does not exhibit concentration oscillations in a closed reactor. Of course, this conclusion does not exclude the possibility of periodic kinetics in a CSTR where the reaction is kept far from equilibrium by the continuous flow. We have carried out experiments in a CSTR and have observed large amplitude-sustained pH-oscillations that we report here.

In our experiments, we used a water-jacketed, cylindrical-shaped, glass CSTR with a liquid volume of 30 ml. The CSTR was equipped with a pH electrode and a thermistor to measure both the pH and the temperature inside the reactor. A Teflon-covered magnetic stirrer bar was used to ensure uniform mixing. Two input solutions were prepared daily: one contained $Na_2S_2O_4$ of 85% purity (FLUKA) and NaOH, the other contained dilute H_2SO_4. Decomposition of $S_2O_4^{2-}$ in alkaline solution is slow and its decomposition in the reservoir causes only a small change in behavior during the CSTR experiments. The input solutions were kept from air to avoid any effect of O_2. The reactor was fed with these solutions by means of a Desaga peristaltic pump. The mixing ratio of the two input solutions was 1.0 : 1.0. The time–pH data were collected by a computer through a pH meter and an A/D converter with a sampling rate of 1 Hz.

Concentrations, flow rates and temperature were varied systematically over a wide range in order to find sustained oscillations in the pH and in the redox potential. Oscillations were found within a certain range of experimental parameters. Fig. 1, which was obtained under optimized conditions, shows a complex pH–time curve consisting of double peak periods. The period length of oscillations is about one hour. The amplitude exceeds one pH unit. The oscillations could be maintained in the flow-through reactor for a long time, but some small continuous decrease in the amplitude with time can be seen on the oscillatory curve, which could be due to the slow decomposition of $S_2O_4^{2-}$ in the reservoir. Oscillatory behavior could be observed in a rather wide range of experimental constraints, *i.e.* the temperature (25–60 °C), the input concentration of $S_2O_4^{2-}$, and the flow rate [$(3–20) \times 10^{-4}$ s^{-1}]. The shape of the pH–time curves, the period length, and amplitude also depend on the experimental conditions.

In the following, we suggest a mechanism for the oscillatory decomposition. Selected composite reactions are shown in Table 1. Reactions (1)–(3) are known protonation equilibria. Reaction (4) produces some HSO_3^- that initiates the autocatalytic cycle of (6) and (7). Transient formation of $S_3O_6^{2-}$ and its role in the autocatalytic pathway has been demonstrated by Holman and Bennet with an FTIR method.[10] We assume that the autocatalytic route is moderated by reaction (8), which

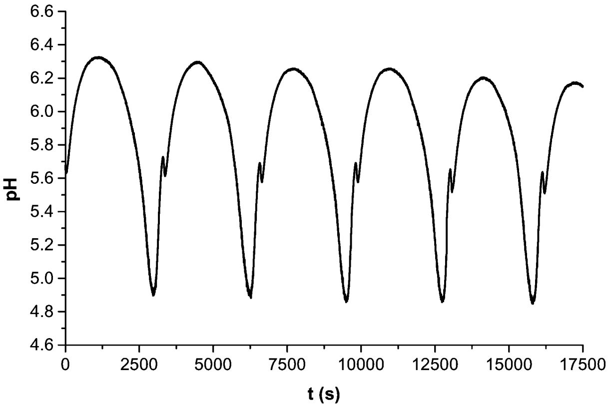

Fig. 1 Measured double peak pH-oscillations in a CSTR. Input concentrations are calculated for the combined feed. $[Na_2S_2O_4]_0 = 0.011$, $[NaOH]_0 = 0.0182$, $[H_2SO_4] = 8.25 \times 10^{-3}$ M, $T = 39.8$ °C, $k_0 = 5.0 \times 10^{-4}$ s^{-1}. The pH of the input $Na_2S_2O_4$ solution containing NaOH was 11.5.

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Table 1 Composite reactions and their rate constants of the $S_2O_4^{2-}$ decomposition

Composite reaction	Rate constant
(1/−1) $S_2O_4^{2-} + H^+ \rightleftharpoons HS_2O_4^-$	$k_1 = 1.0 \times 10^{10}\ M^{-1}\ s^{-1}$
	$k_{-1} = 3.5 \times 10^7\ s^{-1}$
(2/−2) $SO_3^{2-} + H^+ \rightleftharpoons HSO_3^-$	$k_2 = 5.0 \times 10^{10}\ M^{-1}\ s^{-1}$
	$k_{-2} = 3.0 \times 10^3\ s^{-1}$
(3/−3) $SO_2^{2-} + H^+ \rightleftharpoons HSO_2^-$	$k_3 = 1.0 \times 10^{10}\ M^{-1}\ s^{-1}$
	$k_{-3} = 1.0 \times 10^5\ s^{-1}$
(4) $S_2O_4^{2-} + H_2O \rightarrow HSO_3^- + HSO_2^-$	$k_4 = 1.0 \times 10^{-6}\ s^{-1}$
(5) $2HSO_2^- \rightarrow S_2O_3^{2-} + H_2O$	$k_5 = 1.0 \times 10^2\ M^{-1}\ s^{-1}$
(6) $HSO_3^- + HS_2O_4^- \rightarrow S_3O_6^{2-} + H_2O$	$k_6 = 1.0 \times 10^4\ M^{-1}\ s^{-1}$
(7) $S_3O_6^{2-} + H_2O \rightarrow 2HSO_3^- + HSO_2^- + H^+$	$k_7 = 2.0\ s^{-1}$
(8) $S_3O_6^{2-} \rightarrow S_2O_6^{2-} + S$	$k_8 = 0.55\ s^{-1}$
(9) $SO_3^{2-} + S \rightarrow S_2O_3^{2-}$	$k_9 = 1.0 \times 10^2\ M^{-1}\ s^{-1}$
(10) $HSO_3^- + S_2O_3^{2-} \rightarrow SO_4^{2-} + S + HSO_2^-$	$k_{10} = 3.0\ M^{-1}\ s^{-1}$

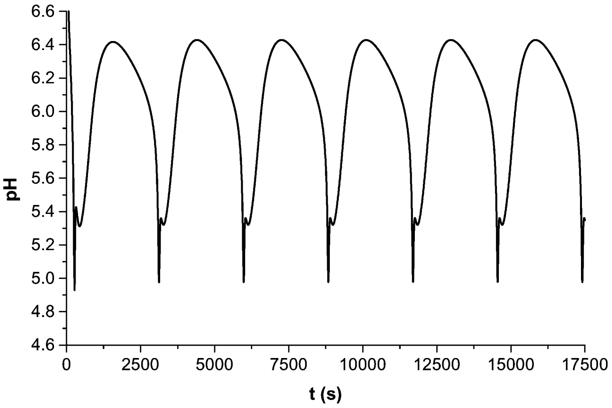

Fig. 2 Calculated pH-oscillations in a CSTR. $[S_2O_4^{2-}]_0 = 0.011$, $[H^+]_0 = 1.0 \times 10^{-7}$ M, $k_0 = 5.0 \times 10^{-4}\ s^{-1}$. Numerical integration was carried out by a semi-implicit Runge–Kutta method with an error parameter of 10^{-5}. Since the 1.0 : 1.0 mixture of the two input solutions was very close to pH = 7 immediately after mixing, we used the $[H^+]_0 = 1.0 \times 10^{-7}$ M value in our calculations.

removes $S_3O_6^{2-}$ from the autocatalytic cycle by transferring it to the much less reactive $S_2O_6^{2-}$. Reaction (10) is also an important negative feedback process because it removes HSO_3^- from the autocatalytic cycle. The governing role of H^+ is also reflected by this mechanism. Since the protonated $HS_2O_4^-$ reacts much faster with HSO_3^- than $S_2O_4^{2-}$ does, the overall process accelerates with increasing H^+ concentration.

The mechanism shown in Table 1 can account for the observed behavior. It reflects that the observed main products of the decomposition are HSO_3^- and $S_2O_3^{2-}$, but some SO_4^{2-} and $S_2O_6^{2-}$ are also formed. The mechanism also accounts for the transient formation of elemental sulfur and for the acidification of the solution during decomposition.

Numerical calculations with the reaction set in Table 1 were carried out taking into account mass action kinetic laws for the composite reactions. The ratios of the rate constants for the forward and reverse steps of the protonation equilibria were chosen to be consistent with the known values of the equilibrium constants of (1) and (2). Other rate constant values were estimated. Simulations resulted in double peak, periodic pH-oscillations very similar to the measured traces. Fig. 2 shows a typical calculated pH–time series. The calculated period length and amplitude are in good agreement with the measured values. Calculations confirm the experimental observation that the periodic behavior is limited to a certain range of experimental constraints.

Oscillatory chemical reaction systems usually consist of two or more reactants. Here we discovered a new sulfur-based pH-oscillatory reaction that demonstrates the possibility of oscillatory decomposition of a single compound. Confirmed oscillations in this type of chemical reaction have not been reported yet. We think that understanding the mechanism of the oscillations in this particular reaction would provide valuable information for the mechanism of the disproportionation and simproportionation of sulfur compounds in general. Furthermore, the study of this reaction will hopefully help to improve the general model suggested recently for the sulfur-based oscillators.[11]

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Notes and references

1 J. Meyer, *Z. Anorg. Chem.*, 1903, **34**, 45.
2 K. Jellinek, *Z. Anorg. Chem.*, 1911, **70**, 93.
3 I. M. Kolthoff and C. S. Miller, *J. Am. Chem. Soc.*, 1941, **63**, 2818.
4 L. Burlamacchi, G. Guarini and E. Tiezzi, *Trans. Faraday Soc.*, 1969, **65**, 496.
5 W. J. Lem and M. Wayman, *Can. J. Chem.*, 1970, **48**, 776.
6 W. J. Lem and M. Wayman, *Can. J. Chem.*, 1970, **48**, 2778.
7 M. Wayman and W. J. Lem, *Can. J. Chem.*, 1971, **49**, 2778.
8 R. G. Rinker, S. Lynn, D. M. Mason and W. H. Corcoran, *Ind. Eng. Chem. Fundam.*, 1965, **4**, 282; (S. Lynn, Ph.D. Thesis, California Institute of Technology, 1952).
9 K. M. Kovács and Gy. Rábai, *J. Phys. Chem. A*, 2001, **105**, 9183.
10 D. A. Holman and D. W. Bennett, *J. Phys. Chem.*, 1994, **98**, 13 300.
11 C. W. Rushing, R. C. Thompson and Q. Gao, *J. Phys. Chem. A*, 2000, **104**, 11 561.