Supplementary Material (ESI) for PCCP

Iodine oxidation by hydrogen peroxide and Bray-Liebhafsky oscillating reaction: effect of the temperature.

Electronic supplementary information

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Content

1. Experimental values of k_{exp}

Table ES1. Experimental values of 10^3 k_{exp} (s^{-1}) at 25°C for $[I_2] = 2\times10^{-4}$ and 4×10^{-4} mol l^{-1}. Fig. ES1 compares the values for $[I_2] = 4\times10^{-4}$ mol l^{-1} with the values calculated with the model.

		$[H_2O_2]$						
$[HClO_4]$	10^4 $[I_2]$	0.002	0.005	0.010	0.020	0.050	0.10	0.20
0.02	2		8.5		6.0			
	4		9.8		7.0			
0.04	2		8.5	8.0	7.5	6.3	5.0	2.8
	4		9.2	8.8	8.2	7.4	5.9	
0.10	2	6.9	7.1	7.2	7.2	6.5	5.7	4.9
	4		7.7	7.8	7.9	7.5	6.7	6.0
0.20	2		5.4	5.5	5.6	5.5	5.1	
	4		6.1	5.6	6.3	6.1	5.5	5.4
0.40	2		3.1	3.3	3.4	3.5	3.4	
	4		3.8	3.4	4.0	4.3	4.0	3.8

Table ES2. Experimental values of 10^3 k_{exp} (s^{-1}) at 39°C for $[I_2] = 2\times10^{-4}$ and 4×10^{-4} mol l^{-1}. Fig. 3 of the main text compares the values for $[I_2] = 4\times10^{-4}$ mol l^{-1} with the values calculated with the model.

		$[H_2O_2]$							
$[HClO_4]$	10^4 $[I_2]$	0.002	0.005	0.010	0.025	0.050	0.10	0.20	0.40
0.04	2		18	25		17	13		
	4		20	27		20	15	6	
0.10	2	26	28	27	24	22	18	12	6
	4	27	29	28	27	25	22	16	9
0.20	2	21	22	22		20	17	15	10
	4		22	23		22	21	18	14
0.40	2	14		14				11	12
	4	15		15				13	13

Table ES3. Experimental values of 10^3 k_{exp} (s^{-1}) at 50°C for $[I_2] = 2\times10^{-4}$ and 4×10^{-4} mol l^{-1}. Fig. 4 of the main text compares the values for $[I_2] = 4\times10^{-4}$ mol l^{-1} with the values calculated with the model.

		$[H_2O_2]$					
$[HClO_4]$	$10^4[I_2]$	0.0091	0.037	0.050	0.15	0.183	0.20
0.112	2	64		52	29		
	4	71		60	42		36
0.212	2	56			39		
	4	60			47		
0.312	2	42	40		34	32	
	4	48	45		40	39	
0.512	2	28		28	26		
	4	32		31	30		30
0.762	2	19				17	
	4	22				20	

2. Rate constant of reaction (R5) at 50°

Liebhafsky *et al.*[1] have tried to measure the value of the rate constant k_5 at 50° using the technique used before[2] at 25°, that is controlling the iodine concentration with the quasi-equilibrium $I_2(s) \rightleftharpoons I_2(aq)$ and the iodide ions concentration with the quasi-equilibrium $Tl^+ + I^- \rightleftharpoons TlI(s)$. Under these conditions, the expected overall reaction is

$$I_2(s) + 2\ Tl^+ + H_2O_2 = 2\ TlI(s) + 2\ H^+ + O_2 \qquad \text{(ES1)}$$

The IOH concentration can be calculated from the quasi-equilibrium (R4), $IOH + I^- + H^+ \rightleftharpoons I_2 + H_2O$, and, if reaction (R5) is the only reaction producing oxygen, the rate constant k_5 can be calculated from $k_5 = (d[O_2]/dt)/[H_2O_2][IOH]$. This method seemed successful at 25°.

At 50°, Liebhafsky had also measured the initial rates of H_2O_2 consumption and H^+ production as well as the amounts of $TlI(s)$ and $TlIO_3(s)$ produced near the end of the reaction. All these measurements should give more information not only about reaction (R5) but also about other reactions in the BL mechanism. However, the following stoichiometric discussion shows that the precision of these measurements was too low. Under Liebhafsky experimental conditions, only negligible amounts of iodate are produced so that they are only two independent stoichiometric relations between the species in significant concentrations, (ES1) and (ES2). The sum of (ES1) and (ES2) gives the H_2O_2 disproportionation.

$$2\ TlI(s) + H_2O_2 + 2\ H^+ = I_2(s) + 2\ Tl^+ + 2\ H_2O \qquad \text{(ES2)}$$

This explains qualitatively why Liebhafsky had obtained amounts of H_2O_2 consumed greater than the amounts of O_2 produced but the quantitative agreement is not good. The results should satisfy two mass balance equations, $\Delta[TlI] = \Delta[H^+]$ and a second one derive as follow. Noting x_1 and x_2 the number of times reactions (ES1) and (ES2) have occurred, we get $\Delta[O_2] = x_1$, $\Delta[H_2O_2] = - x_1 - x_2$, $\Delta[H^+] = 2\ x_1 - 2\ x_2$ and, eliminating x_1 and x_2, $\Delta[H^+] = 2\ \Delta[H_2O_2] + 4\ \Delta[O_2]$. These two mass balance equations are far from being satisfied by the results of Liebhafsky. The less inaccurate values being probably those of $d[O_2]/dt$, we have used them to estimate k_5 by the method applied previously at 25°. Using the iodine solubility at 50°, $[I_2] = 3.1\times10^{-3}$ mol l^{-1}, the solubility product of TlI(s), $[Tl^+][I^-] = 8.7\times10^{-7}$, $[IOH] = [I_2]/(K_4[I^-][H^+])$, with $K_4 = 8.7\times10^{-12}$, and $k_5 = (d[O_2]/dt)/[H_2O_2][IOH]$ the analysis of Liebhafsky measurements give k_5 values between 140 and 250 $M^{-1}\ s^{-1}$ and suggest that k_5 increases with the acidity, in contradiction with his results at 25°. Liebhafsky[1] had proposed $k_5 = 108\ M^{-1}\ s^{-1}$ but this value was an adjustable parameter of his incorrect model for the BL reaction. We have also tried to simulate Liebhafsky results using our model. The qualitative agreement is good and the calculations confirm that the iodate production is negligible under these conditions and that (R5) is the main source of oxygen. However, the quantitative agreement is inevitably bad because the values calculated with the model satisfy the above mass balance equations while the experimental values do not. Finally, we have adopted $k_5 = 150\ M^{-1}\ s^{-1}$ as a likely order of magnitude needing further confirmation.

3. Update of Fig. 2 in Guy Schmitz, PCCP 2010, 12, 6605.

Fig. ES1 shows that agreement between our experimental values of k_{exp} at 25° and the values calculated with the slightly modified set of rate constants in Table II of the main text is as good as in the original fig.2.

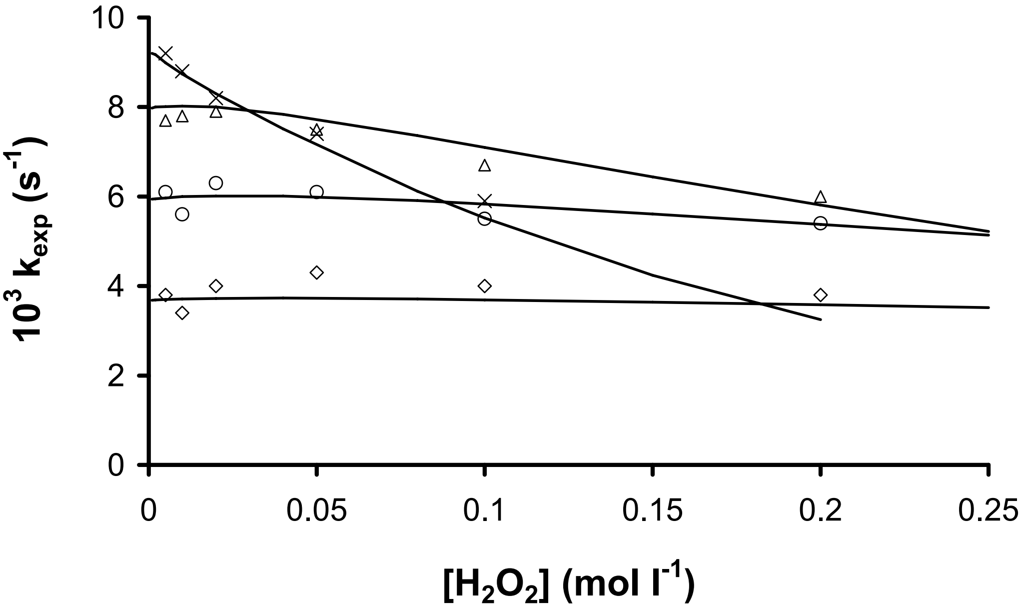

Fig. ES1. Experimental values of k_{exp} at 25° if $[NaIO_3]_o$ = 0.0125 mol l^{-1}, $[HClO_4]_o$ = 0.04 (×), 0.10 (Δ), 0.20 (o), 0.40 (◇) mol l^{-1} and corresponding values calculated with the model (R1)-(R10) and the set of rate constants given in table II of the main text (—).

4. Comparison between the experimental values of Liebhafsky[3] at 50° and the values calculated with the model (R1)-(R10).

Figs ES2 to ES4 compare experimental values read on figs 4 and 5 of reference 3 with the values calculated with the model (R1)-(R10). (The ordinates noted 10^5 [I_2] in Liebhafsky figures are actually 10^4 [I_2] values.) The experimental rates in Fig.ES2 are a little higher than the calculated ones perhaps because Liebhafsky had used iodate concentrations four times higher than ours. Fig.ES3 shows that the values reported by Liebhafsky with an iodate concentration similar to ours give lower rates. A possible explanation of the small effect of the iodate concentration on the rate of reaction (O) was discussed in our previous paper[4].

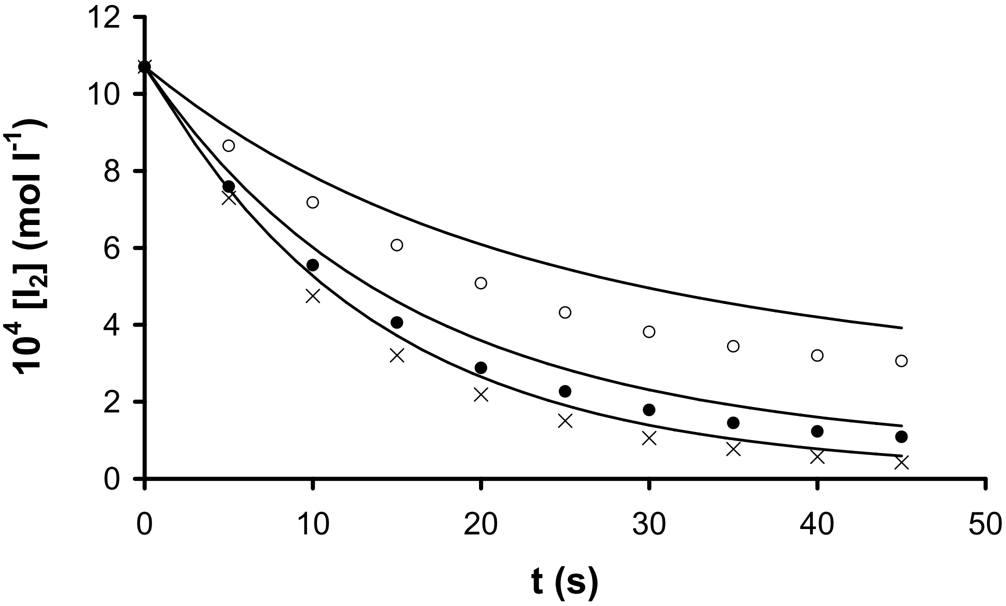

Fig. ES2. Effect of [H_2O_2] if [$HClO_4$] = 0.057 mol l^{-1} and [KIO_3] = 0.053 mol l^{-1} Experimental values[3] if [H_2O_2] = 0.0125 (×), 0.050 (●), 0.20 mol l^{-1} (o) and calculated curves (—).

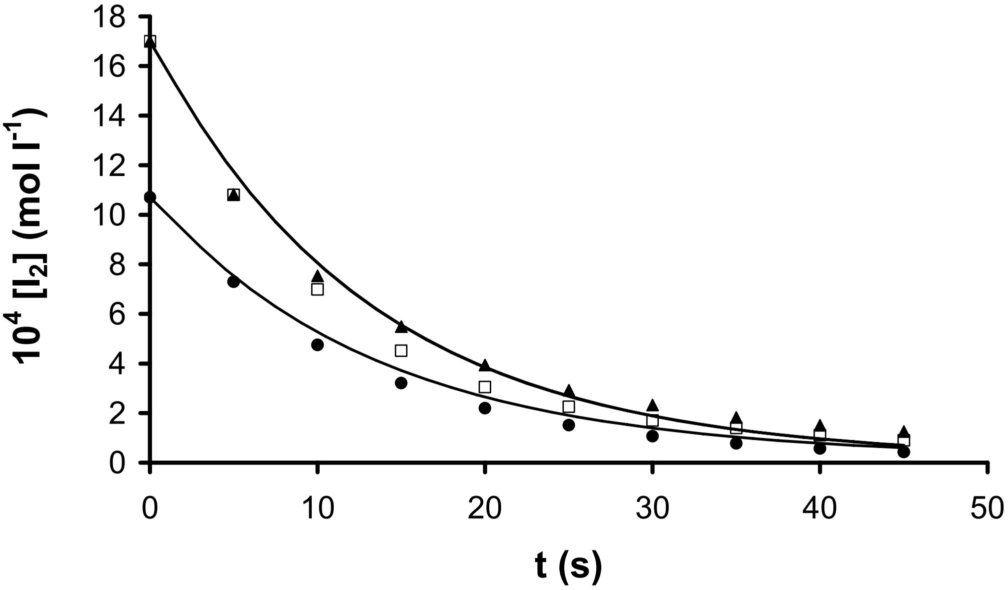

Fig. ES3. Effect of $[KIO_3]_o$ if $[HClO_4]_o = 0.057$ and $[H_2O_2]_o = 0.0125$ mol l^{-1}. Experimental values[3] if $[KIO_3]_o = 0.0135$ (▲), 0.0265 (□), 0.053 mol l^{-1} (●) and calculated curves (—).

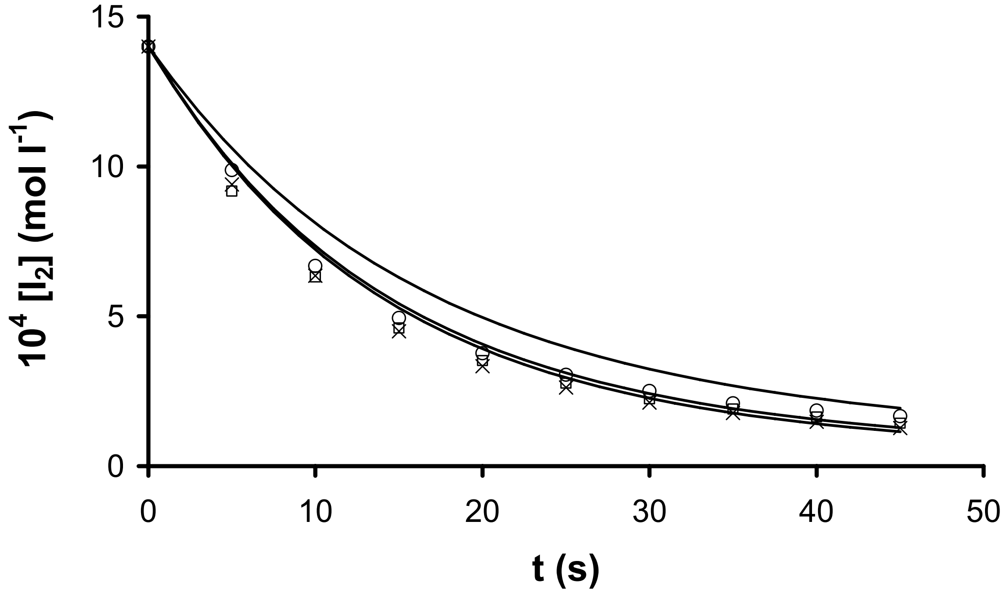

Fig. ES4. Effect of $[HClO_4]_o$ if $[KIO_3]_o = 0.053$ and $[H_2O_2]_o = 0.050$ mol l^{-1}. Experimental values[3] if $[HClO_4]_o = 0.0382$ (o), 0.0764 (□), 0.0957 mol l^{-1} (×) and calculated curves (—).

5. Comparison between the experimental values of Liebhafsky[5] at 0° and the values calculated with the model (R1)-(R10).

The following table compares the k_{exp} values obtained by Liebhafsky at 0° (Table I in ref.5) with the values of k_{exp} calculated with the model for $[I_2] = 4\times10^{-4}$ mol l^{-1}. The rate constants were obtained by extrapolation of the values in Table II of the main text using the Arrhenius law.

N°	$[HClO_4]$	$[KIO_3]$	$[H_2O_2]$	$k_{exp,\ Liebhafsky}$ (min^{-1})	$k_{exp,\ model}$ (min^{-1})	Ratio
81	0.0268	0.214	0.0038	0.046	0.043	0.93
82	0.0134	0.214	0.0038	0.044	0.034	0.78
83	0.0107	0.214	0.0038	0.041	0.031	0.76
60	0.0535	0.00022	0.103	0.0072	0.033[a]	
78	0.0535	0.214	0.00076[b]	0.040	0.044	1.10
32	0.148	0.0142	0.112	0.019	0.027	1.41
71	0.0535	0.214	0.103	0.037	0.028	0.77
73	0.0535	0.214	0.010	0.037	0.046	1.23
74	0.0535	0.214	0.0038	0.039	0.046	1.18
					Mean	1.02

[a] Maximum value after an induction period due to the very small iodate concentration.
[b] If $[I_2]_o = 5\times10^{-4}$, all the H_2O_2 has reacted at the end of the reaction and $[I_2]_{end} = 3.4\times10^{-4}$.

6. Simulation of the effect of the iodine transfer to the gas phase

Ševčik *et al*[6-8] have shown that increasing the rate of stirring can suppress the oscillations and have explained this observation by the increase of the rate of iodine transfer to the gas phase. They have supported this explanation with numerical simulations[8] using the former variant of our model to which they have added reaction (R13). Fig. ES5 shows that the new variant gives even a better agreement with their experimental results. We have calculated the values of log([I_2]/[I^-]) for comparison with the potentials measured with a Pt electrode.

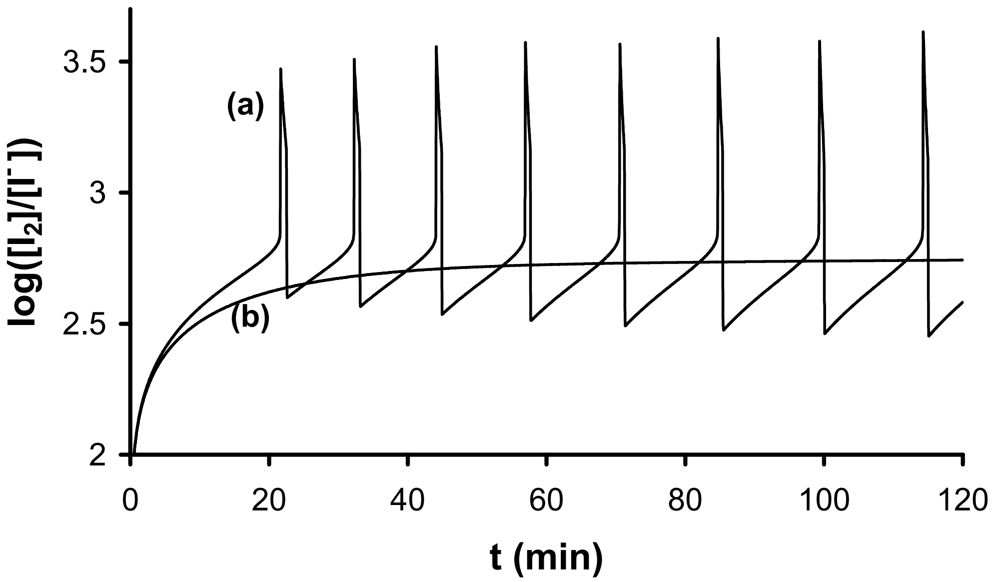

Fig. ES5. Numerical simulation of the effect of the agitation at 60° reported in Fig.1 of reference 8. $[HClO_4]_o = 0.05$, $[KIO_3]_o = 0.32$ and $[H_2O_2]_o = 0.32$ mol l^{-1}. The effect of oxygen was neglected and $k_{13} = 5\times10^{-4}$ for 100 rpm (a) or 1.4×10^{-3} s^{-1} for 800 rpm (b).

7. Simulation of the oxygen production rate

Fig.8 of the main text shows the good agreement between some experimental results obtained by Liebhafsky and our calculated values. This section gives a second example under different conditions. Fig.ES6 is a reproduction of Fig.2 in "Gas Evolution in an Oscillatory Reaction System" by H. A. Liebhafsky, R. Furuichi and G.M. Roe, 1981[9] and Fig.ES7 shows our calculated values. Note that the time scale in Fig.ES6 is in the reverse order and begins at about 42 min so that the initial evolution toward the disproportionation steady state and the first part of smooth catalysis period are not shown. The black dots represent the values of r_{12} calculated from the signal of the flow meter and expressed in scc min^{-1} (scc = cm^3 at 273.15 K and 1 atm.). For comparison, our r_{12} values were converted into the same unit.

The disproportionation steady state is initially stable and becomes unstable later when the hydrogen peroxide concentration has decreased. This explains the three periods in the observed evolution of the iodide ions concentration and shown more clearly in the calculated evolution of the iodine concentration: evolution to the disproportionation steady state, smooth catalysis as long as it is stable and oscillations when it becomes unstable. The mean values of the observed and calculated concentrations are very similar. The amplitude of the calculated oscillations is lower than observed because we have used the same values of k_{11} and k_{12} as in Fig.8 of the main text. With larger values, the amplitude would larger.

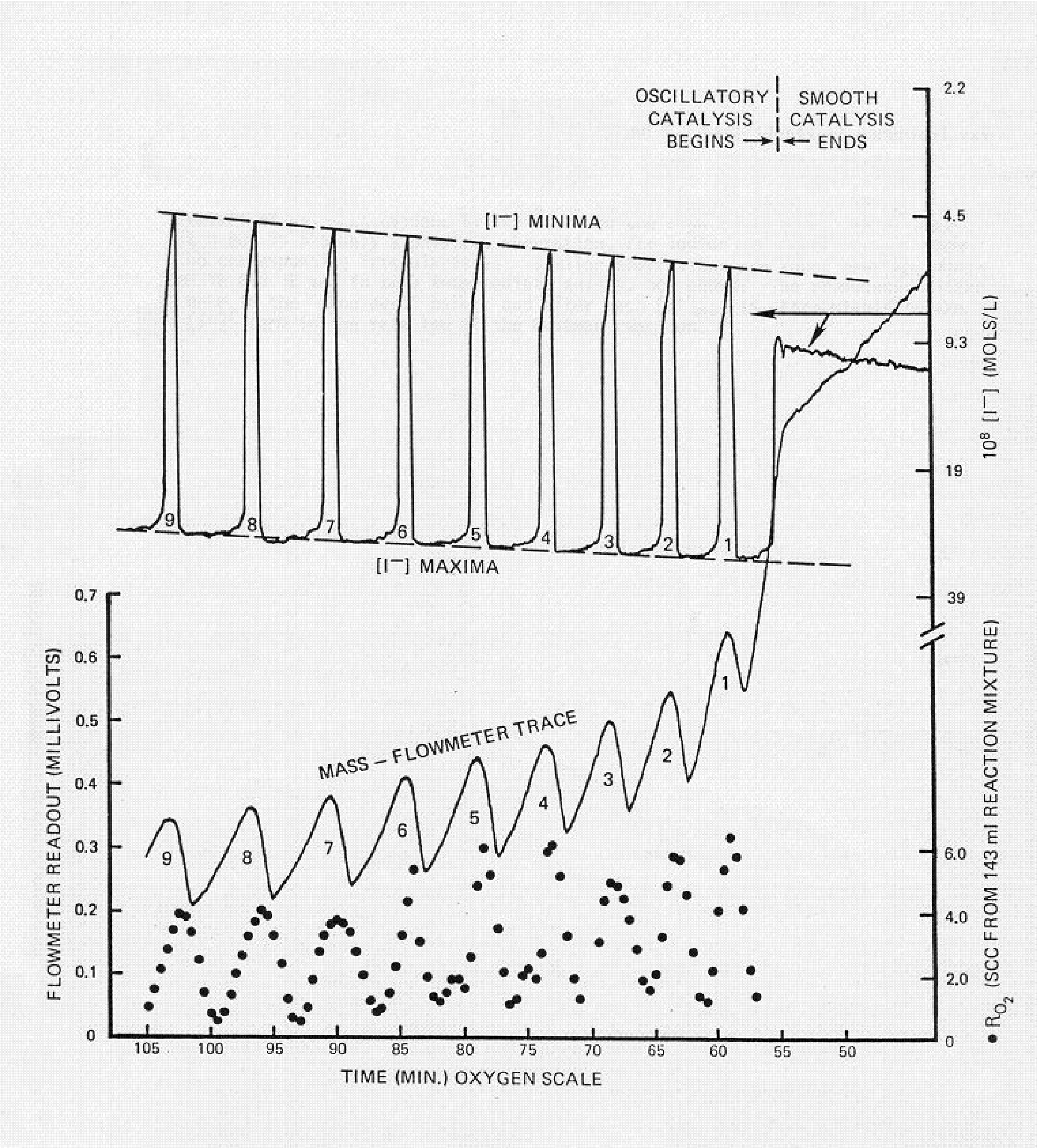

Fig.ES6. Liebhafsky results[9] at 50° for [KIO$_3$]$_o$ = 0.106, [HClO$_4$]$_o$ =0.0573 and [H$_2$O$_2$]$_o$ = 0.58 mol l^{-1}.

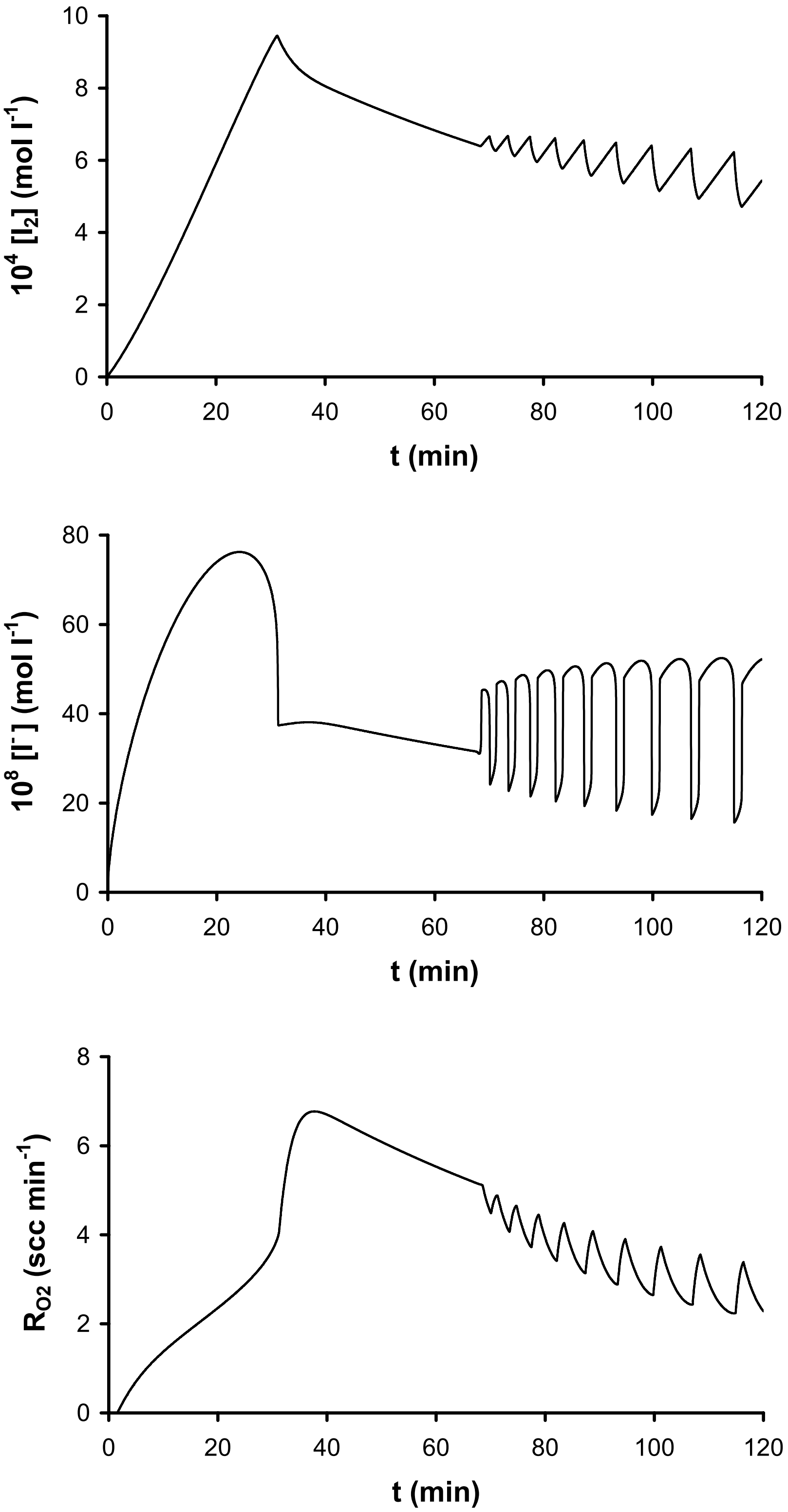

Fig.ES7. Calculated values under the condition of fig.ES6. The rate constants for reactions (R1)-R(10) are given in Table II and $k_{11} = 2\times10^4$, $k_{12} = 5\times10^{-3}$, $k_{13} = 0$ as in Fig.8 of the main text.

8. Simulation of the acidity effect on the oscillations

Fig.ES8 shows that the acidity effect calculated with the model agrees with the experimental observations discussed in the main text.

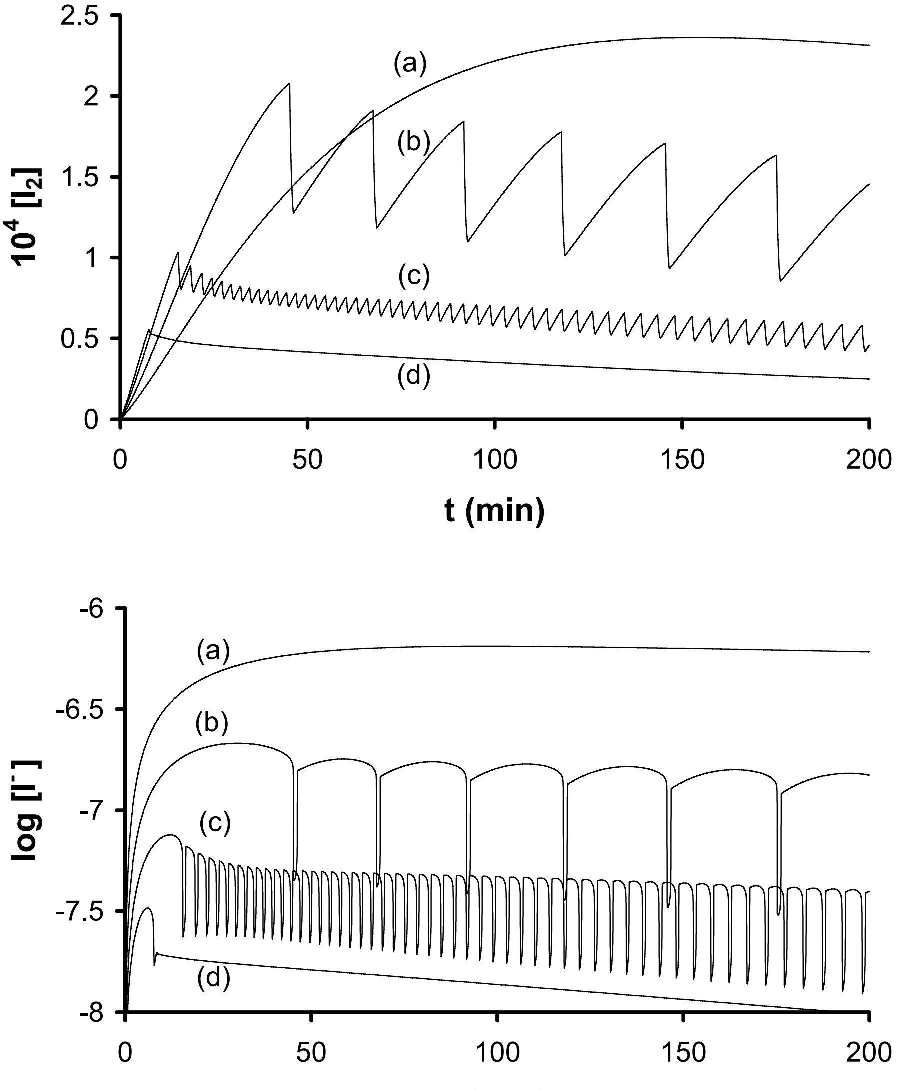

Fig. ES8. Numerical simulation of the acidity effect at 50°. $[NaIO_3]_o = 0.10$, $[H_2O_2]_o = 0.10$ mol l^{-1} and $[HClO_4]_o = 0.03$ (a), 0.06 (b), 0.10 (c), 0.14 mol l^{-1} (d); Rate constants of reactions (R1)-(R10) in Table II of the main text, $k_{11} = 5\times10^4$, $k_{12} = 2\times10^{-3}$ and $k_{13} = 5\times10^{-4}$ s^{-1}.

9. Simulation of the oscillatory system I^-, H_2O_2, $HClO_4$.

Fig. ES9 gives an example of simulation of the oscillations observed by Olexova *et al*[10] in the system I^-, H_2O_2, $HClO_4$. For easier comparison with the experimental results, the calculated iodine concentrations are converted to absorbances at 460 nm using $\varepsilon(I_2) = 730$ at 60°C[11]. The agreement with the results presented in fig.6 of reference 10 is noticeable. The lower part of Fig.ES9 shows also the calculated evolution of log $[I^-]$, very similar to the experimental evolution of the redox potential presented in other figures by these authors.

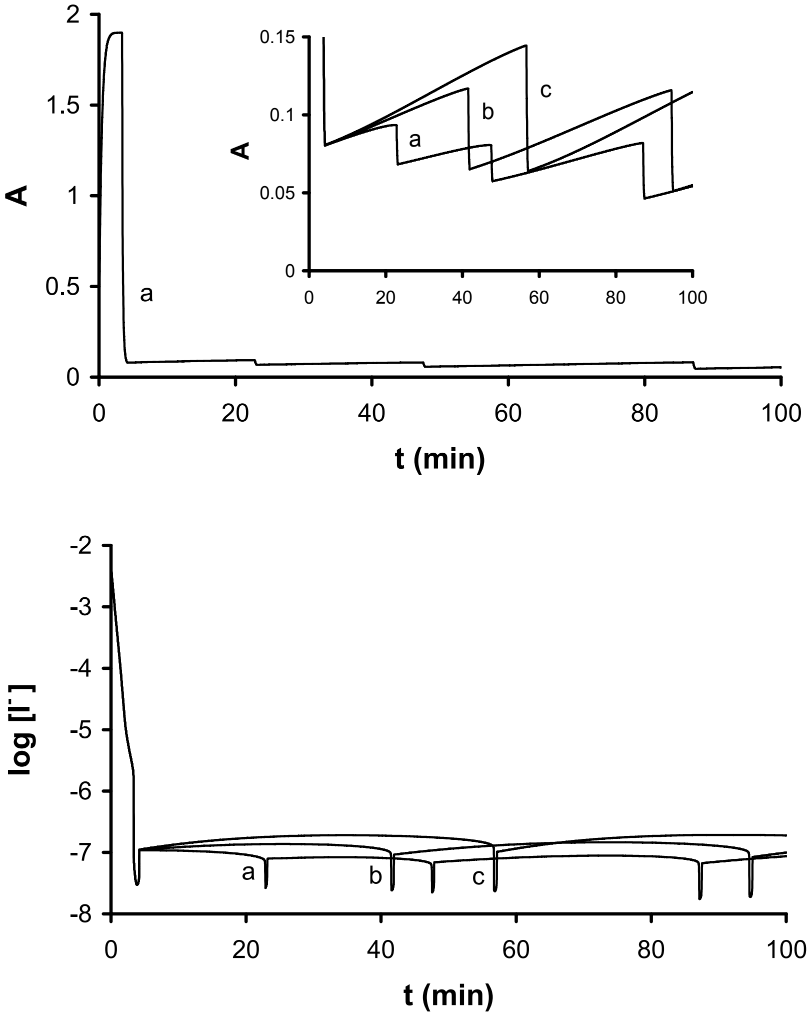

Fig. ES9. Numerical simulation of the oscillatory system I^-, H_2O_2, $HClO_4$ at 60° and effect of the rate of oxygen transfer to the gas phase. $[HClO_4]_o = 0.09$, $[H_2O_2]_o = 0.10$, $[I^-]_o = 5\times10^{-3}$ mol l^{-1}, no iodate initially. Rate constants of reactions (R1)-(R10) in Table II of the main text, $k_{11} = 1\times10^5$ and $k_{12} = 1.5\times10^{-3}$ (a), 2.0×10^{-3} (b) and 2.5×10^{-3} (c). Reaction (R13) was neglected.

10. References

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