Reaction Kinetics, Mechanisms and Catalysis (2022) 135:1171–1186
https://doi.org/10.1007/s11144-022-02155-4

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

Guy E. Schmitz[1] · **Stanley D. Furrow**[2]

Received: 15 November 2021 / Accepted: 3 January 2022 / Published online: 10 January 2022

Abstract

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 → 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–Liebhafsky reaction. H_2O_2 would oxidize HOOI by a radical mechanism.

Keywords I(+3) disproportionation · I(+3) oxidation by H_2O_2 · I_2 oxidation by H_2O_2 · I(+1) reduction by H_2O_2

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_2O_2. Adopting the terminology Up and Down

---

✉ Guy E. Schmitz
guy.schmitz@ulb.be

[1] Ecole Polytechnique, Université Libre de Bruxelles, CP165/63, Av. F. Roosevelt 50, 1050 Brussels, Belgium

[2] Penn State Berks College, The Pennsylvania State University, Reading, PA 19610, USA

reactions proposed by Liebhafsky, we continue to explore the iodine house [11] with 6 floors from I(− 1) to I(+ 5) and an elevator, H_2O_2.

Table 1 is an update of the model proposed in 2010 [12] taking into account our new study of the kinetics of I(+ 3) reactions. The observed effect of $[H^+]$ has consequences for other reactions. A model of iodine reactions must also explain the very unusual kinetics of the oxidation of I_2 by H_2O_2 (reaction O) discussed below. Some kinetic constants were known. Others were adjusted in 2010 to explain this kinetics and we have updated them to take into account the results presented in this work.

The former explanation of the effects of oxygen on the Bray–Liebhafsky (BL) oscillations is also modified. Sharma and Noyes [13] had studied these effects and had even proposed, without success, that they could explain the oscillations. This explanation has been discarded but the importance of oxygen reactions has been confirmed [14–16]. To take these effects into account, the 2010 model included the global reaction $I^- + H^+ + 1/2O_2 \rightarrow HOI$ with an empirical rate law. This reaction seems simple but is actually a complicated light-catalyzed radical reaction that deserves further experimental study. In the meantime, other studies suggest that it involves the HOOI intermediate proposed by Ball and Hnatiw [17] to explain the kinetics of the reduction of I(+ 1) by H_2O_2 in buffered solutions. The existence of this intermediate has been confirmed later [18, 19]. HOOI is also an important intermediate for the explanation of the reduction of iodate by H_2O_2 [20]. The classical rate law of this reduction is no longer valid when the concentration of H_2O_2 is larger than about 0.2–0.3 M and a radical reaction path appears. The reaction $HOI + H_2O_2 \rightarrow I^- + H^+ + O_2 + H_2O$ must be split into $HOI + H_2O_2 \rightleftharpoons HOOI + H_2O$ (R5) and $HOOI \rightleftharpoons I^- + H^+ + O_2$(R6) and a radical reaction path would be initiated by a reaction between HOOI and H_2O_2 [21, 22]. Reaction R6 could also explain the observation of E. Szabo and P. Ševčik [23]. They measured accurately the rate of O_2(g) production during the BL reaction and identified two precursors. One is O_2(aq). The concentration of the other precursor increases with $[H_2O_2]$ and HOOI explains this observation. All these works suggest our new explanation of the effect of oxygen on the BL reaction: R6 is highly reversible and followed by reaction R12. We conclude that HOOI is a member of the iodine house with consequences in many systems.

Some rate constants in Table 1 are calculated using the relation $K_{eq} = k_+/k_-$ between an equilibrium constant and the kinetic constants in the forward and backward directions. It is sometimes justified by the principle of microscopic reversibility. However, many reactions of Table 1 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].

$$HOI + I^- \rightleftharpoons I_2OH^- \tag{4a}$$

$$I_2OH^- + H^+ \rightleftharpoons I_2 + H_2O \tag{4b}$$

The quasi-stationarity of $[I_2OH^-]$ gives $r_{4a} = r_{ab}$ and

Table 1 Units: (mol/l, s)

R1	$IO_3^- + I^- + 2\,H^+ \rightleftharpoons HOI + HOIO$ $r_1 = k_1[IO_3^-][I^-][H^+]^2 - k_{-1}[HOI][HOIO]$	$k_1 = 1300$	$k_{-1} = 210$
R2	$HOIO + I^- + H^+ \rightleftharpoons I_2O + H_2O$ $r_2 = k_2[H^+][HOIO][I^-] - k_{-2}[I_2O]$	$k_2 = 5 \times 10^9$	$k_{-2}/k_3 = 1.0 \times 10^{-7}$
R3	$I_2O + H_2O \rightleftharpoons 2HOI$ $r_3 = k_3[H^+][I_2O] - k_{-3}[H^+][HOI]^2$	Large See Online Appendix	$k_{-3} = 2.44 \times 10^8$
R4	$HOI + I^- + H^+ \rightleftharpoons I_2 + H_2O$ $r_4 = k_4[HOI][I^-] - k_{-4}[I_2]/[H^+]$	$k_4 = 1.7 \times 10^9$	$k_{-4} = 1.8 \times 10^{-3}$
Down reactions			
R5	$HOI + H_2O_2 \rightleftharpoons HOOI + H_2O$ $r_5 = k_5[HOI][H_2O_2] - k_{-5}[HOOI]$	$k_5 = 6$	k_{-5} very small See Online Appendix
R6	$HOOI \rightleftharpoons I^- + H^+ + O_2$ $r_6 = k_6[HOOI] - k_{-6}[I^-][H^+][O_2]$	$k_6 = 1 \times 10^8$	$k_{-6} = 1 \times 10^5$
R7	$HOIO + H_2O_2 \rightarrow HOI + O_2 + H_2O$ $r_7 = k_7[HOIO][H_2O_2]/[H^+]$	$k_7 = 0.5$	irreversible See Online Appendix
R8	$IO_3^- + H^+ + H_2O_2 \rightarrow HOIO + O_2 + H_2O$ $r_8 = (k'_8 + k''_8[H^+])[IO_3^-][H_2O_2]$	$k'_8 = 1.3 \times 10^{-7}$	$k''_8 = 1.5 \times 10^{-5}$
Up reactions			
R9	*Net* $HOIO + H_2O_2 \rightarrow IO_3^- + H^+ + H_2O$ $r_9 = k_9[H_2O_2][HOIO]^2/\{[H^+](1 + a_9[H_2O_2])\}$	$k_9 = 1.7 \times 10^5$	$\alpha_9 = 10$
R10	$I_2O + H_2O_2 \rightarrow HOI + HOIO$ $r_{10} = (k'_{10} + k''_{10}/[H^+])[I_2O][H_2O_2]$	$k'_{10}/k_3 = 0.050$	$k''_{10}/k_3 = 4.1 \times 10^{-3}$
R11	$I^- + H^+ + H_2O_2 \rightarrow HOI + H_2O$ $r_{11} = (k'_{11} + k''_{11}[H^+])[I^-][H_2O_2]$	$k'_{11} = 0.012$	$k''_{11} = 0.17$
Effect of oxygen			
R12	$HOOI + 2\,H_2O_2 \rightarrow HOIO + O_2 + 2\,H_2O$ Global radical reaction beginning with $HOOI + H_2O_2 \rightarrow HOO\cdot + H_2O + IO\cdot$ (R12a) $r_{12} = k_{12a}[HOOI][H_2O_2]$	See Online Appendix	
Side reactions			
R13	$2HOIO \rightarrow IO_3^- + HOI + H^+$ $r_{13} = \left(k'_{13}/[H^+] + k''_{13}/[H^+]^2\right)[HOIO]^2$	$k'_{13} = 0.045$	$k''_{13} = 0.065$
R14	$O_2 \rightleftharpoons O_2(g)$ $r_{14} = \max(0; k_{14}([O_2] - [O_2]_{sat}))$	See Online Appendix	
R15	$I_2 \rightleftharpoons I_2(g)$ $r_{15} = k_{15}[I_2]$	See Online Appendix	
R16	$I_2 + I^- \rightleftharpoons I_3^-$ $r_{16} = 5 \times 10^9([I_2][I^-] - [I_3^-]/K_{16})$	$K_{16} = 713$	
R17	$HIO_3 \rightleftharpoons IO_3^- + H^+$ $r_{17} = 5 \times 10^9(K_{17}[HIO_3] - [IO_3^-][H^+])$	$K_{17} = 0.28$	
R18	$HOI + H^+ \rightleftharpoons H_2OI^+$ $r_{18} = 5 \times 10^9(K_{18}[HOI][H^+] - [H_2OI^+])$	$K_{18} = 0.3$	
R19	$HOIO + H^+ \rightleftharpoons H_2OIO^+$ $r_{19} = 5 \times 10^9(K_{19}[HOIO][H^+] - [H_2OIO^+])$	$K_{19} < 0.1$	

$$r_{4a} = \frac{k_{4a}k_{4b}[HOI][I^-]\left[H^+\right] - k_{-4a}k_{-4b}\left[I_2\right]}{k_{-4a} + k_{4b}\left[H^+\right]}$$

The rate law in Table 1 is observed when $k_{4b}\left[H^+\right] \gg k_{-4a}$. At equilibrium $k_{4a}k_{4b}$ $[HOI]_{eq}[I^-]_{eq}[H^+]_{eq} = k_{-4a}k_{-4b}$ $[I_2]_{eq}$. This kinetic expression must be equivalent to the thermodynamic expression of the equilibrium. It follows that $k_{4a}k_{4b}/k_{-4a}k_{-4b} = K_{eq}$ and, with numbering of Table 1, $k_4/k_{-4} = K_4$. We have applied this principle of equivalence between the kinetic and thermodynamic expressions of the equilibrium to other quasi-elementary reactions in Table 1.

Section "I(+3) disproportionation" proposes a new interpretation of our kinetic study of the reaction 2HOIO → IO_3^- + HOI + H^+ (R13) published previously [26]. Section "I(+3) autocatalytic disproportionation" presents a new kinetic study of the reaction HOI + HOIO → IO_3^- + I^- + $2H^+$ (-R1) and the next section presents a new kinetic study of the oxidation of I(+3) by H_2O_2 (R9). Section "Oxidation of I2 by H_2O_2 with iodate added initially (Reaction O)" shows that the model in Table 1 with updated values of some kinetic constant explains also our former results. If there is no iodate initially, the $I_2 + H_2O_2$ reaction begins with a non-reproducible induction period. It is discussed in section "Oxidation of I2 by H_2O_2 without iodate added initially" on the basis of our recent calculations [27] of the nullclines corresponding to the model in Table 1. Section "I(+1) reduction by H_2O_2" shows that this induction period allows measurements of the kinetic constant of the reaction HOI + H_2O_2 → HOOI + H_2O (R5). Appendix (in the Supplementary Information) gives details about the calculations of the kinetic constants given in Table 1.

Experiments and calculations

The I(+3) solutions are prepared as explained before [28] by the reaction of weighed amounts of I_2 and KIO_3 in concentrated H_2SO_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 MΩ water is supplied by a Barnstead Micropore ST model. The initial concentrations $[H^+]$ are calculated using the Pitzer model of the H_2SO_4 solutions. The absorbance measurements are made with an Agilent Cary 60 scanning spectrophotometer. The addition of the samples of I(+3) in H_2SO_4 to the aqueous phase (of composition depending on the kind of experiment) being exothermic, the aqueous phase is cooled before mixing so that the temperature after mixing is close to 25 °C. The spectrophotometer cell is thermostatically controlled at 25 °C and contains a small stirrer.

The sample of I(+3) (20 to 30 mg) must be added quickly to the aqueous phase (3 to 5 cm^3). Mixing in the reverse order causes a local overheating giving some fast initial reactions and wrong results. Two mixing methods were used. The "syringe" method consists of placing the aqueous phase in a cell with a small circular opening, injecting the sample of I(+3) with a fast mixing syringe, closing the cell with a Teflon stopper, inverting the cell to mix well and place it in the spectrophotometer. This cell is tight and allows absorbances measurements up to large conversions, but the first measurements can only be made about 15–20 s after the injection of the I(+ 3) sample. The "paddle" method consists of placing the cooled aqueous phase in a cell with a wide opening (1 cm^2) and weighing the I(+ 3) sample on a small paddle. It is introduced quickly into the cell, shaken briefly to mix well, and a Teflon cover is placed over the cell. The cell also contains a small stirrer. This method allows absorbances measurements after less than 5 s and gives accurate values at small conversions, but the cell is not tight and the absorbances are sometimes too small at large conversion. Both method were used for the measurements of the rate of disproportionation of I(+ 3) in the presence of crotonic acid, which is relatively slow, and for the measurements of the rate of autocatalytic disproportionation which begins with an induction period. They gave similar results. Oxidation of I(+ 3) by H_2O_2 is faster and we used the "paddle" method.

The spectrophotometer results are transferred to a computer and the analytical calculations are done with Excel. The differential equations associated with the model are integrated using the *ode15s* function of Matlab specially adapted to stiff differential equations. The main program calls the *fminsearch* function which determines the kinetic constants minimizing the sum of squares of the difference between the absorbances measured and calculated by *ode15s*. Calculations usually take less than 2 min and the relative error on the iodine mass balance is less than 10^{-13}.

I(+ 3) disproportionation

The I(+ 3) disproportionation is autocatalytic as explained in the next section. To study the kinetics of reaction $2HOIO \rightarrow IO_3^- + HOI + H^+$ (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.

$$HOI + CA \rightarrow HOICA \tag{1}$$

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

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

[I(+ 3)] represents the total concentration $[I(+3)] = [HOIO] + [H_2OIO^+] = (1 + K_{19}[H^+])[HOIO]$ so that $k_{13} = (1 + K_{19}\ [H^+])^2\ k_{exp,\ disp}$. The integration of the kinetic law (2) gives the equation below which makes it possible to calculate $k_{exp,\ disp}$ 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_∞ by extrapolation of the A values at long term.

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

We also analyzed the experimental results using Matlab to integrate the differential equations associated with the model in Table 1 without the H_2O_2 reactions but with reaction (1) added. The *fminsearch* function adjusts the kinetic constant k_{13} to minimize the sum of squares $\sum\left(A_{calc} - A_{exp}\right)^2$ where $A_{calc} = \varepsilon_{I(+3)}$ $[I(+3)] + \varepsilon_{I(+5)}$ $[I(+5)] + \varepsilon_{CA}$ $[CA] + \varepsilon_{HOICA}$ $[HOICA]$. New measurements gave $\varepsilon_{I(+3)} = 121$, $\varepsilon_{I(+5)} = 11.4$, $\varepsilon_{CA} = 6.40$ and $\varepsilon_{HOICA} = 399$ at 275 nm. The agreement between the rate constants calculated with the order two rate law or with Matlab is excellent.

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

$$HOIO \rightleftharpoons H^+ + OIO^- \tag{R20}$$

$$HOIO + OIO^- \rightarrow IO_3^- + HOI \tag{R21}$$

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

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

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

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

The large effect of $[H^+]$ on $k_{exp,disp}$ could be explained by the factor $(1 + K_{19}$ $[H^+])^2$ if $K_{19} \sim 3\ M^{-1}$. 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 $[H_2OIO^+] \ll [HOIO]$ under our experimental conditions and explain the effect of $[H^+]$ on $k_{exp,disp}$ by the formation of the intermediate $I_2O_4H^-$, similar to the oxide I_2O_3 known in the gas phase. Its formation will be supported by our new study of the I(+3) oxidation by H_2O_2 discussed below.

$$HOIO + OIO^- \rightleftharpoons I_2O_4H^- \tag{R22}$$

$$I_2O_4H^- \rightarrow IO_3^- + HOI \tag{R23}$$

$$I_2O_4H^- + OH^- \rightarrow IO_3^- + IO^- + H_2O \tag{R24}$$

Reaction R13 is obtained by combining these reactions with the acid–base quasi-equilibria,. Assuming $[I_2O_4H^-] = K_{22}[HOIO][OIO^-]$, we obtain $r_{13} = \left(k_{23} + k_{24}[OH^-]\right) K_{22}[HOIO][OIO^-]$ or $r_{13} = \left(k'_{13}/[H^+] + k''_{13}\Big/[H^+]^2\right)[HOIO]^2$ where $k'_{13} = k_{23}K_{20}K_{22}$ and

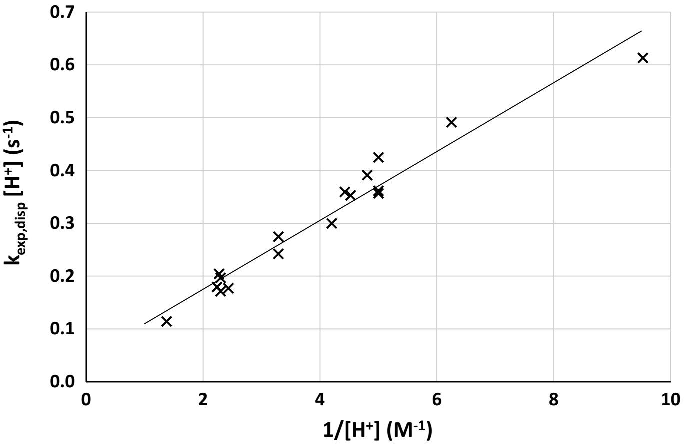

Fig. 1 Effect of the acidity on the rate constant of reaction (R13). Experimental values (×) and linear regression line (—) giving $k'_{13} = 0.045\,s^{-1}$ and $k''_{13} = 0.065\,M\,s^{-1}$. I(+3) autocatalytic disproportionation

$k''_{13} = k_{24}K_wK_{20}K_{22}$. The experiments give $k_{exp,disp}=r_{13}/[HOIO]^2$ and the plot of $k_{exp,disp}$ [H^+] as a function of 1/[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}.

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 $2HOIO + HOI \rightarrow IO_3^- + H^+ + 2HOI$. 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 $[I(+3)]_0$ at high acidities. Then, it goes through a maximum shown in Fig. 2 and the main reaction becomes $HOIO + 2HOI \rightarrow IO_3^- + H^+ + I_2 + H_2O$. When [HOIO] becomes small, some HOI remains and the direction of reactions (R2) and (R3) is reversed. [HOI] decreases very slowly according to $5HOI \rightarrow IO_3^- + H^+ + 2I_2 + 2H_2O$. The overall stoichiometry is $5I(+3) \rightarrow 3IO_3^- + 3H^+ + I_2 + H_2O$ but the experimental values of [I_2] at the end of the experiments is always lower than $[I(+3)]_0/5$ because the disproportionation of I(+ 1) is very slow under our experimental conditions. Fig. 2 gives examples of evolutions over time.

Matlab simulates the experimental curves and the function *fminsearch* adjusts k_{-1} and the initial value of [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

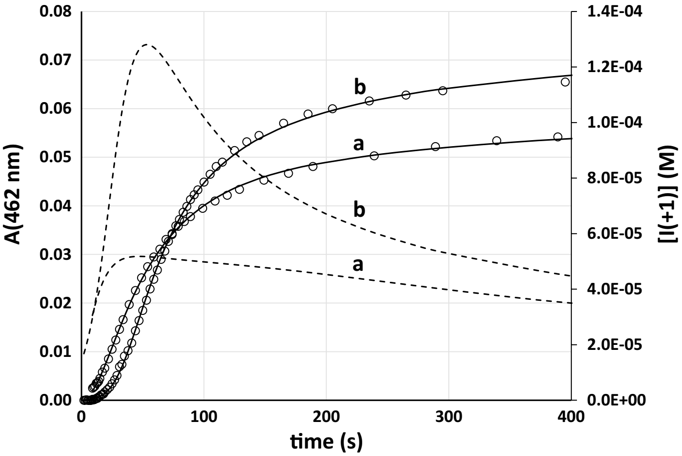

Fig. 2 Left hand scale: Experimental (o) and calculated (—) absorbances at 462 nm at low (**a**) and high (**b**) acidities. $[H_2SO_4] = 0.068$ M and $[I(+3)]_0 = 4.34 \times 10^{-4}$ M (**a**). $[H_2SO_4] = 0.76$ M and $[I(+3)]_0 = 5.41 \times 10^{-4}$ M (—). Right hand scale: Calculated I(+1) concentrations (- - -)

$[I(+1)] = \left(1 + K_{18}\left[H^+\right]\right)$ [HOI] and $[I(+3)] = \left(1 + K_{19}\left[H^+\right]\right)$ [HOIO]. Thus, the individual concentrations [HOI] and [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 $[H^+]^2$. Consequently, k_{-1} must be independent of $[H^+]$. If $K_{19} > 0.1$ M^{-1}, the calculated values of k_{-1} increase with $[H^+]$ as shown in Fig. 3 and, moreover, the fit of the experimental curves becomes

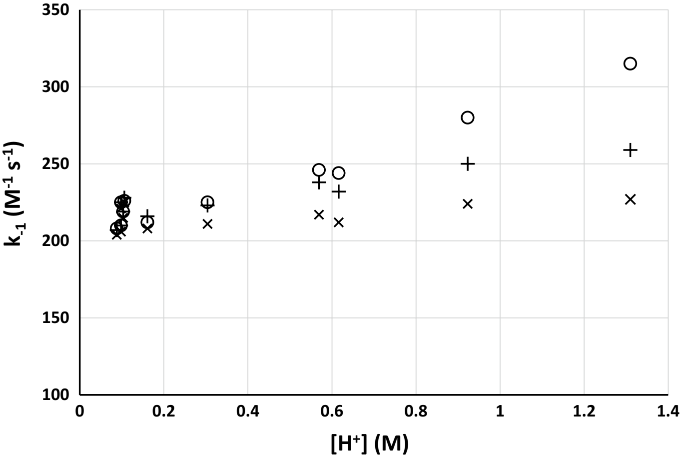

Fig. 3 Values of k_{-1} adjusted by Matlab if $K_{18} = 0.5$ M^{-1} and $K_{19} = 0$ (O), $K_{18} = 0.3$ M^{-1} and $K_{19} = 0.2$ M^{-1} (+), $K_{18} = 0.3$ M^{-1} and $K_{19} = 0$ (×)

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

Oxidation of I(+3) by H_2O_2

When a sample of I(+3) is added to an acidic solution of H_2O_2, the main reaction is the oxidation $HOIO + H_2O_2 \rightarrow IO_3^- + H^+ + H_2O$ (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 $[H^+]$. The rate constants k_9 in Table 2 were calculated for the rate law $r_9 = k_9[HOIO]^2\left[H_2O_2\right]/\left[H^+\right]$ 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 $k_9 = (1.7 \pm 0.2) \times 10^5\ M^{-1}\ s^{-1}$ (t-Student 95% confidence interval). New measurements of the molar absorption coefficient of HOIO at 275 nm gave $\varepsilon(HOIO) = 121 \pm 2$. Other values used in this work are $\varepsilon(H_2O_2) = 5.7$, $\varepsilon(IO_3^-) = 11.4$, $\varepsilon(HOI) = 107$ and $\varepsilon(I_2) = 121$ at 275 nm.

We had shown that H_2O_2 reduces the HOI monomer and oxidizes its dimer I_2O. The rate law of the HOIO disproportionation with an excess of CA discussed above and the kinetic law of HOIO oxidation by H_2O_2 suggest that the HOIO reactions are similar to those of HOI. HOIO also forms a dimer and H_2O_2 reduces its monomer and oxidizes its dimer. Also, the effect of $[H^+]$ on these reactions suggests that this dimer is $I_2O_4H^-$ introduced above that reacts according to (R24).

Table 2 Rate constants of the HOIO oxidation by H_2O_2 (units: mol/l and s)

$[H_2SO_4]$	$[H^+]$	$[H_2O_2]_0 \times 10^4$	$[HOIO]_0 \times 10^4$	$[HIO_3]_0 \times 10^4$	$k_9 \times 10^{-5}$
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

$$I_2O_4H^- + H_2O_2 \rightarrow IO_3^- + HOIO + H_2O \tag{R25}$$

The oxidation R25 is much faster than the disproportionation of HOIO from the smallest values of $[H_2O_2]$ and the quasi-stationarity of $[I_2O_4H^-]$ gives $(k_{-22}+k_{25}[H_2O_2])\,[I_2O_4H^-]=k_{22}\,[HOIO][OIO^-]$ and the rate law

$$r_{25} = \frac{k_{25}k_{22}K_{20}[HOIO]^2\left[H_2O_2\right]}{\left(k_{-22} + k_{25}\left[H_2O_2\right]\right)\left[H^+\right]}$$

This expression explains the rate law of R9 in Table 1 with $k_9=k_{24}k_{22}K_{20}/k_{-22}$ and $\alpha_9=k_{24}/k_{-22}$. The term in $\alpha_9\,[H_2O_2]$ has no effect on the results in Table 2 because the concentration of H_2O_2 was small but will be important to simulate the H_2O_2 effect on the rate of reaction O (Fig. 4).**

Oxidation of I_2 by H_2O_2 with iodate added initially (Reaction O)

The oxidation of iodine by H_2O_2 without iodate added initially begins with a non-reproducible period of induction discussed below. It is suppressed and a fast oxidation of I_2 is observed if iodate is added initially. We had carried out more than a thousand experiments in a wide range of concentrations and temperatures and published the main results previously [12, 31]. When the initial iodate concentration is about 0.005 to 0.1 M, the rates are complicated functions of acidity, $[H_2O_2]$ and $[I_2]$ but are independent of the iodate concentration. To analyze these rates, it is convenient to define the function $k_{exp}=-d(\ln[I_2])/dt$ although the reaction is not exactly of order 1 with respect to $[I_2]$. Fig. 5 shows values of k_{exp} at 25 °C if $[I_2]=4\times10^{-4}$ M. The values of k_{exp} do not directly give values of kinetic constants, only relations between them. A modification of one constant requires readjusting the

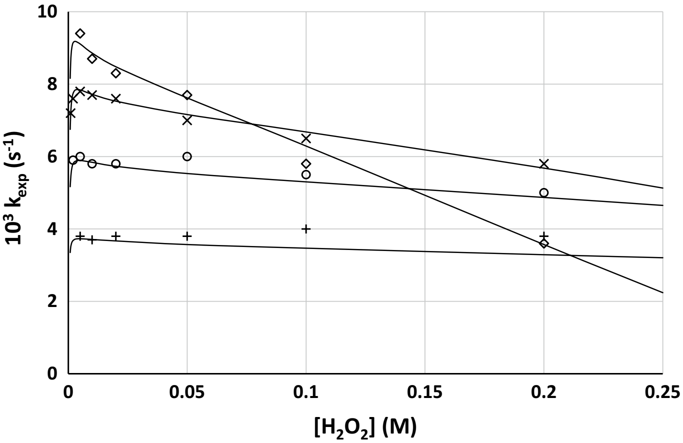

Fig. 4 Experimental rate constants of the I_2 oxidation by H_2O_2 at 25 °C with about 0.01 mol/l iodate added initially. $[HClO_4]=0.04$ (open diamond), 0.10 (×), 0.20 (O), 0.40 M (+) and values calculated with the model in Table 1 (lines)

kinetic constants of the reactions R3, R7 and R10. The previously published model [12, 31] explained our results but we had to modify the values of some kinetic constants to take into account our new results. The proposed model with updated rate constants explains not only our new experimental results but also the previous ones. Our model centered on the reactions of HOI and I_2O is robust in the sense that slight modifications of it can be compensated by adjustments of some kinetic constants. Fig. 4 shows that the rate constants in Table 1 give excellent simulations of the k_{exp} values. Note the decrease in k_{exp} when the concentration of the reagent H_2O_2 increases.

Oxidation of I_2 by H_2O_2 without iodate added initially

H_2O_2 does not react directly with I_2. An acidic solution containing only I_2 and H_2O_2 gives a quasi-steady state corresponding to the slow decomposition $H_2O_2 \rightarrow H_2O + O_2$. To obtain the oxidation of I_2, 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^+ but can also appear spontaneously after a more or less long time. Fig. 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 $I^- + H^+ + 1/2O_2 \rightarrow HOI$ 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 bifurcation occurring when the concentration of oxygen in solution reaches a critical value. Anything that promotes the transfer of oxygen to the gas phase delays the transition. This explains that it occurs later if the contact surface between the solution and the gas phase is increased and if the solution is stirred [32–34].

An essential feature of the proposed model is the competition between the Down reactions R5 followed by R6 and the Up reaction R10. The concentration of the intermediate I_2O is very small in aqueous solutions, is quasi-stationary and approximately proportional to $[HOI]^2$. 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 approximately proportional to [HOI]. If [HOI] is small, H_2O_2 mainly reacts as a reducing agent. If [HOI] is large, H_2O_2 mainly reacts as an oxidant. The reaction R4 being a quasi-equilibrium, $[I^-]$ must be small enough for H_2O_2 to act mainly as an oxidant giving reaction O.

It is difficult to quantify the effect of oxygen. The transfer reaction R14 to the gas phase is an over-simplification and the solution can become highly supersaturated in oxygen. Complicated phenomena of transfer at the interface and germination-growth of bubbles must be taken into account. Moreover, the rate of oxidation of iodide is photocatalyzed and depends on complicated radical reactions [36]. Finally, it can be noted that the reaction $2H_2O_2 \rightarrow 2H_2O + {}^1O_2$ is thermodynamically possible [37]. We could produce singlet oxygen which would react much faster with iodide. These complications explain that the induction period of the oxidation of I_2 by H_2O_2

without iodate added initially seems stochastic [34, 35]. A phenomenon seems stochastic when it depends on parameters that we ignore or do not control. A qualitative explanation of the transition between the quasi-steady state and the reaction O when the oxygen concentration reaches a critical value is already a success of the proposed model.

I(+1) reduction by H_2O_2 (reactions R5 and R6)

Furrow [38] measured the absorbances at 354 and 460 nm of solutions of I_2 and H_2O_2 without iodate during the quasi-stationary period. These absorbances allow to calculate the concentrations of I_2 and I_3^-, then that of I^- and finally that of HOI corresponding to the quasi-equilibrium R4. The sum of the reactions R5 + R6 + R11 gives the decomposition $H_2O_2 \rightarrow H_2O + O_2$ and Furrow assumed that their rates are equal during this period giving $k_5[HOI] = \left(k'_{11} + k''_{11}\left[H^+\right]\right)[I^-]$. The values of k'_{11} and k''_{11} being known, k_5 can be calculated. Furrow obtained $k_5 = 3\ M^{-1}\ s^{-1}$ but its values were widely dispersed. We recalculated his results using updated values of the parameters ($\varepsilon(I_2, 354) = 17$; $\varepsilon(I_3^-, 354) = 26{,}250$; $\varepsilon(H_2O_2, 354)$; $K_4 = 10^{11}\ M^{-2}$ when $I = 0.10$ M) and plotted $k_{11}\ [I^-]/[HOI]$, where $k_{11} = k'_{11} + k''_{11}\left[H^+\right]$, as a function of [HOI]. If the above equality was verified, the values of $k_{11}\ [I^-]/[HOI]$ would be independent of [HOI]. Fig. 5 shows on the contrary a decrease when [HOI] increases. This explains why the values calculated ignoring this dependence were so dispersed.

The model in Table 1 explains this effect of [HOI]. Numerical simulations show that reactions R2 and R10 cannot be neglected. Their sum gives the same global reaction as R11, $I^- + H^+ + H_2O_2 \rightarrow HOI + H_2O$. If R3 was an equilibrium and if we could neglect the effect of R12, we would have $k_5\ [HOI]\ [H_2O_2] = k_{11}\ [I^-]\ [H_2O_2] + k_{10}\ [I_2O]\ [H_2O_2]$ giving $k_{11}\ [I^-]/[HOI] = k_5 - k_{10}\ k_{-3}/k_3\ [HOI]$. This approximate expression explains the effect of [HOI] seen in Fig. 5

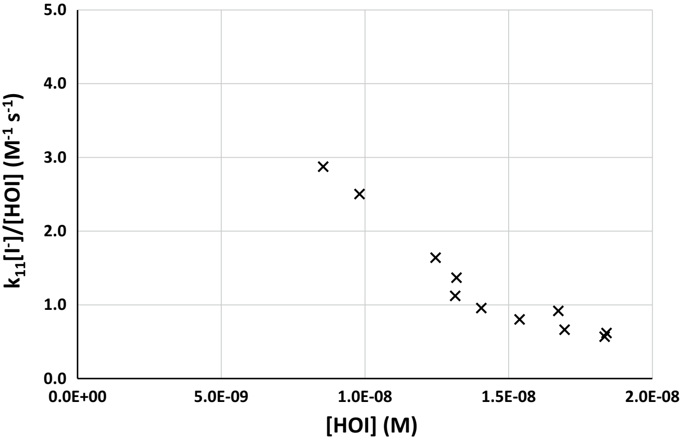

Fig. 5 Analysis of Furrow's results [38] explained in the text

and suggests $k_5 \sim 5\ M^{-1}\ s^{-1}$ or a little larger by extrapolation at [HOI] → 0. The numerical simulations of these experiments taking the k_{exp} values for reaction O into account give $k_5 = 6\ M^{-1}\ s^{-1}$. The electronic supplement shows a comparison between the experimental values and the values calculated with the model in Table 1.

Liebhafsky [39] measured the rate of oxygen production due to the reaction $HOI + H_2O_2 \rightarrow I^- + H^+ + O_2 + H_2O$ (R5+R6) in the presence of solid iodine and an excess of Tl^+ ions. The concentration of iodine in solution was equal to its solubility, the concentration of iodide was fixed by equilibrium $Tl^+ + I^- \rightleftharpoons TlI(s)$ and that of HOI by reaction (R4). He deduced the values of $k_5 = (d[O_2]/dt)/([HOI][H_2O_2]$ in Fig. 6 giving on average $k_5 = 37\ M^{-1}\ s^{-1}$. We recalculated his results [12] using more recent values of the equilibrium constants, but keeping Liebhafsky calculations assumptions, and proposed $k_5 = 23\ M^{-1}\ s^{-1}$, a value significantly greater than $k_5 = 6\ M^{-1}\ s^{-1}$ adopted above.

The effect of $[H^+]$ revealed by Fig. 6 suggests that the dispersion of the k_5 values obtained by Liebhafsky is not due to experimental inaccuracies and that the system is more complicated than he thought. This is confirmed by numerical simulations using the model in Table 1 supplemented by reaction (3) and with $[I_2]$ fixed by the solubility of iodine. Under these conditions, oxygen is produced not only by reaction R5 followed by R6 but also by reactions R7 and R12. $d[O_2]/dt > r_5$ explains that the values of k_5 obtained by Liebhafsky are too large. The model also explains a surprising observation reported by Liebhafsky. If he added only Tl^+, the iodide concentration became very small, the rate of oxygen production much too high, and iodate was produced [ref. 39, bottom of p. 3504]. To avoid this, he had to add a large amount of solid TlI(s). If $k_{12} \sim 10^7\ M^{-1}\ s^{-1}$, order of magnitude estimated in the appendix, an important reaction path is R2+R3+R4+R5+R12 giving overall $2I^- + 2H^+ + 3H_2O_2 \rightarrow I_2 + O_2 + 4H_2O$ and the observed decrease in $[I^-]$. The addition of solid TlI(s) was necessary to avoid this decrease and to obtain the overall

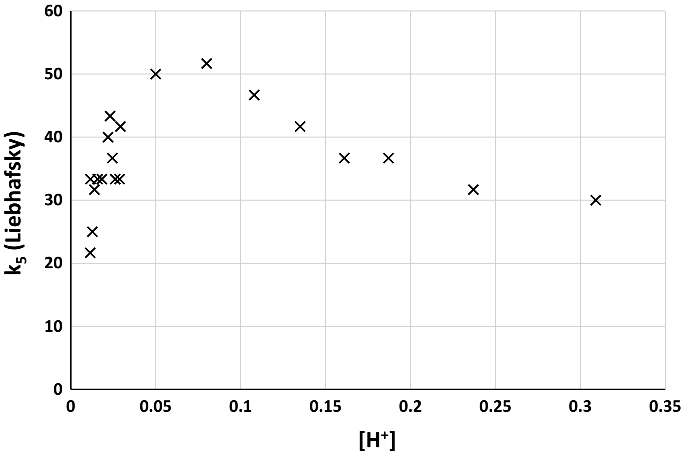

Fig. 6 k_5 values ($M^{-1}\ s^{-1}$) given by Liebhafsky in Ref. [39], p. 3506, Table 2

reaction $2TlI(s) + 2H^+ + 3H_2O_2 \rightarrow 2Tl^+ + I_2 + O_2 + 4H_2O$. This reaction greatly contributes to the production of oxygen and varies $[H^+]$. The model explains Liebhafsky observations, shows that the system he studied gives too large values of k_5 and is too complicated to allow an exact measurement.

Shin, Lee and von Gunten [40] studied the reaction between H_2O_2 and I_2 in buffered solutions between pH 4 and pH 12. They confirmed that this reaction is catalyzed by the buffers. The large differences between the values of the kinetic constants published in the literature can, in part, be explained by the effect of the nature and the concentration of the buffers. These authors obtained $k_5 = 29 \pm 5\ M^{-1}\ s^{-1}$ but this value was obtained in acetic buffers and the value in unbuffered solutions is certainly smaller. In addition, the extrapolation to pH 1 of results obtained above pH 4 is very approximate. The value $k_5 = 6\ M^{-1}\ s^{-1}$ that we propose is therefore compatible with the results of Shin, Lee and von Gunten.

Conclusion

The model in Table 1 explains the kinetics of the reactions in acidic solutions of iodine compounds at oxidation states from − 1 to + 5 with each other and with H_2O_2. The new experiments confirm the existence of the HOOI intermediate compound proposed previously [17–22]. The effect of acidity on the disproportionation of HOIO and on its oxidation by H_2O_2 shows that OIO^- is much more reactive than HOIO and suggests that the mechanism of these reactions involves an intermediate compound noted $I_2O_4H^-$ (reaction R22). This model, with updated kinetic constants, also quantitatively explains the kinetics of many reactions previously studied under very different conditions and especially the complicated kinetics of the oxidation of I_2 by H_2O_2 with or without iodate added initially. This model becomes more and more likely that it allows to explain a greater number of experiments of different types. None of these results suggest radical reactions in the dark, except in the mechanism of the oxidation of iodide by oxygen. Light, including that of a spectrophotometer, can initiate radical reactions briefly discussed in the appendix (in the Supplementary Information) which deserve further work.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11144-022-02155-4.

References

1. Comprehensive Chemical Kinetics 2004, Volume 40, Chapter 14, Instability, periodic reactions, and chaos.
2. Schuster HG, Just W (2005) Deterministic chaos—an introduction, 4th edn. Wiley, Weinheim
3. Čupić ŽD, Taylor AF, Horváth D, Orlik M, Epstein IR (2020) Advances in oscillating reactions. Front Chem 9:292
4. Ivanović-Šasić AZ, Marković VM, Anić SR, Lj Z, Kolar-Anić and Ž. D. Čupić, (2011) Structures of chaos in open reaction systems. Phys Chem Chem Phys 13:20162–20171

5. Bosland L, Cantrel L, Girault N, Clement B (2010) Modeling of iodine Radiochemistry in the ASTEC severe accident code: description and application to FPT-2 Phebus test. Nuclear Technol 171:88–107
6. Fortina C, Fèvre-Nolleta V, Cousin F, Lebègue P, Louisa F (2019) Box modelling of gas-phase atmospheric iodine chemical reactivity in case of a nuclear accident. Atmos Environ 214:116838
7. Saha S, Roy S, Mathi P, Mondal JA (2020) Adsorption of iodine species (I_3^-, I^-, and IO_3^-) at the nuclear paint monolayer−water interface and its relevance to a nuclear accident scenario. J Phys Chem A 124:6726–6734
8. Mahajan AS, Shaw M, Oetjen H, Hornsby KE, Carpenter LJ, Kaleschke L, Tian-Kunze X, Lee JD, Moller SJ, Edwards P, Commane R, Ingham T, Heard DE, Plane JMC (2010) Evidence of reactive iodine chemistry in the Arctic boundary layer. J Geophys Res 115:D20303
9. Badia A, Reeves CE, Baker AR, Saiz-Lopez A, Volkamer R, Koenig TK, Apel EC, Hornbrook RS, Carpenter LJ, Andrews SJ, Sherwen T, von Glasow R (2019) Importance of reactive halogens in the tropical marine atmosphere: a regional modelling study using WRF-Chem. Atmos Chem Phys 19:3161–3189
10. Inamdar S, Tinel L, Chance R, Carpenter LJ, Sabu P, Chacko R, Tripathy SC, Kerkar AU, Sinha AK, Venkateswaran Bhaskar P, Sarkar A, Roy R, Sherwen T, Cuevas C, Saiz-Lopez A, Ram K, Mahajan AS (2020) Estimation of reactive inorganic iodine fluxes in the Indian and Southern Ocean marine boundary layer. Atmos Chem Phys 20:12093–12114
11. Schmitz G, Furrow SD (2018) Kinetics of reactions of iodine inorganic compounds in acidic solutions. In: Physical Chemistry 2018, Proceedings of the 14th Int. Conf. Fundam. Appl. Aspects Phys. Chem. Belgrade, Sept 24–28, Society of Physical Chemists of Serbia pp 271–278
12. Schmitz G (2010) Iodine oxidation by hydrogen peroxide in acidic solutions, Bray–Liebhafsky reaction and other related reactions. Phys Chem Chem Phys 12:6605–6615
13. Sharma KR, Noyes RM (1976) Oscillations in chemical systems. 13. A detailed molecular mechanism for the Bray–Liebhafsky reaction of iodate and hydrogen peroxide. J Am Chem Soc 98(15):4345–4361
14. Schmitz G (1999) Effects of oxygen on the Bray–Liebhafsky reaction. Phys Chem Chem Phys 1:4605
15. Ševčik P, Kissimonová K, Adamčikova L (2000) Oxygen production in the oscillatory Bray–Liebhafsky reaction. J Phys Chem A 104:3958–3963
16. Ševčik P, Adamčikova L (1998) Effect of a gas bubbling and stirring on the oscillating Bray–Liebhafsky reaction. J Phys Chem A 102:1288–1291
17. Ball JM, Hnatiw JB (2001) The reduction of l_2 by H_2O_2 in aqueous solution. Can J Chem 79:304–311
18. Schmitz G (2008) Buffers catalysis of the iodine(+1) reduction by hydrogen peroxide In Physical Chemistry 2008, Proceedings of the 9th Int. Conf. Fundam. Appl. Aspects Phys. Chem. Society of Physical Chemists of Serbia, Belgrade pp. 219–224
19. Schmitz G (2009) Iodine(+1) reduction by hydrogen peroxide, Russian. J Phys Chem 83(9):1447
20. Schmitz G, Furrow SD (2012) Kinetics of the iodate reduction by hydrogen peroxide and relation with the Briggs–Rauscher and Bray–Liebhafsky oscillating reactions. Phys Chem Chem Phys 14:5711–5717
21. Schmitz G, Furrow SD (2014) Iodine Inorganic Reactions in Acidic Solutions and Oscillating Reactions, Physical Chemistry 2014, Proceedings of the 12th Int. Conf. Fundam. Appl. Aspects Phys. Chem. Society of Physical Chemists of Serbia, Belgrade pp 320–326
22. Schmitz G, Furrow SD (2016) Bray–Liebhafsky and non-catalyzed Briggs–Rauscher oscillating reactions. Russ J Phys Chem A 90(2):271–275
23. Szabo E, Ševčík P (2013) Reexamination of gas production in the Bray−Liebhafsky reaction: what happened to O_2 pulses? J Phys Chem A 117:10604–10614
24. Schmitz G, Lente G (2020) Fundamental concepts in chemical kinetics. ChemTexts 6(1):1
25. Schmitz G (2004) Inorganic reactions of iodine(+1) in acidic solutions. Int J Chem Kinet 36:480
26. Schmitz G, Furrow SD (2013) Kinetics of iodous acid disproportionation. Int J Chem Kinet 48(8):525–530
27. Schmitz G, Nullclines (2021) A Simple Explanation of Complicated Phenomena, In Physical Chemistry 2021, Proceedings of the 15th Int. Conf. Fundam. Appl. Aspects Phys. Chem., pp. 222–229, Belgrade, Sept 20–24, Society of Physical Chemists of Serbia, 2021. ISBN 978-86-82475-40-8.
28. Schmitz G, Noszticzius Z, Hollo G, Wittmann M, Furrow SD (2018) Reactions of iodate with iodine in concentrated sulfuric acid. Formation of I(+3) and I(+1) compounds. Chem Phys Lett 691:44

29. Furrow SD, Cervellati R, Amadori G (2002) New substrates for the oscillating Briggs–Rauscher reaction. J Phys Chem A 106:5841–5850
30. Schmitz G (2008) Inorganic reactions of iodine(III) in acidic solutions and free energy of iodous acid formation. Int J Chem Kinet 40:647–652
31. Schmitz G (2011) Iodine oxidation by hydrogen peroxide and Bray–Liebhafsky oscillating reaction: effect of the temperature. Phys Chem Chem Phys 13:7102–7111
32. Olexová A, Mrákavová M, Melicherčík M, Treindl L (2006) The autocatalytic oxidation of iodine with hydrogen peroxide in relation to the Bray–Liebhafsky oscillatory reaction. Collect Czech Chem Commun 71:91–106
33. Olexová A, Mrákavová M, Melicherčík M, Treindl L (2010) Oscillatory system I^-, H_2O_2, $HClO_4$: the modified form of the Bray–Liebhafsky reaction. J Phys Chem A 114:7026–7029
34. Stanisavljev DR, Stevanović KZ, Bubanja IM (2018) Outsized stochasticity of iodine oxidation with hydrogen peroxide and its implications on the reaction mechanism. Chem Phys Lett 706:120–126
35. Stevanović KZ, Bubanja IM, Stanisavljev DR (2019) Is iodine oxidation with hydrogen peroxide coupled with nucleation processes? J Phys Chem C 123:16671–16680
36. Jortner J, Ottolenghi M, Stein G (1962) The effect of oxygen on the photochemistry of the iodide ion in aqueous solutions. J Phys Chem 66:2042–2045
37. Nardello V, Briviba K, Sies H, Aubry J-M (1998) Identification of the precursor of singlet oxygen ($^1O_2$, $^1\Delta_g$) involved in the disproportionation of hydrogen peroxide catalyzed by calcium hydroxide. Chem Commun 5:599–600
38. Furrow SD (1987) Reactions of iodine intermediates in iodate-hydrogen peroxide oscillators. J Phys Chem 91:2129–2135
39. Liebhafsky HA (1932) The catalytic decomposition of hydrogen peroxide by the iodine-iodide couple. III. The rate of oxidation, in acid solution, of hydrogen peroxide by iodine. J Am Chem Soc 54:3499–3508
40. Shin J, Lee Y, von Gunten U (2020) Kinetics of the reaction between hydrogen peroxide and aqueous iodine: implications for technical and natural aquatic systems. Water Res 179:115852
41. Schmitz G (1909) Kinetics and mechanism of the iodate-iodide reaction and other related reactions. Phys Chem Chem Phys 1999:1
42. Furuichi R, Liebhafsky HA (1975) Bull Chem Soc Jpn 48:745
43. Schmitz G (2000) Kinetics of the Dushman reaction at low I^- concentrations. Phys Chem Chem Phys 2:4041
44. Liebhafsky HA, Mohammad A (1933) The kinetics of the reduction in acidic solution of hydrogen peroxide by iodide ion. J Am Chem Soc 55:3977–3986
45. Lozar J, Lafage B (1994) Kinetics of the oxidation of iodide ions by oxygenated water using spectrophotometry with a microcomputer. Bulletin de l'Union des Physiciens 88(764):895–902
46. Stanisavljev DR, Milenković MC, Mojović MD, Popović-Bijelić AD (2011) Oxygen centered radicals in iodine chemical oscillators. J Phys Chem A 115:7955–7958
47. Stanisavljev DR, Milenković MC, Popović-Bijelić AD, Mojović MD (2013) Radicals in the Bray–Liebhafsky oscillatory reaction. J Phys Chem A 117:3292–3295
48. Kéki S, Székely G, Beck MT (2003) The effect of light on the Bray–Liebhafsky reaction. J Phys Chem A 107:73–75
49. Stanbury DM (2018) Comment on the principle of detailed balancing in complex mechanisms and its application to iodate reactions. J Phys Chem A 122:3956–3957