

# Reaction Kinetics, Mechanisms and Catalysis

## Kinetics and mechanism of I(+3) reactions and consequences for other iodine reactions

--Manuscript Draft--

<b>Manuscript Number:</b>	REAC-D-21-00559R1
<b>Full Title:</b>	Kinetics and mechanism of I(+3) reactions and consequences for other iodine reactions
<b>Article Type:</b>	Full Paper
<b>Corresponding Author:</b>	Guy Schmitz Universite Libre de Bruxelles Brussels, BELGIUM
<b>Corresponding Author Secondary Information:</b>	
<b>Corresponding Author's Institution:</b>	Universite Libre de Bruxelles
<b>Corresponding Author's Secondary Institution:</b>	
<b>First Author:</b>	Guy Schmitz
<b>First Author Secondary Information:</b>	
<b>Order of Authors:</b>	Guy Schmitz Stanley D. Furrow
<b>Order of Authors Secondary Information:</b>	
<b>Funding Information:</b>	
<b>Abstract:</b>	This article presents new kinetic studies of the disproportionation of I(+3) and of its oxidation by $H_2O_2$ . It also provides an update of the previously proposed model for reactions of iodine compounds with oxidation numbers from -1 to +5 with each other and with $H_2O_2$ . This model explains the kinetics of several reactions, including the oxidation of iodine by $H_2O_2$ . We show that the reduction of HOI by $H_2O_2$ results from $HOI + H_2O_2 \rightarrow HOOI + H_2O$ followed by the reversible reaction $HOOI \rightleftharpoons I^- + H^+ + O_2$ . An analysis of previous measurements of the kinetic constant $k(HOI + H_2O_2)$ explains the large differences between the values proposed in the literature and gives $k(HOI + H_2O_2) = 6 M^{-1} s^{-1}$ . The reversibility of the reaction $HOOI \rightleftharpoons I^- + H^+ + O_2$ suggests a new explanation for the effect of oxygen on the Bray-Liebafsky reaction. HOOI would be oxidized by $H_2O_2$ following a radical mechanism.
<b>Response to Reviewers:</b>	See attached file

Ms. No. REAC-D-21-00559. Responses to reviewer.

*1) Reference 27 on nullclines plays a prominent role in the logic of this manuscript, but I have been unable to locate it. Please provide a DOI for the reference.*

This communication was published only recently and reference 27 has been completed and added on Research Gate.

*2) In Table 1, reaction 8 is stoichiometrically equivalent to the sum of reactions 1, 5, and 6. Thus we have  $K_1K_5K_6 = K_8$ .  $K_1$  and  $K_6$  can be calculated from the rate constants in the Table, and  $K_5$  can be calculated from  $k_5$  in the Table and  $k_{-5}$  in the Appendix. The result is  $K_8 = 1.2 \times 10^8$ .  $\Delta G^\circ$  for reaction 8 can also be calculated from the  $\Delta_f G^\circ$  values in the NBS tables and the value for HOIO in Schmitz's 2008 paper. This  $\Delta G^\circ$  value is equivalent to a value of  $2.5 \times 10^9$  for  $K_8$ , which differs from the value calculated from the rate constants by a factor of 20. This deviation is excessive and needs to be resolved prior to publication.*

This comment is very interesting and we have redone the calculations of the reviewer. The NBS values are:  $\Delta_f G^\circ(\text{IO}_3^-) = -132.6$  kJ/mol,  $\Delta_f G^\circ(\text{H}_2\text{O}_2, \text{aq}) = -134.03$  kJ/mol,  $\Delta_f G^\circ(\text{O}_2, \text{aq}) = 16.4$  kJ/mol and  $\Delta_f G^\circ(\text{H}_2\text{O}) = -237.13$  kJ/mol. Our 2008 value is  $\Delta_f G^\circ(\text{HOIO}) = -95$  kJ/mol. These values give  $\Delta_r G^\circ(\text{R8}) = -49.1$  kJ/mol and  $K_8 = 4 \times 10^8$ . A.J.Bard, R.Parsons and J.Jordan, Standard Potentials in Aqueous Solutions, IUPAC, Marcel Dekker Inc., 1985, give  $\Delta_f G^\circ(\text{IO}_3^-) = -134.9$  kJ/mol, in better agreement with the experimental values of  $\text{K}(\text{IO}_3^- + 5 \text{I}^- + 6 \text{H}^+ = 3 \text{I}_2 + 3 \text{H}_2\text{O}) = 10^{47}$  [ref. 30]. Then,  $\Delta_r G^\circ(\text{R8}) = -46.8$  kJ/mol and  $K_8 = 1.6 \times 10^8$ . Note also that our value of  $\Delta_f G^\circ(\text{HOIO})$  is approximate and that the kinetic constants are estimated if  $\gamma = 0.75$ . The agreement between the thermodynamic value of  $K_8$  and the value of  $K_1K_5K_6$  deduced from the kinetic constants is therefore very good.

We thank the reviewer for this comment because we had neglected the reversibility of the reaction R8 without noticing that this implies to neglect also the reversibility of R6, which our estimation of the kinetic constants shows.

*3) In the Appendix, page 27, the authors state that  $k_{-13}$  can be calculated. The authors should report the value.*

This value is added in the appendix.

*4) The discussion of  $k_{13}$  on p 8 shows a pH dependence for the reaction that differs from the authors' 2013 publication. The manuscript should discuss the difference and explain why the current dependence is preferred.*

We have changed the interpretation of our 2013 results because our new results show that the value of the formation constant of  $\text{H}_2\text{OIO}^+$  is small:  $K_{19} < 0.1$ . The effect of pH is that observed in 2013 and figure 1 shows that it is perfectly explained by the new mechanism. A sentence is added in the text to clarify this difference.

5) *Reaction 13 was a source of contention in a prior paper: Stanbury, D. M. Comment on the Principle of Detailed Balancing in Complex Mechanisms and Its Application to Iodate Reactions. J. Phys. Chem. A, 2018, 122, 3956-3957. The authors should take the opportunity to resolve the issues exposed in that prior paper.*

This excellent article by Stanbury is added as reference 49. Our reaction R13 is the inverse of its reaction (3) and the relation  $K_{13} = K_2K_3 / K_1$  in the appendix satisfies the principle of detailed balancing. The definition of this principle refers to the elementary steps which give the overall reaction but these elementary steps are often unknown. This is why we prefer to justify the relations  $K_{eq} = k_f / k_b$  by the equivalence between the thermodynamic and kinetic expressions of an equilibrium. This equivalence is discussed in the introduction of this article and in reference 24.

6) *I see that  $K_2K_3K_5K_6 = K_7$ . Thus, the value of  $k_{-7}$  can be calculated and should be included in the simulations. Likewise, the values of  $k'_{-8}$  and  $k''_{-8}$  can be calculated, should be reported, and should be included in the simulations.*

We have added in the appendix the sentences "  $K_2K_3K_5K_6 = K_7$  and  $K_5K_6 = 1.6 \times 10^7$  give  $K_7 = 3.2 \times 10^{15}$  showing that R17 is practically irreversible. This is also true for the others  $H_2O_2$  reactions."

7) *Units should be included in the axis labels in Figs. 1, 3, 5, and 6. The caption to Figure 1 should include the units for the rate constants.*

Units are added to all figures.

8) *On page 18, second line of the Conclusion states "compounds at oxidation degrees...". Proper terminology would use "states" or "numbers" rather than "degrees".*

"States" replaces "degrees".

# Kinetics and mechanism of I(+3) reactions and consequences for other iodine reactions

Guy E. Schmitz<sup>a</sup> and Stanley D. Furrow<sup>b</sup>

<sup>a</sup> Université Libre de Bruxelles, Ecole Polytechnique, CP165/63, Av. F. Roosevelt 50, 1050 Brussels, Belgium

<sup>b</sup> Penn State Berks College, The Pennsylvania State University, Reading, Pennsylvania 19610, United States

## Abstract

This article presents new kinetic studies of the disproportionation of I(+3) and of its oxidation by H<sub>2</sub>O<sub>2</sub>. It also provides an update of the previously proposed model for reactions of iodine compounds with oxidation numbers from -1 to +5 with each other and with H<sub>2</sub>O<sub>2</sub>. This model explains the kinetics of several reactions, including the oxidation of iodine by H<sub>2</sub>O<sub>2</sub>. We show that the reduction of HOI by H<sub>2</sub>O<sub>2</sub> results from  $\text{HOI} + \text{H}_2\text{O}_2 \rightarrow \text{HOOI} + \text{H}_2\text{O}$  followed by the reversible reaction  $\text{HOOI} \rightleftharpoons \text{I}^- + \text{H}^+ + \text{O}_2$ . An analysis of previous measurements of the kinetic constant  $k(\text{HOI} + \text{H}_2\text{O}_2)$  explains the large differences between the values proposed in the literature and gives  $k(\text{HOI} + \text{H}_2\text{O}_2) = 6 \text{ M}^{-1}\text{s}^{-1}$ . The reversibility of the reaction  $\text{HOOI} \rightleftharpoons \text{I}^- + \text{H}^+ + \text{O}_2$  suggests a new explanation for the effect of oxygen on the Bray-Liebafsky reaction. H<sub>2</sub>O<sub>2</sub> would oxidize HOOI by a radical mechanism.

## Introduction

Studies of systems involving iodine reactions, such as periodic and chaotic reactions [1-4], the consequences of a nuclear accident [5-7] and the marine boundary layer chemistry [8-10] require the understanding of simpler sub-systems. The models of these complicated systems involve a large number of reactions with unknown or poorly known rate constants and the aim of our work is to reduce their number. We present new measurements of the kinetics of I(+3) reactions in acidic solutions as well as a new analysis of previous results for inorganic reactions of iodine compounds between them and with H<sub>2</sub>O<sub>2</sub>. Adopting the

1 terminology Up and Down reactions proposed by Liebhafsky, we continue to explore the  
2 iodine house [11] with 6 floors from I(-1) to I(+5) and an elevator, H<sub>2</sub>O<sub>2</sub>.  
3

4 Table I is an update of the model proposed in 2010 [12] taking into account our new  
5 study of the kinetics of I(+3) reactions. The observed effect of [H<sup>+</sup>] has consequences for  
6 other reactions. A model of iodine reactions must also explain the very unusual kinetics of  
7 the oxidation of I<sub>2</sub> by H<sub>2</sub>O<sub>2</sub> (reaction O) discussed below. Some kinetic constants were  
8 known. Others were adjusted in 2010 to explain this kinetics and we have updated them to  
9 take into account the results presented in this work.  
10

11 The former explanation of the effects of oxygen on the Bray-Liebhafsky (BL)  
12 oscillations is also modified. Sharma and Noyes [13] had studied these effects and had even  
13 proposed, without success, that they could explain the oscillations. This explanation has  
14 been discarded but the importance of oxygen reactions has been confirmed [14-16]. To take  
15 these effects into account, the 2010 model included the global reaction  $I^- + H^+ + \frac{1}{2} O_2 \rightarrow HOI$   
16 with an empirical rate law. This reaction seems simple but is actually a complicated light-  
17 catalyzed radical reaction that deserves further experimental study. In the meantime, other  
18 studies suggest that it involves the HOOI intermediate proposed by Ball and Hnatiw [17] to  
19 explain the kinetics of the reduction of I(+1) by H<sub>2</sub>O<sub>2</sub> in buffered solutions. The existence of  
20 this intermediate has been confirmed later [18, 19]. HOOI is also an important intermediate  
21 for the explanation of the reduction of iodate by H<sub>2</sub>O<sub>2</sub> [20]. The classical rate law of this  
22 reduction is no longer valid when the concentration of H<sub>2</sub>O<sub>2</sub> is larger than about 0.2-0.3 M  
23 and a radical reaction path appears. The reaction  $HOI + H_2O_2 \rightarrow I^- + H^+ + O_2 + H_2O$  must be  
24 split into  $HOI + H_2O_2 \rightleftharpoons HOOI + H_2O$  (R5) and  $HOOI \rightleftharpoons I^- + H^+ + O_2$  (R6) and a radical reaction  
25 path would be initiated by a reaction between HOOI and H<sub>2</sub>O<sub>2</sub> [21, 22]. Reaction R6 could  
26 also explain the observation of E. Szabo and P. Ševčík [23]. They measured accurately the  
27 rate of O<sub>2</sub>(g) production during the BL reaction and identified two precursors. One is O<sub>2</sub>(aq).  
28 The concentration of the other precursor increases with [H<sub>2</sub>O<sub>2</sub>] and HOOI explains this  
29 observation. All these works suggest our new explanation of the effect of oxygen on the BL  
30 reaction: R6 is highly reversible and followed by reaction R12. We conclude that HOOI is a  
31 member of the iodine house with consequences in many systems.  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56

57 Some rate constants in Table I are calculated using the relation  $K_{eq} = k_+/k_-$  between an  
58 equilibrium constant and the kinetic constants in the forward and backward directions. It is  
59  
60  
61  
62  
63  
64  
65

sometimes justified by the principle of microscopic reversibility. However, many reactions of Table I are not elementary and the use of this principle may be open to criticism. We have offered another proof introducing the concept of quasi-elementary reaction [24]. It is defined as a reaction with a well-defined stoichiometry and rate orders corresponding to this stoichiometry. Take reaction R4 as an example. It is the sum of reactions (4a) and (4b) [25].



The quasi-stationarity of  $[\text{I}_2\text{OH}^-]$  gives  $r_{4a} = r_{4b}$  and

$$r_{4a} = \frac{k_{4a}k_{4b} [\text{HOI}][\text{I}^-][\text{H}^+] - k_{-4a}k_{-4b}[\text{I}_2]}{k_{-4a} + k_{4b}[\text{H}^+]}$$

The rate law in Table I is observed when  $k_{4b} [\text{H}^+] \gg k_{-4a}$ . At equilibrium  $k_{4a}k_{4b} [\text{HOI}]_{\text{eq}}[\text{I}^-]_{\text{eq}}[\text{H}^+]_{\text{eq}} = k_{-4a}k_{-4b} [\text{I}_2]_{\text{eq}}$ . This kinetic expression must be equivalent to the thermodynamic expression of the equilibrium. It follows that  $k_{4a}k_{4b}/k_{-4a}k_{-4b} = K_{\text{eq}}$  and, with numbering of Table I,  $k_4/k_{-4} = K_4$ . We have applied this principle of equivalence between the kinetic and thermodynamic expressions of the equilibrium to other quasi-elementary reactions in Table I.

The section "I(+3) disproportionation" proposes a new interpretation of our kinetic study of the reaction  $2 \text{HOIO} \rightarrow \text{IO}_3^- + \text{HOI} + \text{H}^+$  (R13) published previously [26]. The section "I(+3) autocatalytic disproportionation" presents a new kinetic study of the reaction  $\text{HOI} + \text{HOIO} \rightarrow \text{IO}_3^- + \text{I}^- + 2 \text{H}^+$  (-R1) and the next section presents a new kinetic study of the oxidation of I(+3) by  $\text{H}_2\text{O}_2$  (R9). The section "Oxidation of  $\text{I}_2$  by  $\text{H}_2\text{O}_2$  with iodate added initially (Reaction O)" shows that the model in Table I with updated values of some kinetic constant explains also our former results. If there is no iodate initially, the  $\text{I}_2 + \text{H}_2\text{O}_2$  reaction begins with a non-reproducible induction period. It is discussed in section "Oxidation of  $\text{I}_2$  by  $\text{H}_2\text{O}_2$  without iodate added initially" on the basis of our recent calculations [27] of the nullclines corresponding to the model in Table I. Section "I(+1) reduction by  $\text{H}_2\text{O}_2$ " shows that this induction period allows measurements of the kinetic constant of the reaction  $\text{HOI} + \text{H}_2\text{O}_2 \rightarrow \text{HOOI} + \text{H}_2\text{O}$  (R5). The appendix gives details about the calculations of the kinetic constants given in Table I.

Table I (units: mol/l, s)

R1	$\text{IO}_3^- + \text{I}^- + 2 \text{H}^+ \rightleftharpoons \text{HOI} + \text{HOIO}$ $r_1 = k_1[\text{IO}_3^-][\text{I}^-][\text{H}^+]^2 - k_{-1}[\text{HOI}][\text{HOIO}]$	$k_1 = 1300$	$k_{-1} = 210$
R2	$\text{HOIO} + \text{I}^- + \text{H}^+ \rightleftharpoons \text{I}_2\text{O} + \text{H}_2\text{O}$ $r_2 = k_2[\text{H}^+][\text{HOIO}][\text{I}^-] - k_{-2}[\text{I}_2\text{O}]$	$k_2 = 5 \times 10^9$	$k_{-2}/k_3 = 1.0 \times 10^{-7}$
R3	$\text{I}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons 2 \text{HOI}$ $r_3 = k_3[\text{H}^+][\text{I}_2\text{O}] - k_{-3}[\text{H}^+][\text{HOI}]^2$	Large see appendix	$k_{-3} = 2.44 \times 10^8$
R4	$\text{HOI} + \text{I}^- + \text{H}^+ \rightleftharpoons \text{I}_2 + \text{H}_2\text{O}$ $r_4 = k_4[\text{HOI}][\text{I}^-] - k_{-4}[\text{I}_2]/[\text{H}^+]$	$k_4 = 1.7 \times 10^9$	$k_{-4} = 1.8 \times 10^{-3}$
	<i>Down reactions</i>		
R5	$\text{HOI} + \text{H}_2\text{O}_2 \rightleftharpoons \text{HOOI} + \text{H}_2\text{O}$ $r_5 = k_5[\text{HOI}][\text{H}_2\text{O}_2] - k_{-5}[\text{HOOI}]$	$k_5 = 6$	$k_{-5}$ very small see appendix
R6	$\text{HOOI} \rightleftharpoons \text{I}^- + \text{H}^+ + \text{O}_2$ $r_6 = k_6[\text{HOOI}] - k_{-6}[\text{I}^-][\text{H}^+][\text{O}_2]$	$k_6 = 1 \times 10^8$	$k_{-6} = 1 \times 10^5$
R7	$\text{HOIO} + \text{H}_2\text{O}_2 \rightarrow \text{HOI} + \text{O}_2 + \text{H}_2\text{O}$ $r_7 = k_7[\text{HOIO}][\text{H}_2\text{O}_2]/[\text{H}^+]$	$k_7 = 0.5$	irreversible see appendix
R8	$\text{IO}_3^- + \text{H}^+ + \text{H}_2\text{O}_2 \rightarrow \text{HOIO} + \text{O}_2 + \text{H}_2\text{O}$ $r_8 = (k'_8 + k''_8[\text{H}^+])[\text{IO}_3^-][\text{H}_2\text{O}_2]$	$k'_8 = 1.3 \times 10^{-7}$	$k''_8 = 1.5 \times 10^{-5}$
	<i>Up reactions</i>		
R9	<b>Net:</b> $\text{HOIO} + \text{H}_2\text{O}_2 \rightarrow \text{IO}_3^- + \text{H}^+ + \text{H}_2\text{O}$ $r_9 = k_9[\text{H}_2\text{O}_2][\text{HOIO}]^2 / \{[\text{H}^+](1 + \alpha_9[\text{H}_2\text{O}_2])\}$	$k_9 = 1.7 \times 10^5$	$\alpha_9 = 10$
R10	$\text{I}_2\text{O} + \text{H}_2\text{O}_2 \rightarrow \text{HOI} + \text{HOIO}$ $r_{10} = (k'_{10} + k''_{10}/[\text{H}^+])[\text{I}_2\text{O}][\text{H}_2\text{O}_2]$	$k'_{10}/k_3 = 0.050$	$k''_{10}/k_3 = 4.1 \times 10^{-3}$
R11	$\text{I}^- + \text{H}^+ + \text{H}_2\text{O}_2 \rightarrow \text{HOI} + \text{H}_2\text{O}$ $r_{11} = (k'_{11} + k''_{11}[\text{H}^+])[\text{I}^-][\text{H}_2\text{O}_2]$	$k'_{11} = 0.012$	$k''_{11} = 0.17$

	<i>Effect of oxygen</i>		
R12	$\text{HOOI} + 2 \text{H}_2\text{O}_2 \rightarrow \text{HOIO} + \text{O}_2 + 2 \text{H}_2\text{O}$ Global radical reaction beginning with $\text{HOOI} + \text{H}_2\text{O}_2 \rightarrow \text{HOO}^\bullet + \text{H}_2\text{O} + \text{IO}^\bullet \quad (\text{R12a})$ $r_{12} = k_{12a} [\text{HOOI}] [\text{H}_2\text{O}_2]$	see appendix	
	<i>Side reactions</i>		
R13	$2 \text{HOIO} \rightarrow \text{IO}_3^- + \text{HOI} + \text{H}^+$ $r_{13} = (k'_{13}/[\text{H}^+] + k''_{13}/[\text{H}^+]^2) [\text{HOIO}]^2$	$k'_{13} = 0.045$	$k''_{13} = 0.065$
R14	$\text{O}_2 \rightleftharpoons \text{O}_2(\text{g})$ $r_{14} = \max(0; k_{14} ([\text{O}_2] - [\text{O}_2]_{\text{sat}}))$	see appendix	
R15	$\text{I}_2 \rightleftharpoons \text{I}_2(\text{g})$ $r_{15} = k_{15} [\text{I}_2]$	see appendix	
R16	$\text{I}_2 + \text{I}^- \rightleftharpoons \text{I}_3^-$ $r_{16} = 5 \times 10^9 ([\text{I}_2][\text{I}^-] - [\text{I}_3^-]/K_{16})$	$K_{16} = 713$	
R17	$\text{HIO}_3 \rightleftharpoons \text{IO}_3^- + \text{H}^+$ $r_{17} = 5 \times 10^9 (K_{17} [\text{HIO}_3] - [\text{IO}_3^-][\text{H}^+])$	$K_{17} = 0.28$	
R18	$\text{HOI} + \text{H}^+ \rightleftharpoons \text{H}_2\text{OI}^+$ $r_{18} = 5 \times 10^9 (K_{18} [\text{HOI}] [\text{H}^+] - [\text{H}_2\text{OI}^+])$	$K_{18} = 0.3$	
R19	$\text{HOIO} + \text{H}^+ \rightleftharpoons \text{H}_2\text{OIO}^+$ $r_{19} = 5 \times 10^9 (K_{19} [\text{HOIO}] [\text{H}^+] - [\text{H}_2\text{OIO}^+])$	$K_{19} < 0.1$	

### Experiments and calculations

The I(+3) solutions are prepared as explained before [28] by the reaction of weighed amounts of  $\text{I}_2$  and  $\text{KIO}_3$  in concentrated  $\text{H}_2\text{SO}_4$ . They contain about 1 to 2% I(+1). The calculation of the initial composition of the experimental solutions takes this into account. The other reagents are of the best purity commercially available and are used without further purification. The 18 M $\Omega$  water is supplied by a Barnstead Micropore ST model. The initial concentrations  $[\text{H}^+]$  are calculated using the Pitzer model of the  $\text{H}_2\text{SO}_4$  solutions. The absorbance measurements are made with an Agilent Cary 60 scanning spectrophotometer.



1 The addition of the samples of I(+3) in H<sub>2</sub>SO<sub>4</sub> to the aqueous phase (of composition  
2 depending on the kind of experiment) being exothermic, the aqueous phase is cooled before  
3 mixing so that the temperature after mixing is close to 25°C. The spectrophotometer cell is  
4 thermostatically controlled at 25°C and contains a small stirrer.  
5  
6

7  
8 The sample of I(+3) (20 to 30 mg) must be added quickly to the aqueous phase (3 to 5  
9 cm<sup>3</sup>). Mixing in the reverse order causes a local overheating giving some fast initial reactions  
10 and wrong results. Two mixing methods were used. The "syringe" method consists of placing  
11 the aqueous phase in a cell with a small circular opening, injecting the sample of I(+3) with a  
12 fast mixing syringe, closing the cell with a Teflon stopper, inverting the cell to mix well and  
13 place it in the spectrophotometer. This cell is tight and allows absorbances measurements  
14 up to large conversions, but the first measurements can only be made about 15 - 20 s after  
15 the injection of the I(+3) sample. The "paddle" method consists of placing the cooled  
16 aqueous phase in a cell with a wide opening (1 cm<sup>2</sup>) and weighing the I(+3) sample on a small  
17 paddle. It is introduced quickly into the cell, shaken briefly to mix well, and a Teflon cover is  
18 placed over the cell. The cell also contains a small stirrer. This method allows absorbances  
19 measurements after less than 5 s and gives accurate values at small conversions, but the cell  
20 is not tight and the absorbances are sometimes too small at large conversion. Both method  
21 were used for the measurements of the rate of disproportionation of I(+3) in the presence of  
22 crotonic acid, which is relatively slow, and for the measurements of the rate of autocatalytic  
23 disproportionation which begins with an induction period. They gave similar results.  
24  
25 Oxidation of I(+3) by H<sub>2</sub>O<sub>2</sub> is faster and we used the "paddle" method.  
26  
27

28  
29 The spectrophotometer results are transferred to a computer and the analytical  
30 calculations are done with Excel. The differential equations associated with the model are  
31 integrated using the *ode15s* function of Matlab specially adapted to stiff differential  
32 equations. The main program calls the *fminsearch* function which determines the kinetic  
33 constants minimizing the sum of squares of the difference between the absorbances  
34 measured and calculated by *ode15s*. Calculations usually take less than two minutes and the  
35 relative error on the iodine mass balance is less than 10<sup>-13</sup>.  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

### I(+3) disproportionation

The I(+3) disproportionation is autocatalytic as explained in the next section. To study the kinetics of reaction  $2 \text{HOIO} \rightarrow \text{IO}_3^- + \text{HOI} + \text{H}^+$  (R13), we carried out experiments with crotonic acid (CA) [26]. It reacts very quickly with HOI according to reaction (1) to form an iodohydrin HOICA.



Reaction (R13) becomes the rate determining step giving the kinetic law (2) when the concentration of CA is large enough. We used  $[\text{CA}]_0 = 5 \times 10^{-3}$  to  $1.2 \times 10^{-2}$  M and  $[\text{I}(+3)]_0 = 5 \times 10^{-4}$  to  $2 \times 10^{-3}$  M. The kinetic constant of reaction (1),  $k_{\text{CA}} = 4730 \text{ M}^{-1}\text{s}^{-1}$ , has been measured previously [29].

$$-\frac{d[\text{I}(+3)]}{dt} = 2 k_{\text{exp,disp}} [\text{I}(+3)]^2 \quad (2)$$

$[\text{I}(+3)]$  represents the total concentration  $[\text{I}(+3)] = [\text{HOIO}] + [\text{H}_2\text{OIO}^+] = (1 + K_{19} [\text{H}^+])[\text{HOIO}]$  so that  $k_{13} = (1 + K_{19} [\text{H}^+])^2 k_{\text{exp,disp}}$ . The integration of the kinetic law (2) gives the equation below which makes it possible to calculate  $k_{\text{exp,disp}}$  by making as only assumption that the absorbance measured at 275 nm varies linearly with the extent of the reaction [26]. However, it is necessary to estimate the value of  $A_\infty$  by extrapolation of the A values at long term.

$$\frac{A_\infty - A_0}{A_\infty - A_t} = 1 + 2 k_{\text{exp,disp}} [\text{I}(+3)]_0 t$$

We also analyzed the experimental results using Matlab to integrate the differential equations associated with the model in Table I without the  $\text{H}_2\text{O}_2$  reactions but with reaction (1) added. The *fminsearch* function adjusts the kinetic constant  $k_{13}$  to minimize the sum of squares  $\sum (A_{\text{calc}} - A_{\text{exp}})^2$  where  $A_{\text{calc}} = \epsilon_{\text{I}(+3)} [\text{I}(+3)] + \epsilon_{\text{I}(+5)} [\text{I}(+5)] + \epsilon_{\text{CA}} [\text{CA}] + \epsilon_{\text{HOICA}} [\text{HOICA}]$ . New measurements gave  $\epsilon_{\text{I}(+3)} = 121$ ,  $\epsilon_{\text{I}(+5)} = 11.4$ ,  $\epsilon_{\text{CA}} = 6.40$  and  $\epsilon_{\text{HOICA}} = 399$  at 275 nm. The agreement between the rate constants calculated with the order two rate law or with Matlab is excellent.

The rate constant  $k_{\text{exp,disp}}$  increases very quickly with decreasing acidity [26]. We had explained this effect by reaction (R20) followed by reaction (R21).





The acidity constant of HOIO is unknown but its order of magnitude is  $K_{20} = 10^{-5}$  to  $10^{-6}$  M [30] so that  $[\text{OIO}^-] = K_{20} [\text{HOIO}]/[\text{H}^+]$  is much smaller than  $[\text{HOIO}]$  under our experimental conditions.

$$r_{21} = k_{21} [\text{HOIO}] [\text{OIO}^-] = k_{21} \frac{K_{20}}{[\text{H}^+]} [\text{HOIO}]^2$$

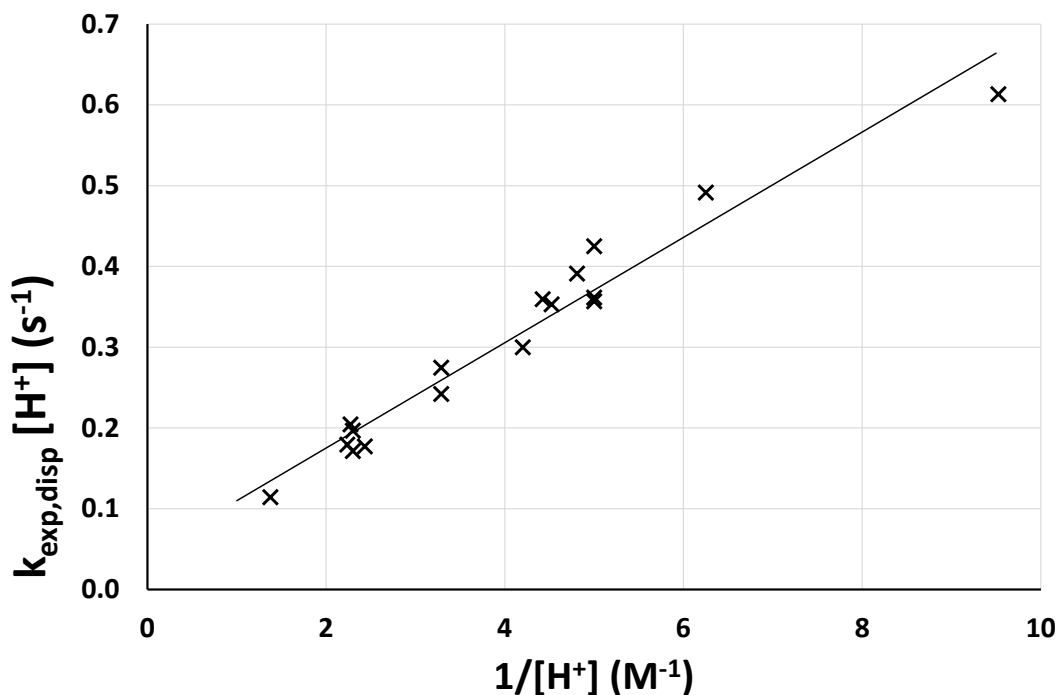
and  $[\text{HOIO}] = [\text{I(+3)}] / (1 + K_{19} [\text{H}^+])$  give

$$k_{\text{exp,disp}} = \frac{k_{21} K_{20}}{[\text{H}^+] (1 + K_{19} [\text{H}^+])^2}$$

The large effect of  $[\text{H}^+]$  on  $k_{\text{exp,disp}}$  could be explained by the factor  $(1 + K_{19} [\text{H}^+])^2$  if  $K_{19} \sim 3 \text{ M}^{-1}$ . However, the study of the autocatalytic disproportionation rate of I(+3) in the next section shows that  $K_{19}$  is much smaller so that this explanation must be discarded and we propose a new explanation of our 2013's results. We assume  $[\text{H}_2\text{OIO}^+] \ll [\text{HOIO}]$  under our experimental conditions and explain the effect of  $[\text{H}^+]$  on  $k_{\text{exp,disp}}$  by the formation of the intermediate  $\text{I}_2\text{O}_4\text{H}^-$ , similar to the oxide  $\text{I}_2\text{O}_3$  known in the gas phase. Its formation will be supported by our new study of the I(+3) oxidation by  $\text{H}_2\text{O}_2$  discussed below.



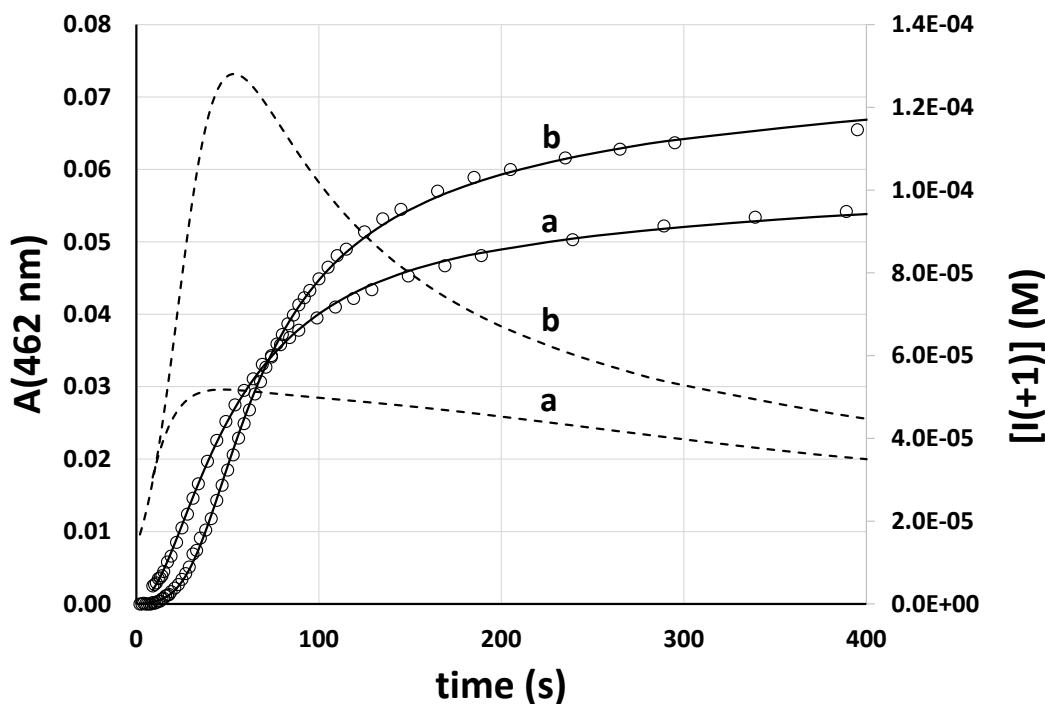
Reaction R13 is obtained by combining these reactions with the acid-base quasi-equilibria,. Assuming  $[\text{I}_2\text{O}_4\text{H}^-] = K_{22} [\text{HOIO}] [\text{OIO}^-]$ , we obtain  $r_{13} = (k_{23} + k_{24} [\text{OH}^-]) K_{22} [\text{HOIO}] [\text{OIO}^-]$  or  $r_{13} = (k'_{13}/[\text{H}^+] + k''_{13}/[\text{H}^+]^2) [\text{HOIO}]^2$  where  $k'_{13} = k_{23} K_{20} K_{22}$  and  $k''_{13} = k_{24} K_w K_{20} K_{22}$ . The experiments give  $k_{\text{exp,disp}} = r_{13} / [\text{HOIO}]^2$  and the plot of  $k_{\text{exp,disp}} [\text{H}^+]$  as a function of  $1/[\text{H}^+]$  in Fig.1 shows that this equation explains our former results. The intercept and slope give the values of  $k'_{13}$  and  $k''_{13}$ .



**Fig.1.** Effect of the acidity on the rate constant of reaction (R13). Experimental values (×) and linear regression line (—) giving  $k'_{13} = 0.045 \text{ s}^{-1}$  and  $k''_{13} = 0.065 \text{ M s}^{-1}$ .

### I(+3) autocatalytic disproportionation

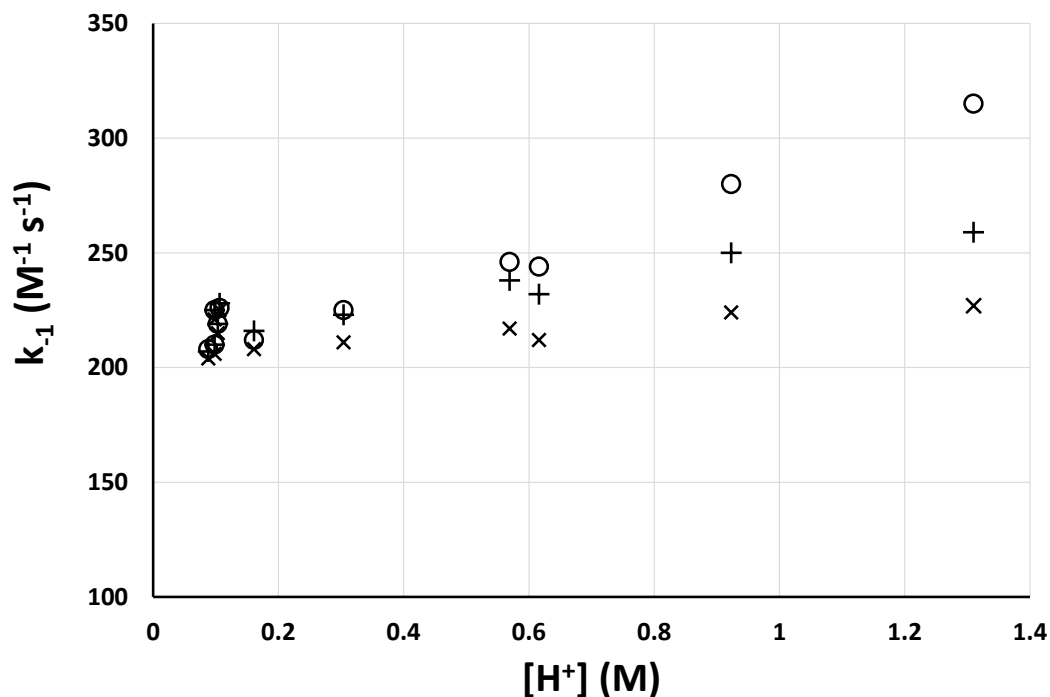
The kinetic of the I(+3) disproportionation without added CA is not simple. At the beginning, the main reaction is (R-1) followed by the fast reactions (R2) and (R3) giving the autocatalytic reaction  $2 \text{HOIO} + \text{HOI} \rightarrow \text{IO}_3^- + \text{H}^+ + 2 \text{HOI}$ . The induction period depends on the concentration of I(+1) in the preparation of I(+3) and overlaps the period required for the solution to be well mixed so that there are no mixing problems. The concentration [HOI] increases and can become as large as 20% of  $[\text{I}(+3)]_0$  at high acidities. Then, it goes through a maximum shown in Fig.2 and the main reaction becomes  $\text{HOIO} + 2 \text{HOI} \rightarrow \text{IO}_3^- + \text{H}^+ + \text{I}_2 + \text{H}_2\text{O}$ . When [HOIO] becomes small, some HOI remains and the direction of reactions (R2) and (R3) is reversed. [HOI] decreases very slowly according to  $5 \text{HOI} \rightarrow \text{IO}_3^- + \text{H}^+ + 2 \text{I}_2 + 2 \text{H}_2\text{O}$ . The overall stoichiometry is  $5 \text{I}(+3) \rightarrow 3 \text{IO}_3^- + 3 \text{H}^+ + \text{I}_2 + \text{H}_2\text{O}$  but the experimental values of  $[\text{I}_2]$  at the end of the experiments is always lower than  $[\text{I}(+3)]_0/5$  because the disproportionation of I(+1) is very slow under our experimental conditions. Fig.2 gives examples of evolutions over time.



**Fig.2.** Left hand scale: Experimental (O) and calculated (—) absorbances at 462 nm at low (a) and high (b) acidities.  $[\text{H}_2\text{SO}_4] = 0.068 \text{ M}$  and  $[\text{I}(+3)]_0 = 4.34 \times 10^{-4} \text{ M}$  (a).  $[\text{H}_2\text{SO}_4] = 0.76 \text{ M}$  and  $[\text{I}(+3)]_0 = 5.41 \times 10^{-4} \text{ M}$  (b). Right hand scale: Calculated  $\text{I}(+1)$  concentrations (- - -).

Matlab simulates the experimental curves and the function *fminsearch* adjusts  $k_{-1}$  and the initial value of  $[\text{I}(+1)]$ . The electronic supplement gives the results. The effect on  $k_{-1}$  of likely modifications of the kinetic constants, including  $k_{13}$ , is lower than the experimental inaccuracies. On the other hand,  $k_{-1}$  depends on the values of  $K_{18}$  and  $K_{19}$ . The concentrations known experimentally or calculated by mass balances are the total concentrations  $[\text{I}(+1)] = (1 + K_{18} [\text{H}^+]) [\text{HOI}]$  and  $[\text{I}(+3)] = (1 + K_{19} [\text{H}^+]) [\text{HOIO}]$ . Thus, the individual concentrations  $[\text{HOI}]$  and  $[\text{HOIO}]$  calculated by Matlab depend on  $K_{18}$  and  $K_{19}$  and, therefore, also the value of  $k_{-1}$ . To estimate the values of  $K_{18}$  and  $K_{19}$  we apply the principle of equivalence between the kinetic and thermodynamic expressions of an equilibrium. The kinetic of the reaction (R1) in the forward direction is well known [41]: its rate is proportional to  $[\text{H}^+]^2$ . Consequently,  $k_{-1}$  must be independent of  $[\text{H}^+]$ . If  $K_{19} > 0.1 \text{ M}^{-1}$ , the calculated values of  $k_{-1}$  increase with  $[\text{H}^+]$  as shown in Fig.3 and, moreover, the fit of the experimental curves

1 becomes bad if  $K_{19} > 0.5 \text{ M}^{-1}$ . We therefore neglect  $K_{19}$ . Fig. 3 also shows that  $k_{-1}$  is nearly  
 2 independent of  $[\text{H}^+]$  if  $K_{18} \sim 0.3 \text{ M}^{-1}$ . We had estimated previously  $K_{18} \sim 0.5 \text{ M}^{-1}$  [25] and these  
 3 results suggest to decrease slightly this value. These experiments give  $k_{-1} = 210 \pm 6 \text{ M}^{-1} \text{ s}^{-1}$  (t-  
 4 Student 95% confidence interval).  
 5  
 6  
 7  
 8  
 9



10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

**Fig.3.** Values of  $k_{-1}$  adjusted by Matlab if  $K_{18} = 0.5 \text{ M}^{-1}$  and  $K_{19} = 0$  (O),  $K_{18} = 0.3 \text{ M}^{-1}$  and  $K_{19} = 0.2 \text{ M}^{-1}$  (+),  $K_{18} = 0.3 \text{ M}^{-1}$  and  $K_{19} = 0$  (x).

### Oxidation of I(+3) by H<sub>2</sub>O<sub>2</sub>

When a sample of I(+3) is added to an acidic solution of H<sub>2</sub>O<sub>2</sub>, the main reaction is the oxidation  $\text{HOIO} + \text{H}_2\text{O}_2 \rightarrow \text{IO}_3^- + \text{H}^+ + \text{H}_2\text{O}$  (R9). The amount of iodine produced is negligible showing that the reduction of HOIO by reaction R7 is much slower. The results show that the rate of R9 is proportional to the square of the concentration [HOIO] and inversely proportional to [H<sup>+</sup>]. The rate constants  $k_9$  in Table II were calculated for the rate law  $r_9 = k_9 [\text{HOIO}]^2 [\text{H}_2\text{O}_2] / [\text{H}^+]$  using the Matlab function *fminsearch* minimizing the sum of the squares of the deviations between the calculated and measured absorbances of HOIO at 275 nm over time. The electronic supplement gives examples. The average value is  $k_9 = (1.7 \pm$

0.2) $\times 10^5 \text{ M}^{-1}\text{s}^{-1}$  (t-Student 95% confidence interval). New measurements of the molar absorption coefficient of HOIO at 275 nm gave  $\varepsilon(\text{HOIO}) = 121 \pm 2$ . Other values used in this work are  $\varepsilon(\text{H}_2\text{O}_2) = 5.7$ ,  $\varepsilon(\text{IO}_3^-) = 11.4$ ,  $\varepsilon(\text{HOI}) = 107$  and  $\varepsilon(\text{I}_2) = 121$  at 275 nm.

**Table II.** Rate constants of the HOIO oxidation by  $\text{H}_2\text{O}_2$  (units: mol/l and s)

$[\text{H}_2\text{SO}_4]$	$[\text{H}^+]$	$[\text{H}_2\text{O}_2]_0 \times 10^4$	$[\text{HOIO}]_0 \times 10^4$	$[\text{HIO}_3]_0 \times 10^4$	$k_9 \times 10^{-5}$
0.064	0.083	10.4	5.0	1.5	1.3
0.074	0.096	6.0	5.8	1.6	2.0
0.077	0.099	12	5.8	1.7	1.6
0.087	0.111	24	6.6	1.9	2.1
0.092	0.117	6.4	5.6	2.3	1.7
0.099	0.125	36	7.4	2.1	1.8
0.11	0.138	6.5	5.0	1.2	1.8
0.11	0.138	6.5	4.6	1.1	2.1
0.24	0.29	6.0	5.0	1.5	1.4
0.26	0.32	5.7	4.3	1.0	2.9
0.27	0.33	81	4.6	1.9	1.5
0.28	0.34	5.7	5.0	1.1	1.0
0.45	0.54	5.7	4.6	1.1	1.9
0.45	0.54	5.7	4.7	1.1	1.8
0.46	0.56	81	4.2	1.7	1.1

We had shown that  $\text{H}_2\text{O}_2$  reduces the HOI monomer and oxidizes its dimer  $\text{I}_2\text{O}$ . The rate law of the HOIO disproportionation with an excess of CA discussed above and the kinetic law of HOIO oxidation by  $\text{H}_2\text{O}_2$  suggest that the HOIO reactions are similar to those of HOI. HOIO also forms a dimer and  $\text{H}_2\text{O}_2$  reduces its monomer and oxidizes its dimer. Also, the effect of  $[\text{H}^+]$  on these reactions suggests that this dimer is  $\text{I}_2\text{O}_4\text{H}^-$  introduced above that reacts according to (R24).



The oxidation R25 is much faster than the disproportionation of HOIO from the smallest values of  $[\text{H}_2\text{O}_2]$  and the quasi-stationarity of  $[\text{I}_2\text{O}_4\text{H}^-]$  gives  $(k_{-22} + k_{25} [\text{H}_2\text{O}_2]) [\text{I}_2\text{O}_4\text{H}^-] = k_{22} [\text{HOIO}][\text{OIO}^-]$  and the rate law

$$r_{25} = \frac{k_{25} k_{22} K_{20} [\text{HOIO}]^2 [\text{H}_2\text{O}_2]}{(k_{-22} + k_{25} [\text{H}_2\text{O}_2]) [\text{H}^+]}$$

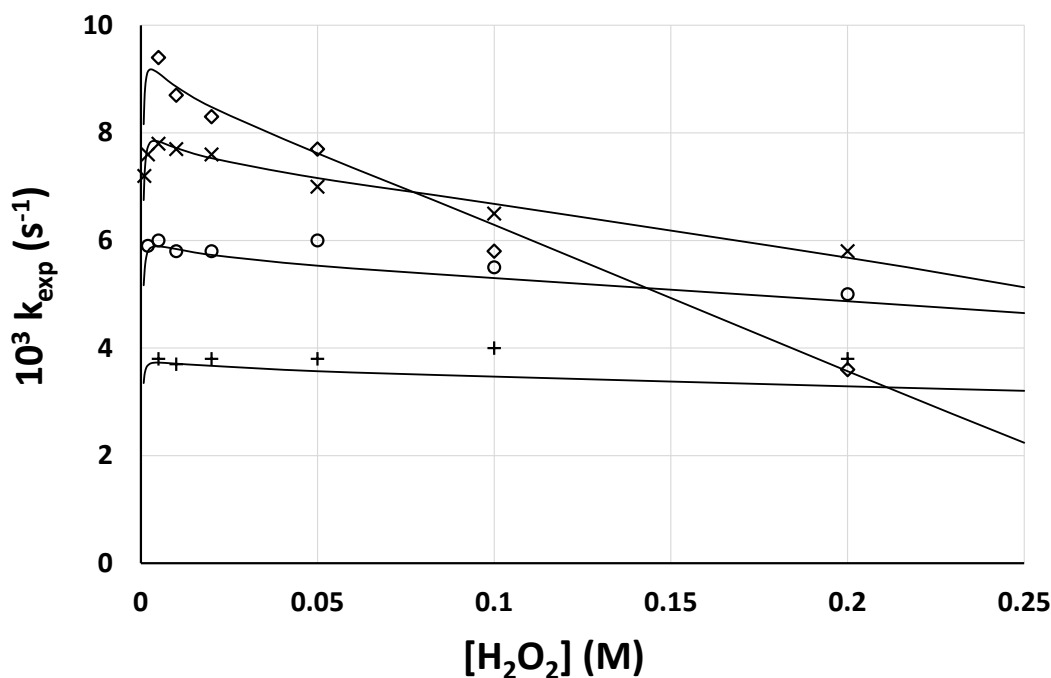
1  
2 This expression explains the rate law of R9 in Table I with  $k_9 = k_{24}k_{22}K_{20}/k_{-22}$  and  $\alpha_9 = k_{24}/k_{-22}$ .

3  
4 The term in  $\alpha_9 [H_2O_2]$  has no effect on the results in table II because the concentration of  
5  
6  $H_2O_2$  was small but will be important to simulate the  $H_2O_2$  effect on the rate of reaction O.  
7  
8  
9

### 10 **Oxidation of $I_2$ by $H_2O_2$ with iodate added initially (Reaction O)**

11  
12 The oxidation of iodine by  $H_2O_2$  without iodate added initially begins with a non-  
13 reproducible period of induction discussed below. It is suppressed and a fast oxidation of  $I_2$  is  
14 observed if iodate is added initially. We had carried out more than a thousand experiments  
15 in a wide range of concentrations and temperatures and published the main results  
16 previously [12, 31]. When the initial iodate concentration is about 0.005 to 0.1 M, the rates  
17 are complicated functions of acidity,  $[H_2O_2]$  and  $[I_2]$  but are independent of the iodate  
18 concentration. To analyze these rates, it is convenient to define the function  $k_{exp} = -d(\ln[I_2])$   
19 / dt although the reaction is not exactly of order 1 with respect to  $[I_2]$ . Figure 5 shows values  
20 of  $k_{exp}$  at 25 ° if  $[I_2] = 4 \times 10^{-4}$  M. The values of  $k_{exp}$  do not directly give values of kinetic  
21 constants, only relations between them. A modification of one constant requires readjusting  
22 the kinetic constants of the reactions R3, R7 and R10. The previously published model [12,  
23 31] explained our results but we had to modify the values of some kinetic constants to take  
24 into account our new results. The proposed model with updated rate constants explains not  
25 only our new experimental results but also the previous ones. Our model centered on the  
26 reactions of HOI and  $I_2O$  is robust in the sense that slight modifications of it can be  
27 compensated by adjustments of some kinetic constants. Fig.4 shows that the rate constants  
28 in Table I give excellent simulations of the  $k_{exp}$  values. Note the decrease in  $k_{exp}$  when the  
29 concentration of the reagent  $H_2O_2$  increases.  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65





**Fig.4.** Experimental rate constants of the I<sub>2</sub> oxidation by H<sub>2</sub>O<sub>2</sub> at 25°C with about 0.01 mol/l iodate added initially. [HClO<sub>4</sub>] = 0.04 (◇), 0.10 (×), 0.20 (O), 0.40 M (+) and values calculated with the model in Table I (lines).

#### Oxidation of I<sub>2</sub> by H<sub>2</sub>O<sub>2</sub> without iodate added initially

H<sub>2</sub>O<sub>2</sub> does not react directly with I<sub>2</sub>. An acidic solution containing only I<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> gives a quasi-steady state corresponding to the slow decomposition H<sub>2</sub>O<sub>2</sub> → H<sub>2</sub>O + O<sub>2</sub>. To obtain the oxidation of I<sub>2</sub>, the concentration in iodide must be decreased. This can be obtained by addition of iodate as in the previous section, by precipitation of AgI(s) or by formation of HgI<sup>+</sup> but can also appear spontaneously after a more or less long time. Figure 6 of reference [31] gave an example and the electronic supplement gives another one. Since the only concentration that changes significantly during the quasi-steady period is that of produced oxygen, we explained the transition to reaction O by the oxidation of iodide by oxygen. We had shown that the reaction I<sup>-</sup> + H<sup>+</sup> + ½ O<sub>2</sub> → HOI with an empirical rate law allows to explain the experimental observations [12, 31]. The direct oxidation of iodide is much too slow but a radical pathway can be fast. Studying the nullclines calculated with the model in Table 1 [27] we concluded that the transition is explained by a saddle-node

1 bifurcation occurring when the concentration of oxygen in solution reaches a critical value.  
 2 Anything that promotes the transfer of oxygen to the gas phase delays the transition. This  
 3 explains that it occurs later if the contact surface between the solution and the gas phase is  
 4 increased and if the solution is stirred [32-34].  
 5  
 6

7  
 8 An essential feature of the proposed model is the competition between the Down  
 9 reactions R5 followed by R6 and the Up reaction R10. The concentration of the intermediate  
 10  $I_2O$  is very small in aqueous solutions, is quasi-stationary and approximately proportional to  
 11  $[HOI]^2$ . The ratio between the rates  $r_{10} = k_{10} [I_2O] [H_2O_2]$  and  $r_5 = k_5 [HOI] [H_2O_2]$  is therefore  
 12 approximately proportional to  $[HOI]$ . If  $[HOI]$  is small,  $H_2O_2$  mainly reacts as a reducing agent.  
 13 If  $[HOI]$  is large,  $H_2O_2$  mainly reacts as an oxidant. The reaction R4 being a quasi-equilibrium,  
 14  $[I^-]$  must be small enough for  $H_2O_2$  to act mainly as an oxidant giving reaction O.  
 15  
 16

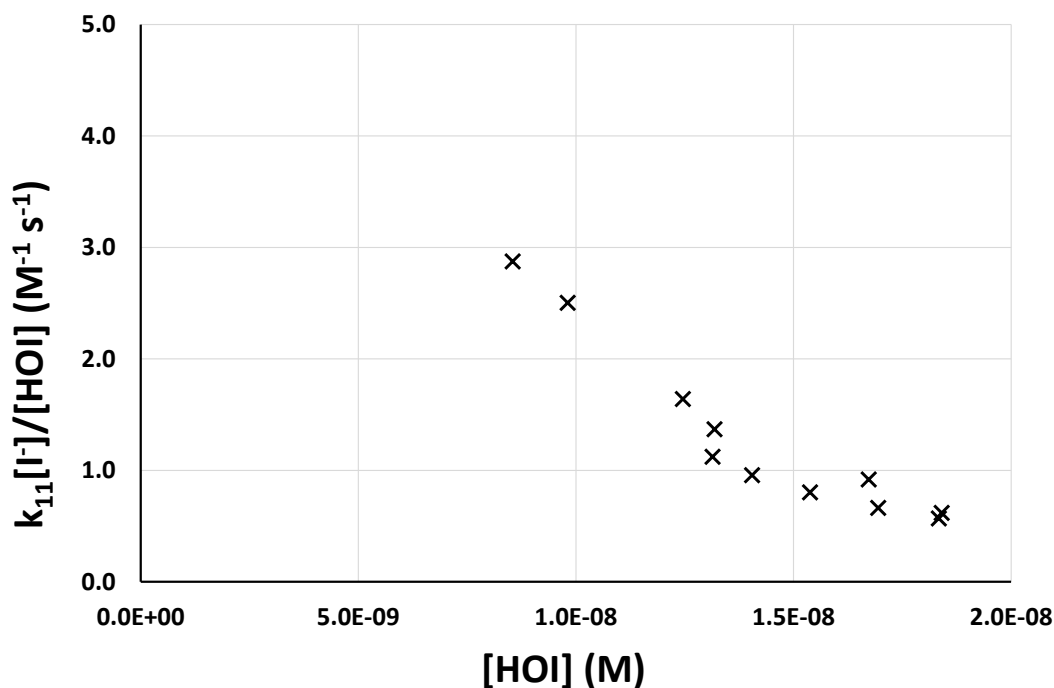
17  
 18 It is difficult to quantify the effect of oxygen. The transfer reaction R14 to the gas  
 19 phase is an over-simplification and the solution can become highly supersaturated in oxygen.  
 20 Complicated phenomena of transfer at the interface and germination-growth of bubbles  
 21 must be taken into account. Moreover, the rate of oxidation of iodide is photocatalyzed and  
 22 depends on complicated radical reactions [36]. Finally, it can be noted that the reaction  
 23  $2 H_2O_2 \rightarrow 2 H_2O + {}^1O_2$  is thermodynamically possible [37]. We could produce singlet oxygen  
 24 which would react much faster with iodide. These complications explain that the induction  
 25 period of the oxidation of  $I_2$  by  $H_2O_2$  without iodate added initially seems stochastic [34-35].  
 26 A phenomenon seems stochastic when it depends on parameters that we ignore or do not  
 27 control. A qualitative explanation of the transition between the quasi-steady state and the  
 28 reaction O when the oxygen concentration reaches a critical value is already a success of the  
 29 proposed model.  
 30  
 31  
 32  
 33  
 34  
 35  
 36  
 37  
 38  
 39  
 40  
 41  
 42  
 43  
 44  
 45  
 46

#### 47 **I(+1) reduction by $H_2O_2$ (reactions R5 and R6)**

48  
 49 Furrow [38] measured the absorbances at 354 and 460 nm of solutions of  $I_2$  and  $H_2O_2$   
 50 without iodate during the quasi-stationary period. These absorbances allow to calculate the  
 51 concentrations of  $I_2$  and  $I_3^-$ , then that of  $I^-$  and finally that of  $HOI$  corresponding to the quasi-  
 52 equilibrium R4. The sum of the reactions R5 + R6 + R11 gives the decomposition  $H_2O_2 \rightarrow H_2O$   
 53 +  $O_2$  and Furrow assumed that their rates are equal during this period giving  $k_5 [HOI] = (k'_{11} +$   
 54  $k''_{11} [H^+]) [I^-]$ . The values of  $k'_{11}$  and  $k''_{11}$  being known,  $k_5$  can be calculated. Furrow obtained  
 55  
 56  
 57  
 58  
 59  
 60  
 61  
 62  
 63  
 64  
 65

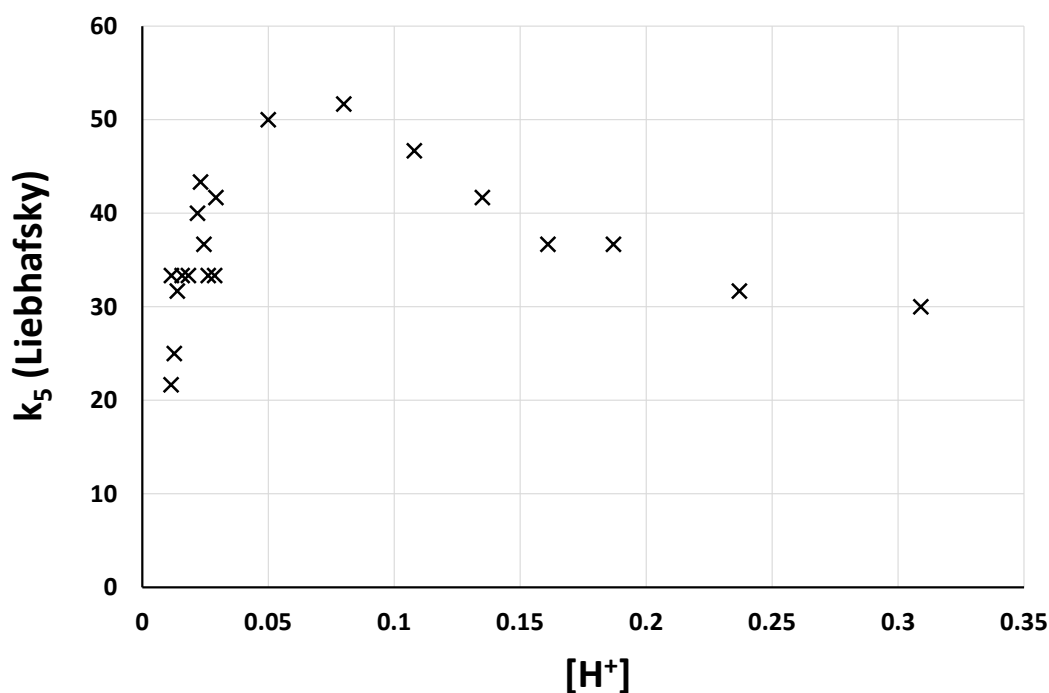
1  $k_5 = 3 \text{ M}^{-1} \text{ s}^{-1}$  but its values were widely dispersed. We recalculated his results using updated  
 2 values of the parameters ( $\varepsilon(\text{I}_2, 354) = 17$ ;  $\varepsilon(\text{I}_3^-, 354) = 26250$ ;  $\varepsilon(\text{H}_2\text{O}_2, 354)$ ;  $K_4 = 10^{11} \text{ M}^{-2}$  when  $\text{I} =$   
 3  $0.10 \text{ M}$ ) and plotted  $k_{11} [\text{I}^-] / [\text{HOI}]$ , where  $k_{11} = k'_{11} + k''_{11} [\text{H}^+]$ , as a function of  $[\text{HOI}]$ . If the  
 4 above equality was verified, the values of  $k_{11} [\text{I}^-] / [\text{HOI}]$  would be independent of  $[\text{HOI}]$ . Fig.  
 5 5 shows on the contrary a decrease when  $[\text{HOI}]$  increases. This explains why the values  
 6 calculated ignoring this dependence were so dispersed.  
 7  
 8  
 9  
 10  
 11

12 The model in Table I explains this effect of  $[\text{HOI}]$ . Numerical simulations show that  
 13 reactions R2 and R10 cannot be neglected. Their sum gives the same global reaction as R11,  
 14  $\text{I}^- + \text{H}^+ + \text{H}_2\text{O}_2 \rightarrow \text{HOI} + \text{H}_2\text{O}$ . If R3 was an equilibrium and if we could neglect the effect of  
 15 R12, we would have  $k_5 [\text{HOI}][\text{H}_2\text{O}_2] = k_{11} [\text{I}^-] [\text{H}_2\text{O}_2] + k_{10} [\text{I}_2\text{O}][\text{H}_2\text{O}_2]$  giving  $k_{11} [\text{I}^-] / [\text{HOI}] =$   
 16  $k_5 - k_{10} k_{-3}/k_3 [\text{HOI}]$ . This approximate expression explains the effect of  $[\text{HOI}]$  seen in Fig. 5  
 17 and suggests  $k_5 \sim 5 \text{ M}^{-1} \text{ s}^{-1}$  or a little larger by extrapolation at  $[\text{HOI}] \rightarrow 0$ . The numerical  
 18 simulations of these experiments taking the  $k_{\text{exp}}$  values for reaction O into account give  $k_5 = 6$   
 19  $\text{M}^{-1} \text{ s}^{-1}$ . The electronic supplement shows a comparison between the experimental values  
 20 and the values calculated with the model in Table I.  
 21  
 22  
 23  
 24  
 25  
 26  
 27  
 28  
 29  
 30  
 31



32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56 **Fig.5.** Analysis of Furrow's results [38] explained in the text.  
57  
58  
59  
60  
61  
62  
63  
64  
65

1  
2  
3 Liebhafsky [39] measured the rate of oxygen production due to the reaction  $\text{HOI} +$   
4  $\text{H}_2\text{O}_2 \rightarrow \text{I}^- + \text{H}^+ + \text{O}_2 + \text{H}_2\text{O}$  (R5 + R6) in the presence of solid iodine and an excess of  $\text{TI}^+$  ions.  
5  
6 The concentration of iodine in solution was equal to its solubility, the concentration of iodide  
7  
8 was fixed by equilibrium  $\text{TI}^+ + \text{I}^- \rightleftharpoons \text{TI}(\text{s})$  and that of HOI by reaction (R4). He deduced the  
9  
10 values of  $k_5 = (d[\text{O}_2]/dt) / ([\text{HOI}] [\text{H}_2\text{O}_2])$  in figure 6 giving on average  $k_5 = 37 \text{ M}^{-1}\text{s}^{-1}$ . We  
11  
12 recalculated his results [12] using more recent values of the equilibrium constants, but  
13  
14 keeping Liebhafsky calculations assumptions, and proposed  $k_5 = 23 \text{ M}^{-1}\text{s}^{-1}$ , a value  
15  
16 significantly greater than  $k_5 = 6 \text{ M}^{-1}\text{s}^{-1}$  adopted above.  
17  
18  
19  
20



45 **Fig.6.**  $k_5$  values ( $\text{M}^{-1}\text{s}^{-1}$ ) given by Liebhafsky in ref. 39, p.3506, Table II.

46  
47  
48 The effect of  $[\text{H}^+]$  revealed by Figure 6 suggests that the dispersion of the  $k_5$  values  
49  
50 obtained by Liebhafsky is not due to experimental inaccuracies and that the system is more  
51  
52 complicated than he thought. This is confirmed by numerical simulations using the model in  
53  
54 Table I supplemented by reaction (3) and with  $[\text{I}_2]$  fixed by the solubility of iodine. Under  
55  
56 these conditions, oxygen is produced not only by reaction R5 followed by R6 but also by  
57  
58 reactions R7 and R12.  $d[\text{O}_2]/dt > r_5$  explains that the values of  $k_5$  obtained by Liebhafsky are  
59  
60  
61  
62  
63  
64  
65

1 too large. The model also explains a surprising observation reported by Liebhafsky. If he  
 2 added only  $\text{TI}^+$ , the iodide concentration became very small, the rate of oxygen production  
 3 much too high, and iodate was produced [ref. 39, bottom of p.3504]. To avoid this, he had to  
 4 add a large amount of solid  $\text{TII(s)}$ . If  $k_{12} \sim 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , order of magnitude estimated in the  
 5 appendix, an important reaction path is  $\text{R2} + \text{R3} + \text{R4} + \text{R5} + \text{R12}$  giving overall  $2 \text{ I}^- + 2 \text{ H}^+ + 3$   
 6  $\text{H}_2\text{O}_2 \rightarrow \text{I}_2 + \text{O}_2 + 4 \text{ H}_2\text{O}$  and the observed decrease in  $[\text{I}^-]$ . The addition of solid  $\text{TII(s)}$  was  
 7 necessary to avoid this decrease and to obtain the overall reaction  $2 \text{ TII(s)} + 2 \text{ H}^+ + 3 \text{ H}_2\text{O}_2 \rightarrow$   
 8  $2 \text{ TI}^+ + \text{I}_2 + \text{O}_2 + 4 \text{ H}_2\text{O}$ . This reaction greatly contributes to the production of oxygen and  
 9 varies  $[\text{H}^+]$ . The model explains Liebhafsky observations, shows that the system he studied  
 10 gives too large values of  $k_5$  and is too complicated to allow an exact measurement.

11  
 12  
 13  
 14  
 15  
 16  
 17  
 18  
 19  
 20 Shin, Lee and von Gunten [40] studied the reaction between  $\text{H}_2\text{O}_2$  and  $\text{I}_2$  in buffered  
 21 solutions between  $\text{pH} = 4$  and  $\text{pH} = 12$ . They confirmed that this reaction is catalyzed by the  
 22 buffers. The large differences between the values of the kinetic constants published in the  
 23 literature can, in part, be explained by the effect of the nature and the concentration of the  
 24 buffers. These authors obtained  $k_5 = 29 \pm 5 \text{ M}^{-1}\text{s}^{-1}$  but this value was obtained in acetic  
 25 buffers and the value in unbuffered solutions is certainly smaller. In addition, the  
 26 extrapolation to  $\text{pH} = 1$  of results obtained above  $\text{pH} = 4$  is very approximate. The value  $k_5 =$   
 27  $6 \text{ M}^{-1}\text{s}^{-1}$  that we propose is therefore compatible with the results of Shin, Lee and von  
 28 Gunten.  
 29  
 30  
 31  
 32  
 33  
 34  
 35  
 36  
 37  
 38  
 39

## 40 Conclusion

41 The model in Table I explains the kinetics of the reactions in acidic solutions of iodine  
 42 compounds at oxidation states from -1 to +5 with each other and with  $\text{H}_2\text{O}_2$ . The new  
 43 experiments confirm the existence of the  $\text{HOOI}$  intermediate compound proposed previously  
 44 [17-22]. The effect of acidity on the disproportionation of  $\text{HOIO}$  and on its oxidation by  $\text{H}_2\text{O}_2$   
 45 shows that  $\text{OIO}^-$  is much more reactive than  $\text{HOIO}$  and suggests that the mechanism of these  
 46 reactions involves an intermediate compound noted  $\text{I}_2\text{O}_4\text{H}^-$  (reaction R22). This model, with  
 47 updated kinetic constants, also quantitatively explains the kinetics of many reactions  
 48 previously studied under very different conditions and especially the complicated kinetics of  
 49 the oxidation of  $\text{I}_2$  by  $\text{H}_2\text{O}_2$  with or without iodate added initially. This model becomes more  
 50 and more likely that it allows to explain a greater number of experiments of different types.  
 51  
 52  
 53  
 54  
 55  
 56  
 57  
 58  
 59  
 60  
 61  
 62  
 63  
 64  
 65

1 None of these results suggest radical reactions in the dark, except in the mechanism of the  
2 oxidation of iodide by oxygen. Light, including that of a spectrophotometer, can initiate  
3 radical reactions briefly discussed in the appendix which deserve further work.  
4  
5  
6  
7

## 8 **References**

- 9  
10 [1] Comprehensive Chemical Kinetics 2004, Volume 40, Chapter 14, Instability, periodic  
11 reactions, and chaos.  
12  
13 [2] H. G. Schuster and W. Just, Deterministic Chaos - An Introduction, 4th ed., 2005, Wiley-  
14 VCH, Weinheim.  
15  
16 [3] Advances in Oscillating Reactions, Ž. D. Čupić, A. F. Taylor, D. Horváth, M. Orlik and I. R.  
17 Epstein eds. Frontiers in Chemistry 2020.  
18  
19 [4] A. Z. Ivanović-Šasić, V. M. Marković, S. R. Anić, Lj. Z. Kolar-Anić and Ž. D. Čupić, Structures  
20 of chaos in open reaction systems, Phys. Chem. Chem. Phys., 2011, 13, 20162–20171.  
21  
22 [5] L. Bosland, I. Cantrel, N. Girault, and B. Clement, Modeling of iodine Radiochemistry in  
23 the ASTEC severe accident code: description and application to FPT-2 Phebus test, Nuclear  
24 Technology 2010, 171, 88-107.  
25  
26 [6] C. Fortina, V. Fèvre-Nolleta, F. Cousin, P. Lebègue, F. Louisa, Box modelling of gas-phase  
27 atmospheric iodine chemical reactivity in case of a nuclear accident, Atmos. Environment  
28 2019, 214, 116838.  
29  
30 [7] S. Saha, S. Roy, P. Mathi and J. A. Mondal, Adsorption of Iodine Species ( $I_3^-$ ,  $I^-$ , and  $IO_3^-$ ) at  
31 the Nuclear Paint Monolayer–Water Interface and Its Relevance to a Nuclear Accident  
32 Scenario, J. Phys. Chem. A 2020, 124, 6726–6734.  
33  
34 [8] A. S. Mahajan, M. Shaw, H. Oetjen, K. E. Hornsby, L. J. Carpenter, L. Kaleschke, X. Tian-  
35 Kunze, J. D. Lee, S. J. Moller, P. Edwards, R. Commane, T. Ingham, D. E. Heard and J. M. C.  
36 Plane, Evidence of reactive iodine chemistry in the Arctic boundary layer, J. Geophys.  
37 Research 2010, 115, D20303.  
38  
39 [9] A. Badia, C. E. Reeves, A. R. Baker, A. Saiz-Lopez, R. Volkamer, T. K. Koenig, E. C. Apel, R. S.  
40 Hornbrook, L. J. Carpenter, S. J. Andrews, T. Sherwen and R. von Glasow, Importance of  
41 reactive halogens in the tropical marine atmosphere: a regional modelling study using WRF-  
42 Chem, Atmos. Chem. Phys. 2019, 19, 3161–3189.  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

- 1 [10] S. Inamdar, L. Tinel, R. Chance, L. J. Carpenter, P. Sabu, R. Chacko, S. C. Tripathy, A. U.  
2 Kerkar, A. K. Sinha, P. Venkateswaran Bhaskar, A. Sarkar, R. Roy, T. Sherwen, C. Cuevas, A.  
3 Saiz-Lopez, K. Ram and A. S. Mahajan, Estimation of reactive inorganic iodine fluxes in the  
4 Indian and Southern Ocean marine boundary layer, *Atmos. Chem. Phys.* 2020, 20, 12093–  
5 12114.  
6  
7  
8  
9  
10 [11] G. Schmitz and S.D. Furrow, Kinetics of reactions of iodine inorganic compounds in  
11 acidic solutions, In *Physical Chemistry 2018, Proceedings of the 14th Int. Conf. Fundam. Appl.*  
12 *Aspects Phys. Chem.*, 271-278, Belgrade, Sept 24-28, Society of Physical Chemists of Serbia,  
13 2018.  
14  
15  
16  
17 [12] G. Schmitz, Iodine oxidation by hydrogen peroxide in acidic solutions, Bray-Liebhafsky  
18 reaction and other related reactions, *Phys. Chem. Chem. Phys.* 2010, 12, 6605-6615.  
19  
20  
21 [13] K. R. Sharma and R. M. Noyes, Oscillations in chemical systems. 13. A detailed molecular  
22 mechanism for the Bray-Liebhafsky reaction of iodate and hydrogen peroxide, *J. Am. Chem.*  
23 *Soc.* 1976, 98 (15), 4345-4361.  
24  
25  
26 [14] G. Schmitz, Effects of oxygen on the Bray-Liebhafsky reaction, *Phys. Chem. Chem. Phys.*  
27 1999, 1, 4605.  
28  
29  
30 [15] P. Ševčík, K. Kissimonová and L. Adamčíkova, Oxygen Production in the Oscillatory Bray-  
31 Liebhafsky Reaction, *J. Phys. Chem. A* 2000, 104, 3958-3963.  
32  
33 [16] P. Ševčík and L. Adamčíkova, Effect of a Gas Bubbling and Stirring on the Oscillating  
34 Bray-Liebhafsky Reaction, *J. Phys. Chem. A* 1998, 102, 1288-1291.  
35  
36 [17] J.M. Ball, J.B. Hnatiw, The reduction of I<sub>2</sub> by H<sub>2</sub>O<sub>2</sub> in aqueous solution, *Can. J. Chem.*  
37 2001, 79, 304-311.  
38  
39 [18] G. Schmitz, Buffers catalysis of the iodine(+1) reduction by hydrogen peroxide In  
40 *Physical Chemistry 2008, Proceedings of the 9th Int. Conf. Fundam. Appl. Aspects Phys.*  
41 *Chem.*, pp. 219-224, Society of Physical Chemists of Serbia, Belgrade, 2008.  
42  
43 [19] G. Schmitz, Iodine(+1) Reduction by Hydrogen Peroxide, *Russian J. Phys. Chem.*, 2009,  
44 83(9), 1447.  
45  
46 [20] G. Schmitz and S. D. Furrow, Kinetics of the iodate reduction by hydrogen peroxide and  
47 relation with the Briggs-Rauscher and Bray-Liebhafsky oscillating reactions, *Phys. Chem.*  
48 *Chem. Phys.* 2012, 14, 5711-5717.  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

- 1 [21] G. Schmitz and S.D. Furrow - Iodine Inorganic Reactions in Acidic Solutions and  
2 Oscillating Reactions, Physical Chemistry 2014, Proceedings of the 12th Int. Conf. Fundam.  
3 Appl. Aspects Phys. Chem., pp. 320-326, Society of Physical Chemists of Serbia, Belgrade  
4 2014.  
5  
6  
7  
8 [22] G. Schmitz and S. D. Furrow, Bray-Liebhafsky and Non-Catalyzed Briggs-Rauscher  
9 Oscillating Reactions, Russ. J. Phys. Chem. A, 2016, 90(2), 271-275.  
10  
11 [23] E. Szabo and P. Ševčík, Reexamination of Gas Production in the Bray-Liebhafsky  
12 Reaction: What Happened to O<sub>2</sub> Pulses? J. Phys. Chem. A 2013, 117, 10604–10614.  
13  
14 [24] G. Schmitz and G. Lente, Fundamental Concepts in Chemical Kinetics, ChemTexts 2020,  
15 6(1), 1.  
16  
17 [25] G. Schmitz, Inorganic Reactions of Iodine(+1) in Acidic Solutions, Int. J. Chem. Kinet.,  
18 2004, 36, 480.  
19  
20 [26] G. Schmitz and S. D. Furrow, Kinetics of iodous acid disproportionation, Int. J. Chem.  
21 Kinet., 2013, 48(8), 525-530.  
22  
23 [27] G. Schmitz, Nullclines. A Simple Explanation of Complicated Phenomena, In Physical  
24 Chemistry 2021, *Proceedings of the 15th Int. Conf. Fundam. Appl. Aspects Phys. Chem.*, pp.  
25 222-229, Belgrade, Sept 20-24, Society of Physical Chemists of Serbia, 2021. ISBN 978-86-  
26 82475-40-8.  
27  
28 [28] G. Schmitz, Z. Noszticzius, G. Hollo, M. Wittmann and S. D. Furrow, Reactions of Iodate  
29 with Iodine in Concentrated Sulfuric Acid. Formation of I(+3) and I(+1) Compounds, Chem.  
30 Phys. Lett. 2018, 691, 44.  
31  
32 [29] S. D. Furrow, R. Cervellati and G. Amadori, New Substrates for the Oscillating Briggs-  
33 Rauscher Reaction, J. Phys. Chem. A 2002, 106, 5841-5850.  
34  
35 [30] G. Schmitz, Inorganic Reactions of Iodine(III) in Acidic Solutions and Free Energy of  
36 Iodous Acid Formation, Int. J. Chem. Kinet., 2008, 40, 647-652.  
37  
38 [31] G. Schmitz, Iodine oxidation by hydrogen peroxide and Bray-Liebhafsky oscillating  
39 reaction: effect of the temperature, Phys. Chem. Chem. Phys. 2011, 13, 7102-7111.  
40  
41 [32] A. Olexová, M. Mrákavová, M. Melicherčík and L. Treindl, The autocatalytic oxidation of  
42 iodine with hydrogen peroxide in relation to the Bray-Liebhafsky oscillatory reaction, Collect.  
43 Czech. Chem. Commun. 2006, 71, 91–106.  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65



- 1 [33] A. Olexová, M. Mrákavová, M. Melicherčík and L. Treindl, Oscillatory System I<sup>-</sup>, H<sub>2</sub>O<sub>2</sub>,  
2 HClO<sub>4</sub>: The Modified Form of the Bray-Liebhafsky Reaction, J. Phys. Chem. A 2010, 114,  
3 7026–7029.  
4  
5  
6 [34] D. R. Stanisavljev, K. Z. Stevanović and I. M. Bubanja, Outsized stochasticity of iodine  
7 oxidation with hydrogen peroxide and its implications on the reaction mechanism, Chem.  
8 Phys. Letters 2018, 706, 120-126.  
9  
10 [35] K. Z. Stevanović, I. M. Bubanja and D. R. Stanisavljev, Is Iodine Oxidation with Hydrogen  
11 Peroxide Coupled with Nucleation Processes? J. Phys. Chem. C 2019, 123, 16671-16680.  
12  
13 [36] J. Jortner, M. Ottolenghi and G. Stein, The Effect of Oxygen on the Photochemistry of  
14 the Iodide Ion in Aqueous Solutions, J. Phys. Chem. 1962, 66, 2042-2045.  
15  
16 [37] V. Nardello, K. Briviba, Helmut Sies and J.-M. Aubry, Identification of the precursor of  
17 singlet oxygen (<sup>1</sup>O<sub>2</sub>, <sup>1</sup>Δ<sub>g</sub>) involved in the disproportionation of hydrogen peroxide catalyzed  
18 by calcium hydroxide, Chem. Commun., 1998, 599-600.  
19  
20 [38] S. D. Furrow, Reactions of Iodine Intermediates in Iodate-Hydrogen Peroxide Oscillators,  
21 J. Phys. Chem. 1987, 91, 2129-2135.  
22  
23 [39] H. A. Liebhafsky, The Catalytic Decomposition of Hydrogen Peroxide by the Iodine-  
24 Iodide Couple. III. The Rate of Oxidation, In Acid Solution, of Hydrogen Peroxide by Iodine, J.  
25 Amer. Chem. Soc. 1932, 54, 3499-3508.  
26  
27 [40] J. Shin, Y. Lee, U. von Gunten, Kinetics of the reaction between hydrogen peroxide and  
28 aqueous iodine: Implications for technical and natural aquatic systems, Water Research  
29 2020, 179, 115852.  
30  
31 [41] G. Schmitz, Kinetics and mechanism of the iodate-iodide reaction and other related  
32 reactions, Phys. Chem. Chem. Phys. 1999, 1, 1909.  
33  
34 [42] R. Furuichi and H. A. Liebhafsky, Bull. Chem. Soc. Japan, 1975, 48, 745.  
35  
36 [43] G. Schmitz, Kinetics of the Dushman reaction at low I<sup>-</sup> concentrations, Phys. Chem.  
37 Chem. Phys., 2000, 2, 4041.  
38  
39 [44] H.A. Liebhafsky and A. Mohammad, The kinetics of the reduction in acidic solution of  
40 hydrogen peroxide by iodide ion, J. Am. Chem. Soc. 1933, 55, 3977-3986.  
41  
42 [45] J. Lozar and B. Lafage, Kinetics of the oxidation of iodide ions by oxygenated water using  
43 spectrophotometry with a microcomputer, Bulletin de l'Union des Physiciens 1994, 88(764),  
44 895-902.  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

[46] D. R. Stanisavljev, M. C. Milenković, Miloš D. Mojović, and Ana D. Popović-Bijelić, Oxygen Centered Radicals in Iodine Chemical Oscillators, *J. Phys. Chem. A* 2011, 115, 7955–7958

[47] D. R. Stanisavljev, M. C. Milenković, Ana D. Popović-Bijelić, and Miloš D. Mojović, Radicals in the Bray–Liebhafsky Oscillatory Reaction, *J. Phys. Chem. A* 2013, 117, 3292–3295.

[48] S. Kéki, G. Székely and M. T. Beck, The Effect of Light on the Bray-Liebhafsky Reaction, *J. Phys. Chem. A* 2003, 107, 73-75.

[49] D. M. Stanbury, Comment on the Principle of Detailed Balancing in Complex Mechanisms and Its Application to Iodate Reactions. *J. Phys. Chem. A*, 2018, 122, 3956-3957.

## Appendix. Rate constants

### *Ionic strength effect*

Equilibrium constants depend on the ionic strength and consequently the kinetic constants also depend on it [24]. It is not possible to take this effect exactly into account but we note that most monovalent ions have an activity coefficient  $\gamma$  near 0.70-0.75 in the range of ionic strengths of most of our experiments (0.1 to 0.2 M) and we use values of the kinetic constants estimated if  $\gamma \sim 0.7$ . This is an approximation but better than ignoring the effect of the ionic strength. We use a superscript ° for values at zero ionic strength.

### *Reaction R1*

The complicated rate law of the iodate reduction by iodide has been discussed before [41]. In non-buffered solutions and when  $[I^-]$  is lower than about  $10^{-6}$  M, the rate law reduces to the expression in Table I. Furuichi and Liebhafsky [42] have obtained  $r_{+1} = 4500 \gamma^4 [IO_3^-][I^-][H^+]^2$  giving  $k_{+1}$  between 1100 and 1400  $M^{-3} s^{-1}$  if  $\gamma$  is between 0.70 and 0.75 and one of us [43] has obtained  $k_{+1} = (1200 \pm 150) M^{-3} s^{-1}$  if the ionic strength is 0.2 M.

New measurements of  $k_{-1}$  are given in section "I(+3) autocatalytic disproportionation".

### *Reactions R2 and R3*

The rates of these reactions depend on four parameters not measured directly and the aim of the following discussion is to estimate them.  $I_2O$  is an intermediate in quasi-stationary concentration giving  $r_2 = r_3 + r_{10}$  and equation (A1).

$$[I_2O] = \frac{k_2[H^+][HOIO][I^-] + k_{-3}[H^+][HOI]^2}{k_{-2} + k_3[H^+] + (k'_{10} + k''_{10}/[H^+])[H_2O_2][H^+]}$$
(A1)

By introducing this expression into the expressions of the rates  $r_2$ ,  $r_3$  and  $r_{10}$ , we see that they depend on the ratios  $k_{-2}/k_3$ ,  $k'_{10}/k_3$  and  $k''_{10}/k_3$  but not on the value of  $k_3$ . Only the product  $k_3[I_2O]$  can be calculated and, since  $[I_2O]$  is unknown, so is  $k_3$ . It is supposed to be large enough for  $[I_2O]$  to be quasi-stationary. This is why we only give the values of  $k_{-2}/k_3$ ,  $k'_{10}/k_3$  and  $k''_{10}/k_3$  in table I. Our numerical simulations use  $k_3 = 1 \times 10^7$  but a value ten times larger or ten times smaller gives the same results.

K. Stevanović et al [35] criticized reactions (R2) and (R3) and wrote on page 16677: "A closer look at [R3] shows that it is not a redox process and represents simple formation of HOI anhydride ... quite improbable in water solution."  $I_2O$  is not HOI anhydride but its dimer, which is an essential feature of the model as explained in the main text. We had specified [12] that  $I_2O$  is a simple representation of a compound of unknown structure in aqueous solution but very probably hydrated. Forms such as  $I-O-I-OH_2$  or  $H_2O-I-O-I-OH_2$  are kinetically equivalent. These authors also criticized reaction (R3) using thermodynamic arguments based on a supposed value of  $k_3$  but we had specified that the value of  $k_3$  has no effect on the numerical simulations if it is sufficiently large. Thermodynamic arguments cannot be based on an unknown value of a rate constant. The only argument can be based on the sum of (R10) and the reverse of (R3) giving  $HOI + H_2O_2 \rightarrow HOIO + H_2O$  with  $\Delta G_r = -101$  kJ/mol and showing that the oxidation of  $I(+1)$  via  $I_2O$  is possible. None of the arguments presented by these authors allow to rule out reactions of a hydrated form of  $I_2O$ . The proposed mechanism is the only published assumption which explains all the experimental observations.

The disproportionation rate of HOI,  $r_{HOI} = k_{HOI} [HOI]^2$  with  $k_{HOI} = 25 \text{ M}^{-1} \text{ s}^{-1}$  in acidic solutions [12] gives an important relation. The rate  $r_{+2}$  can be neglected under the conditions of this disproportionation and  $[H^+] \gg k_{-2}/k_3$  so that  $r_{HOI} = k_{-2} [I_2O]$ . Then, (A1) gives  $k_{-2}k_3/k_3 = k_{HOI}$ .

A further information is obtained noting that the sum (R1) + (R2) + (R3) gives  $\text{IO}_3^- + 2 \text{I}^- + 3 \text{H}^+ = 3 \text{HOI}$ . The equilibrium constant of this reaction is accurately known at zero ionic strength:  $K_{123}^\circ = 1.3 \times 10^{10}$  giving  $k_1 k_2 k_3 / k_{-1} k_{-2} k_{-3} = \gamma^6 1.3 \times 10^{10}$ . Taking  $k_1 = 1300$ ,  $k_{-1} = 212$  and  $k_{-2} k_{-3} / k_3 = k_{\text{HOI}} = 25$  we obtain  $k_2 = (6 \text{ to } 9) \times 10^9 \text{ M}^{-2} \text{s}^{-1}$  if  $\gamma = 0.7$  to  $0.75$ . Our simulations suggest to decrease slightly this estimated value and we use  $k_2 = 5 \times 10^9 \text{ M}^{-2} \text{s}^{-1}$  at  $0.1 \text{ M}$  ionic strength decreasing to  $3 \times 10^9 \text{ M}^{-2} \text{s}^{-1}$  at  $1.0 \text{ M}$  ionic strength.

#### Reaction R4

The rate constant  $k_{-4} = 1.8 \times 10^{-3} \text{ M s}^{-1}$  was measured by Furrow [38] and confirmed later [12]. The equilibrium constant at zero ionic strength is well known ( $K_4^\circ = 1/5.3 \times 10^{-13}$ ) giving  $k_4 = 1.8 \times 10^{-3} \times (0.7)^2 / 5.3 \times 10^{-13} = 1.7 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$  if  $\gamma = 0.7$ .

#### Reactions R5 and R6

We explain in the main text why the global reaction  $\text{HOI} + \text{H}_2\text{O}_2 = \text{I}^- + \text{H}^+ + \text{O}_2 + \text{H}_2\text{O}$  must be split into R5 and R6.  $K_5^\circ K_6^\circ = 8 \times 10^6$  at zero ionic strength gives  $K_5 K_6 = 1.4 \times 10^7$  if  $\gamma = 0.75$ . The order of magnitude of  $K_6 \sim 10^3$  was estimated before [19] and the value of  $k_5$  is discussed in section "Oxidation of  $\text{I}_2$  by  $\text{H}_2\text{O}_2$  without iodate added initially". These values give  $k_{-5} = k_5 / K_5 = 6 / 1.4 \times 10^4 = 4 \times 10^{-4}$ . This estimation shows that R5 is nearly irreversible under our conditions.  $k_{-6}$  is unknown. We take it sufficiently large ( $10^5$  or  $10^6$ ) to explain the effect of  $\text{O}_2$  on the BL reaction by the reversibility of reaction R6.

We have seen that  $\text{I}_2\text{OH}^-$  is an intermediate of reaction R4 and reaction A2 is known [19].



It is not included in Table I because its rate can be neglected under the experimental conditions of this work.

$$\frac{r_{\text{A2}}}{r_5} = \frac{k_{\text{A2}}[\text{I}_2\text{OH}^-]}{k_5[\text{HOI}]}$$

$k_{\text{A2}} = 1.3 \times 10^4 \text{ M}^{-1} \text{s}^{-1}$  [19] and  $[\text{I}_2\text{OH}^-] = 320 [\text{HOI}][\text{I}^-]$  [25] give  $r_{\text{A2}}/r_5 = 7 \times 10^5 [\text{I}^-]$ .  $[\text{I}^-]$  is always sufficiently small during our experiments to have  $r_{\text{A2}} \ll r_5$ .

#### Reaction R7

1 We have seen that the rate of HOIO disproportionation increases more quickly than  
 2  $1/[H^+]$  and that the rate of HOIO oxidation by  $H_2O_2$  is inversely proportional to  $[H^+]$ . These  
 3 results require a revision of our simulations of the effect of  $[H^+]$  on the kinetics of reaction O  
 4 and we have to assume that the rate of R7 is also inversely proportional to  $[H^+]$  in agreement  
 5 with our conclusion that  $OIO^-$  is much more reactive than HOIO. The rate laws of these  
 6 reactions could be written as functions of  $[OIO^-] = K_{a,HOIO} [HOIO]/[H^+]$  but we did not  
 7 introduce this complication in the rate equations because it would have no effect on the  
 8 numerical simulations.  $k_7$  is adjusted to simulate the kinetics of reaction O.  $K_2K_3K_5K_6 = K_7$  and  
 9  $K_5K_6 = 1.6 \times 10^7$  give  $K_7 = 3.2 \times 10^{15}$  showing that R17 is practically irreversible. This is also true  
 10 for the others  $H_2O_2$  reactions.  
 11  
 12  
 13  
 14  
 15  
 16  
 17  
 18  
 19  
 20  
 21

### 22 *Reactions R8 to R11*

23 We have studied the kinetic of reaction R8 [20] and obtained the classical rate law in  
 24 Table I when the concentration of  $H_2O_2$  is not too large. A new radical pathway appears if it  
 25 is larger than about 0.3 M but this pathway can be neglected under the experimental  
 26 conditions of this work.  
 27  
 28  
 29  
 30

31 The kinetics and possible mechanism of reaction R9 is discussed in the main text. It  
 32 involves the intermediate  $I_2O_4H^-$  but, as long as its concentration remains negligible, it is  
 33 sufficient to consider the overall reaction  $HOIO + H_2O_2 \rightarrow IO_3^- + H^+ + H_2O$  with the kinetic law  
 34 in Table 1. We avoid complications that have no effect on the numerical simulations. The  
 35 value of  $k_9$  was measured experimentally. The term  $\alpha_9 [H_2O_2]$  was negligible in our  
 36 measurements of the rate of reaction R9 and the value of  $\alpha_9$  is chosen to improve the  
 37 simulations of the reaction O. Its effect is small and therefore the indicated value is  
 38 approximate.  
 39  
 40  
 41  
 42  
 43  
 44  
 45  
 46

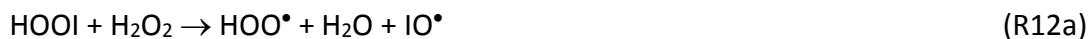
47 As explained when we have discussed reactions R2 and R3, only the ratios  $k'_{10}/k_3$  and  
 48  $k''_{10}/k_3$  have an effect on the simulations. These ratios are adjusted to simulate the kinetics  
 49 of reaction O.  
 50  
 51  
 52

53 The rate constants of reaction R11 were measured by Liebhafsky [44] and confirmed  
 54 later [45].  
 55  
 56  
 57  
 58

### 59 *Reaction R12*

60  
 61  
 62  
 63  
 64  
 65

Reaction R12 explains qualitatively the observed effects of oxygen on the BL reaction by the oxidation of  $I^-$ . The direct reaction is too slow but this oxidation by a radical mechanism can be fast. It could explain that Stanisavljev et al [46, 47] have observed radical reactions during the BL reaction. Reaction R12a is known [20-22] but the reactions following it can only be assumed.



$\text{IO}^\bullet + \text{H}_2\text{O}_2 \rightarrow \text{HOIO} + \text{OH}^\bullet$  can be preferred to  $\text{IO}^\bullet + \text{H}_2\text{O}_2 \rightarrow \text{HOI} + \text{HOO}^\bullet$  because the O-O bond in  $\text{H}_2\text{O}_2$  is much weaker ( $E = 148 \text{ kJ}$ ) than the H-O bond ( $E = 465 \text{ kJ}$ ). The reactions  $2 \text{HOO}^\bullet \rightarrow \text{O}_2 + \text{H}_2\text{O}_2$ ,  $2 \text{OH}^\bullet \rightarrow \text{H}_2\text{O}_2$  and  $\text{OH}^\bullet + \text{H}_2\text{O}_2 \rightarrow \text{HOO}^\bullet + \text{H}_2\text{O}$  are often accepted. We do not hypothesize about these radical reactions and only assume that the oxidation of HOOI by  $\text{H}_2\text{O}_2$  leads to the global reaction  $\text{HOOI} + 2 \text{H}_2\text{O}_2 \rightarrow \text{HOIO} + \text{O}_2 + 2 \text{H}_2\text{O}$  (R12). Reaction R6 being reversible,  $I^- + \text{H}^+ + \text{O}_2 \rightleftharpoons \text{HOOI}$  followed by R12 gives the oxidation of  $I^-$  to HOIO. A likely order of magnitude of  $k_{12a}$  is  $10^7 \text{ M}^{-1} \text{ s}^{-1}$ . The direct isomerization of HOOI seems very slow.

Light photo-catalyzes the oxidation of  $I^-$  by oxygen [36]. We do not discuss this complicated mechanism and just mention that a possible pathway not mentioned before could be the reversibility of R6 followed by  $\text{HOOI} + h\nu \rightarrow \text{OH}^\bullet + \text{IO}^\bullet$ . This photo-catalysis of the iodide oxidation could explain the light effect on the BL reaction [48]. The eventual contribution of  $\text{I}_2 + h\nu \rightarrow 2 \text{I}^\bullet$  seems to depend on the experimental conditions.

### Reaction R13

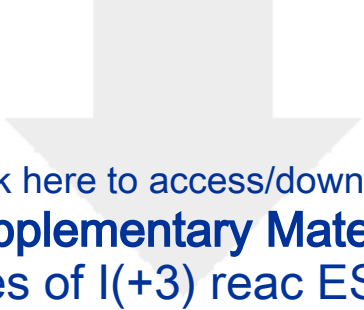
Reaction R13 is much slower than R9 as soon as there is a trace of  $\text{H}_2\text{O}_2$  and this reaction has no effect on the systems studied here. It is however important because it shows that  $\text{OIO}^-$  is much more reactive than HOIO which explains the effect of  $[\text{H}^+]$  on the rate of reactions R7 and R9. The constants  $k'_{13}$  and  $k''_{13}$  are from section "I(+3) disproportionation". Stanbury [49] pointed out that  $\text{R13} = \text{R2} + \text{R3} - \text{R1}$  gives  $K_{13} = K_2K_3/K_1$ , a constraint not always satisfied in mechanisms proposed for iodate reactions. It gives  $k_{-13} = 3 \times 10^{-8} k_{13}$  and shows that the reversibility of R13 can be neglected during our experiments.

### Reactions R14 and R15

1           The solubility of O<sub>2</sub> at 25° in equilibrium with air is 8.3 mg/l = 2.6×10<sup>-4</sup> M. Bubbles of  
2 O<sub>2</sub> may form when [O<sub>2</sub>] > 2.6×10<sup>-4</sup> M / 0.21 = 1.25×10<sup>-3</sup> M. The function *max*( ) in the rate  
3 law is used to avoid a negative rate. The order of magnitude of k<sub>14</sub> and k<sub>15</sub> were discussed  
4 before [31]. We use k<sub>14</sub> ~ 10<sup>-4</sup> s<sup>-1</sup>. r<sub>15</sub> has an effect on the Bray-Liebhafsky oscillations but can  
5 be neglected for the experiments discussed in this work.  
6  
7  
8  
9

### 10 11 *Reactions R16, R17 and R18*

12           The rate expressions of these reactions are multiplied by an arbitrary large factor  
13 5×10<sup>9</sup> because they are close to their equilibrium at the time scale of our experiments. A  
14 detailed critical analysis of the published values of K<sub>16</sub> in the electronic supplement of ref.25  
15 gave K<sub>16</sub> = 713. K<sub>17</sub><sup>o</sup> = 0.156 gives K<sub>17</sub> = 0.28 if γ = 0.75. We had measured K<sub>18</sub> ~ 0.5 [25] but  
16 this value was inaccurate. This work suggests decreasing it slightly.  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65



Click here to access/download  
**Supplementary Material**  
Studies of I(+3) reac ES.docx

