Kinetics of Iodous Acid Disproportionation

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ABSTRACT: The iodous acid disproportionation is autocatalytic, and it is not easy to measure the rate constant of the step $2IO_2H \rightarrow IO_3^- + IOH + H^+$ separately. Hg(II) was used previously to suppress the autocatalytic pathway, but this method presents difficulties discussed in this work. A more effective method is the use of crotonic acid, an effective IOH scavenger. It suppresses side reactions, and a purely second-order rate law is obtained. The rate constant decreases from 5 to 0.2 M^{-1} s^{-1} when the sulfuric acid concentration increases from 0.08 to 0.60 M. The observed decrease could be explained if IO_2^- reacts faster than IO_2H. This may have consequences for the mechanism of the oscillating Bray–Liebhafsky reaction. © 2013 Wiley Periodicals, Inc. Int J Chem Kinet 45: 525–530, 2013

INTRODUCTION

The iodous acid disproportionation in sulfuric acid solutions is autocatalytic [1,2]. This was explained by the mechanism (R1)–(R4):

$$2IO_2H \rightarrow IO_3^- + IOH + H^+ \qquad (R1)$$

$$IOH + IO_2H \rightarrow IO_3^- + I^- + 2H^+ \qquad (R2)$$

$$IO_2H + I^- + H^+ \rightleftharpoons 2IOH \qquad (R3)$$

$$IOH + I^- + H^+ \rightleftharpoons I_2 + H_2O \qquad (R4)$$
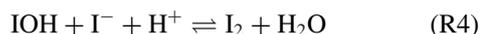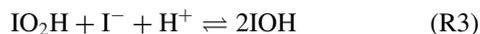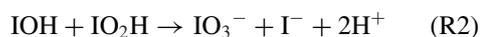
The sum of reactions (R2) and (R3) gives the same stoichiometric result as reaction (R1) with a rate proportional to [IOH][IO$_2$H], and the rate constants are such that this pathway becomes faster than reaction (R1) once a small amount of IOH has formed. An example of autocatalytic behavior is shown in Fig. 1 and

compared with curves calculated as explained in the section Numerical Integrations.

To isolate reaction (R1), one of us [2] has used two methods, one with Hg(II) and the other with crotonic acid. Hg(II) reacts very quickly with iodide ions according to reaction (R5):

$$Hg(II) + I^- \rightleftharpoons HgI^+ \qquad (R5)$$

When reaction (R5) is faster than reaction (R3), the evolution of the system can be described by reactions (R1), (R2), and (R5) with the stoichiometric result (S1). The appearance of HgI$^+$ near 274 nm can be used to measure the rate of reaction (R1):

$$3IO_2H + Hg(II) \rightarrow 2IO_3^- + 3H^+ + HgI^+ \qquad (S1)$$
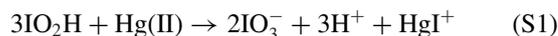
The second method uses crotonic acid (CH$_3$CH:CHCOOH, denoted as CA), which reacts very quickly with IOH producing iodohydrin (CH$_3$CH(OH)CHICOOH, denoted as CAIOH) [2,3].

$$CA + IOH \rightarrow CAIOH \qquad (R6)$$

Figure 1 $[H_2SO_4] = 0.30$ M, $[I(+3)]_o = 8.7 \times 10^{-4}$ M, $[IO_3^-]_o = 5.9 \times 10^{-4}$ M, $[I(+1)]_o = 8.8 \times 10^{-6}$ M. Experimental values (○) and values calculated with Matlab® (——), $k_1 = 0.70$ M^{-1} s^{-1}, other rate constants are given in the text. The insert shows the calculated [IOH] values.

When reaction (R6) is faster than reaction (R2), the evolution of the system can be described by reactions (R1) and (R6) with the stoichiometric result (S2). The appearance of CAIOH at 275 nm can be used to measure the rate of reaction (R1):

$$2IO_2H + CA \rightarrow IO_3^- + H^+ + CAIOH \qquad (S2)$$

Marković et al. have published four papers [4–7], the latest recently in this journal, using the Hg(II) method. Because her results disagree with results obtained formerly, we have analyzed these papers, found several errors, and decided to perform a new study. Assuming that the only net reaction is (S1), Marković states that the rate constant of iodous acid disproportionation can be calculated by Eq. (1), obtained by integration of the second-order rate law $-\,d[IO_2H]/dt = k_{Mark} [IO_2H]^2$.

$$k_{Mark} = \frac{3}{t}\left(\frac{1}{[HgI^+]_\infty - [HgI^+]_t} - \frac{1}{[HgI^+]_\infty}\right) \qquad (1)$$

In the Appendix, we show that the factor 3 in the numerator of this equation should appear in the denominator. Second, this equation assumes that $[HgI^+] = 0$ at $t = 0$. However, as already mentioned by Noszticzius et al. [1], the I(+3) solutions prepared in concentrated sulfuric acid contain always a small amount of I(+1) so that some HgI$^+$ is quickly produced at the beginning of the experiments by reactions (R2) and (R5). This initial I(+1) concentration depends critically on the concentration and purity of the sulfuric acid used to prepare the initial I(+3) solution [8]. Third, k_{Mark} is not equal to k_1 because the global reaction (S1) consumes 3 moles of IO$_2$H so that $-\,d[IO_2H]/dt = 3k_1 [IO_2H]^2$. The distinction between the derivative of a concentra-

tion and a reaction rate [9] is essential as can be seen comparing the two methods. Reaction (S2) consumes only 2 mol of IO$_2$H giving $-\,d[IO_2H]/dt = 2k_1 [IO_2H]^2$, and the rate constants obtained by the two methods can be compared only if we use a factor 2 instead of 3. Finally, we will see that an integrated second-order rate law is applicable only if the Hg(II) concentration is sufficiently high and only at low conversions.

In the Appendix, we derive Eq. (2) by integration of the second-order rate law, where s is the stoichiometric factor 2 or 3.

$$\frac{1}{A_\infty - A_t} = \frac{1 + sk_1[IO_2H]_0 t}{A_\infty - A_0} \qquad (2)$$

When it can be used, this equation is more convenient than numerical integrations. It is directly related to experimental quantities and allows calculating k_1 even if we do not know the contribution of each compound to the absorbance. The only condition is that the absorbance increases linearly with the extent of reaction. A plot of $1/(A_\infty - A_t)$ as a function of t should give a straight line and one could estimate k_1 from its slope. However, this method gives a larger weight to the points at longer times, which are probably less accurate, and a strong dependence of k_1 on the adopted value for A_∞. For this reason, we have used the alternative form (3) and have adjusted k_1 by a nonlinear method minimizing $\Sigma(A_{t,\text{calculated}}/A_{t,\text{experimental}} - 1)^2$. Examples are given in the Supporting Information.

$$A_{t,\text{ calculated}} = A_\infty - \frac{A_\infty - A_0}{1 + sk_1[HIO_2]_0 t} \qquad (3)$$

EXPERIMENTAL

I(+3) solutions were prepared by stirring weighed I$_2$ and KIO$_3$ in concentrated H$_2$SO$_4$ according to the procedure described by Noszticzius et al. [1]. The CA or Hg(II) solutions were measured into separate containers and precooled such that, on mixing with the H$_2$SO$_4$-I(+3) solution, the temperature would rise to 25°C. The two solutions were mixed and added to the spectrometer cell as soon as possible (~20 s). The reaction was sufficiently slow to allow extrapolation to zero time. Spectrophotometric measurements were made on a Shimadzu multispec model 1501 instrument with a cell compartment thermostated at 25°C. KIO$_3$ (Baker analyzed 99.5%), H$_2$SO$_4$ (reagent ACS; 95–98%), and HgSO$_4$ (Acros; 99+%) were used without further purification. CA was recrystallized three times from hot water. CA solutions were prepared from weighed solid just before use.

Table I Kinetic Model

No.	Reaction	Rate Law
R1	$2\,IO_2H \rightarrow IO_3^- + IOH + H^+$	$r_1 = k_1[IO_2H]^2$
R2	$IOH + IO_2 \rightleftharpoons IO_3^- + I^- + 2H+$	$r_2 = k_2[IOH][IO_2H] - k_{-2}[IO_3^-][I^-][H^+]^2$
R3	$IO_2H + I^- + H^+ \rightleftharpoons 2IOH$	$r_3 = k_3[IO_2H][I^-][H^+] - k_{-3}[IOH]^2$
R4	$IOH + I^- + H^+ \rightleftharpoons I_2 + H_2O$	$r_4 = k_4\,[IOH][I^-] - k_{-4}[I_2]/[H^+]$
For the Hg(II) method		
R5	$Hg(II) + I^- \rightleftharpoons HgI^+$	$r_5 = k_5\,[Hg(II)][I^-] - k_{-5}[HgI^+]$
For the CA method		
R6	$CA + IOH \rightarrow CAIOH$	$r_6 = k_6\,[CA][IOH][H^+]$

NUMERICAL INTEGRATIONS

Most of the k_1 values reported in this work were obtained using Eq. (3), and it was necessary to verify the conditions of validity of the second-order rate law. With this aim, the kinetic equations, derived from the model in Table I, were integrated using the routine ode5s of the MATLAB® package.

The preparation of I(+3) with solid I_2 and excess KIO_3 led to a solution with all the I_2 converted to I(+3), excess I(+5), and a minor amount of I(+1). With the crotonic acid runs, a small excess absorbance was present at the beginning, attributable to fast formation of iodohydrin from I(+1). With both the crotonic acid and the Hg(II) runs, the final absorbance was dependent on the relative amounts of I(+1). For both sets of runs, [I(+3)] was calculated from the weight of I_2, then initial I(+1) values of 0.5% to 3% of I(+3) were applied, with corresponding lowering of initial [I(+3)], to best reproduce experimental final absorbances.

The rate constants of reactions (R2)–(R4) are taken from previous works [10,11]: $k_2 = 200\,M^{-1}\,s^{-1}$, $k_{-2} = 1300\,M^{-3}\,s^{-1}$, $k_3 = 4 \times 10^9\,M^{-2}\,s^{-1}$, $k_{-3} = 25\,M^{-1}\,s^{-1}$, $k_4 = 1.8 \times 10^9\,M^{-1}\,s^{-1}$, and $k_{-4} = 1.7 \times 10^{-3}\,M\,s^{-1}$. Reaction (R1) is the sum of (R2) and (R3), so that $K_1 = K_2K_3$ and $k_{-1}/k_1 = k_{-2}k_{-3}/k_2k_3$ (see discussion in the Supporting Information). Using this relation, we have verified that, under our conditions, the reversibility of reaction (R1) can be neglected. The backward rate of reaction (R2) is also very small, since [I⁻] is extremely low, so that the iodate concentration has no effect on the results. Our numerical simulations suggest a very large k_5 value, and we have adopted $k_5 = 10^{10}\,M^{-1}\,s^{-1}$ for a diffusion-controlled reaction. k_{-5} was calculated using $\log K_5 = 12.9$ [12] in agreement with the accepted value $\Delta G_f^\circ(HgI^+) = 39.7$ kJ/mol [13] but very different from the negative value that Marković claims to have deduced from her measurements [7]. Note also that the value $\Delta G_f^\circ(IO_2H)) = -75$ kJ/mol she used (with an error in the reference) for the calculation of K_1 is much too high and that

a more likely estimate is –96 kJ/mol [8]. The reaction $Hg(II) + I_2 + H_2O \rightleftharpoons HgI^+ + IOH + H^+$ was included in the model, but, even diffusion controlled, it had no effect under our experimental conditions. The rate constant $k_6 = 3640\,M^{-2}\,s^{-1}$ was obtained by recalculation of previous results [3,14]. The concentrations obtained by numerical integration were compared with the experimental absorbance values using the following coefficients obtained in this work: $\varepsilon(HgI^+) = 1920$, $\varepsilon(IO_2H) = 124$, and $\varepsilon(IO_3^-) = 13$ at 274 nm for the Hg method and $\varepsilon(CAIOH) = 399$, $\varepsilon(CA) = 6.0$, $\varepsilon(IO_2H) = 120$, and $\varepsilon(IO_3^-) = 11.3$ at 275 nm for the CA method.

EXPERIMENTAL RESULTS

We have analyzed former experimental results [2], obtained by the Hg(II) method, using the methods described in this paper. The results are given in the Supporting Information. The numerical simulations show that the value of the ratio $r_{+5}/r_{+3} = k_5[Hg(II)]_0/k_3[H^+][IO_2H]_0$ is critical. If this ratio is smaller than 1, the reaction is autocatalytic. If it is larger than 1, but not large enough, the autocatalytic shape disappears although the pathway (R2) + (R3) is not suppressed completely. Under these conditions, Eq. (2) seems to be verified but gives rate constants larger than obtained with MATLAB. At low conversions, the pathway (R2) + (R3) becomes negligible only if the ratio r_{+5}/r_{+3} is greater than about 10. At high conversions, reaction (R5) approaches equilibrium, [I⁻] increases with [HgI⁺], and the second-order rate law is never verified. It is also important to note that, when r_{+5}/r_{+3} is not large enough, the k_1 values obtained by numerical simulations depend on the values of the other parameters and, perhaps, on complications not included in the model. On the other hand, numerical simulations of the experiments with CA show that sufficiently high CA concentrations suppress reaction (R2) very efficiently. [I⁻] remains extremely low, and the second-order rate law is verified even at high
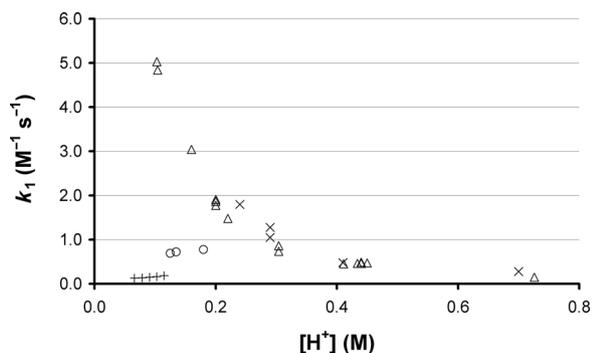
Figure 2 Comparison of different sets of k_1 values: this work CA method ($\triangle$), this work Hg(II) method ($\times$), Marković [6] ($+$), and Marković [7] ($\circ$).

conversions. In conclusion, the CA method is superior to the Hg(II) method.

The details of our results are given in the Supporting Information, and different sets of k_1 values are compared in Fig. 2. The [H$^+$] values were calculated using the Pitzer model for H$_2$SO$_4$ solutions [15]. A small amount of HClO$_4$ was sometimes added and was included in the calculations. The agreement between the values obtained with the CA method and the Hg(II) method with high [Hg(II)] values is good. Our results agree also with the *upper* limits obtained by Noszticzius et al. [1]: 5.4, 2.2, and 2.0 M^{-1} s^{-1} for [H$_2$SO$_4$] = 0.05, 0.10, and 0.15 M. On the other hand, Marković, using the Hg(II) method, has obtained much lower values and her 2010 values [7] are very different from her 2009 values [6]. The values presented in Fig. 2 are $k_{Mark}/3$ because, as explained before, $k_{Mark} = 3k_1$. The activation energies reported in her papers are also very different. These discrepancies probably arise from deviations to the second-order rate law revealed by our numerical simulations and errors in analyzing the measurements.

DISCUSSION AND CONCLUSION

The fast decrease of k_1 when the acidity increases could be explained assuming that IO$_2$H is protonated according to reaction (R7):

$$IO_2H + H^+ \rightleftharpoons IO_2H_2^+ \qquad (R7)$$

Noting [I(+3)] = [IO$_2$H] + [IO$_2$H$_2^+$], we have

$$[IO_2H] = \frac{[I(+3)]}{1 + K_7[H^+]}$$

If IO$_2$H$_2^+$ is much less reactive than IO$_2$H, r_1 is still equal to k_1 [IO$_2$H]^2 and the kinetic equation becomes

$$-\frac{d\,[I(+3)]}{d\,t} = sr_1 = s\frac{k_1}{(1 + K_7[H^+])^2}[I(+3)]^2$$

The experimental k_1 values obtained using the integrated equation 3 would actually be the values of $k_1/(1 + K_7[H^+])^2$. However, the results presented in Fig. 2 would imply a large value of K_7 (about 12 M^{-1}) and this assumption is difficult to reconcile with the results of other kinetic studies. One of them comes from the kinetic study of reaction (R2) showing that the rate r_{+2} is nearly independent of the H$_2$SO$_4$ concentration [2]. If IO$_2$H was largely protonated, IO$_2$H$_2^+$ should be as reactive as IO$_2$H in reaction (R2) and, under the same conditions, much less reactive in reaction (R1). A large value of K_7 would have other unpleasant consequences on the simulations of other systems involving I(+3), and we prefer another explanation to the results in Fig. 2.

The acidity constant of IO$_2$H was never measured, but its order of magnitude is probably K_a(IO$_2$H $\rightleftharpoons$ IO$_2^-$ + H$^+$) = 10^{-5} to 10^{-6} M [8].

If we replace reaction (R1) with IO$_2$H $\rightleftharpoons$ IO$_2^-$ + H$^+$ followed by (R'1), note that [IO$_2^-$] << [IO$_2$H] and substitute [IO$_2^-$] with K_a [IO$_2$H]/[H$^+$], the kinetic equation becomes (4) and the experimental values of k_1 are actually those of $k'_1 K_a/[H^+]$:

$$IO_2H + IO_2^- \rightarrow IO_3^- + IOH \qquad (R'1)$$
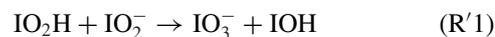
$$-\frac{d\,[I(+3)]}{dt} = sk'_1[IO_2H][IO_2^-]$$

$$= s\frac{k'_1 K_a}{[H^+]}[IO_2H]^2 \qquad (4)$$

We now discuss the consequences of this assumption on the model of the Bray–Liebhafsky (BL) oscillating reaction [10,11]. This model contains the following reactions:

$$2IO_2H \rightleftharpoons I_2O_3 + H_2O \qquad (R8a)$$

$$I_2O_3 + H_2O_2 \rightarrow IO_3^- + H^+ + IO_2H \qquad (R8b)$$

$$I_2O_3 + H_2O \rightarrow IO_3^- + H^+ + IOH \qquad (R8c)$$
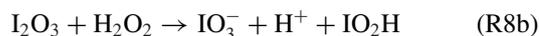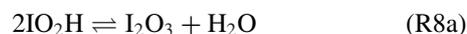
Reactions (R8a) and (R8b) were introduced into the BL model to explain the kinetics of the oxidation of iodine by hydrogen peroxide. The sum of reactions (R8a) and (R8c) gives reaction (R1) and, if (R1) is

replaced with $IO_2H \rightleftharpoons IO_2^- + H^+$ followed by (R′1), these reactions must be modified as follows:

$$IO_2H + IO_2^- \rightleftharpoons I_2O_4H^- \qquad (R'8a)$$

$$I_2O_4H^- + H_2O_2 \rightarrow IO_3^- + IO_2H + H_2O \qquad (R'8b)$$

$$I_2O_4H^- \rightarrow IO_3^- + IOH \qquad (R'8c)$$
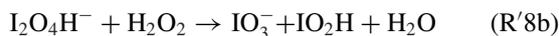
The structure of the intermediate $I_2O_4H^-$ could be
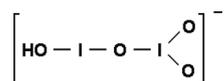
In this case, the rate of IO_2H oxidation by hydrogen peroxide should also decrease when $[H^+]$ increases. We have verified that the model can still simulate the effect of $[H^+]$ on the iodine oxidation by hydrogen peroxide provided it is slightly modified (namely to suppress the effect of $[H^+]$ on reaction noted (R6) in the original BL model). We have also checked directly that the rate of IO_2H oxidation by hydrogen peroxide actually decreases when $[H^+]$ increases. This is not easy because the reaction is very fast, but preliminary results show a strong correlation with the decrease of the rate of IO_2H disproportionation.

Models of complicated systems, like the BL and Briggs–Rusher oscillating reactions, cannot rest only on observations of the oscillations. The kinetic study of several subsystems is essential to construct a more or less correct picture of the reality. This study appends an item to this construction.

APPENDIX: INTEGRATION OF THE SECOND-ORDER RATE LAW

Marković has defined k_{Mark} by

$$-\frac{d[IO_2H]}{dt} = k_{\text{Mark}}[IO_2H]^2$$

or after integration

$$k_{\text{Mark}} = \frac{1}{t}\left(\frac{1}{[IO_2H]_t} - \frac{1}{[IO_2H]_0}\right)$$

The stoichiometric equation (S1) gives

$$[IO_2H]_0 - [IO_2H]_t = 3([HgI^+]_t - [HgI^+]_0)$$

With $[IO_2H] = 0$ at $t = \infty$, we get

$$[IO_2H]_0 = 3([HgI^+]_\infty - [HgI^+]_0)$$

$$[IO_2H]_t = 3([HgI^+]_\infty - [HgI^+]_t)$$

Consequently, the correct form of Marković's equation 1 is (A1):

$$k_{\text{Mark}} = \frac{1}{3t}\left(\frac{1}{[HgI^+]_\infty - [HgI^+]_t}\right.$$
$$\left. - \frac{1}{[HgI^+]_\infty - [HgI^+]_0}\right) \quad (A1)$$

Using Eq. (A1) requires the calculation of $[HgI^+]$, and this is not straightforward. It depends on $\varepsilon(HgI^+)$ and the contribution of other compounds to the measured absorbance. A more convenient form of the integrated second-order rate law can be derived as follows: It is valid under the sole condition that the absorbance varies linearly with the extent of reaction ξ:

$$A = a + b\xi$$

where

$$\xi = \frac{[I(+3)]_0 - [I(+3)]}{s}$$

$s = 3$ for reaction (S1) and $s = 2$ for reaction (S2). At $t = 0$, $\xi_0 = 0$ gives $a = A_0$ so that $A - A_0 = b\xi$. At $t = \infty$, $\xi_\infty = [I(+3)]_0/s$ gives

$$\frac{A_t - A_0}{A_\infty - A_0} = \frac{\xi_t}{\xi_\infty} = \frac{[I(+3)]_0 - [I(+3)]_t}{[I(+3)]_0} \quad (A2)$$

If the rate of reaction is given by

$$-\frac{d[I(+3)]}{dt} = sk_1[I(+3)]^2$$

we get after integration

$$sk_1 t = \frac{1}{[I(+3)]_t} - \frac{1}{[I(+3)]_0}$$

Elimination of $[I(+3)]_t$ between this equation and Eq. (A2) gives Eq. (A3) where k_1 is directly related to experimental quantities:

$$\frac{1}{A_\infty - A_t} = \frac{1 + s\,k_1\,[I(+3)]_0 t}{A_\infty - A_0} \quad (A3)$$

SUPPORTING INFORMATION

The Supporting Information contains a discussion of the equation $k_{-1}/k_1 = k_{-2}k_{-3}/k_2k_3$, the results presented in Fig. 2, and the details of three typical experiments.

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