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# Pitfall of an Initial Rate Study: On the Kinetics and Mechanism of the Reaction of Periodate with Iodide Ions in a Slightly Acidic Medium

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The kinetics of the periodate−iodide reaction has a contradictory history dating back to almost a century. This reaction has been reinvestigated spectrophotometrically in the pH range 3.13−5.55 in both buffered (acetic acid/acetate) and unbuffered solution at $T = 25.0 \pm 0.1$ °C with an $I = 0.5$ M ionic strength. The spectra between 290 and 500 nm were recorded and the reaction was followed until at least 95% of one of the reactants was consumed. The stoichiometry has been found to be strongly dependent on pH, but the rate of the initial step is independent of pH within the pH range studied. An eight-step kinetic model is proposed with four fitted kinetic parameters to take all the important characteristics of the experimental curves into account. On the basis of the model, a perfect reconciliation of the previous contradictory results is presented. It is shown that the kinetic parameters obtained from the initial rate of formation of a product unavoidably leads to misinterpretation of the results in the case of a branching mechanism (and stoichiometry).

## Introduction

There is considerable disagreement in the literature regarding the pH dependence of the periodate−iodide reaction. This reaction occurs in both acidic and neutral media, and this feature provides the analytical distinction between iodate and periodate ions.[1,2] The first kinetic study of this reaction has been carried out by Abel and Fürth almost a century ago.[3] No pH dependence has been found in neutral and slightly acidic media adjusted by acetate buffer. In more acidic medium applying sulfuric acid, however, Abel and Siebenschein have estimated that the rate equation also contains a term that depends on $[H^+]^2$ besides the pH-independent part.[4] Later, Indelli and his co-workers have found that the rate equation contains a term that linearly depends on $[H^+]$ besides the pH-independent path in a slightly acidic medium and that may even be supplemented with a $[H^+]^2$ term in more acidic medium.[5] The essence of their method was to add a slight amount of thiosulfate in the reacting solution to consume all the iodine produced in the system and the time of reappearance of iodine was registered. This procedure was repeated several times during each experiment. The method applied by these authors has raised an important question. If thiosulfate reacts with species present in the reacting system other than iodine with a commensurable rate, then the time of reappearance of iodine is no longer connected uniquely to the periodate−iodide reaction. This situation may happen easily because both iodate and periodate are well-known to react with thiosulfate.[6−8] This possible artifact was also noticed by Marques and Hasty,[9] and they have reinvestigated the periodate−iodide reaction by applying an iodide selective electrode and have found no pH dependence on the rate in the pH range 3.51−5.31 using acetate buffer, in agreement with Abel and Fürth.[3] In a response to their study Ferranti and Indelli have remeasured[10] the kinetics of the periodate−iodide reaction by spectrophotometry at $[H^+]_0 = (1.0-10.0) \times 10^{-4}$ M. The apparent rate coefficients at different $H^+$ concentrations were estimated from the initial rate of formation of total iodine ($[I_2] + [I_3^-]$) determined from the absorbance measured at 468 nm, the corresponding isosbestic point of the system $I_2-I_3^-$. They have found again that the rate equation has both pH-independent and $[H^+]$-dependent terms, in agreement with their previous study. This long and contradictory story has provided us a challenge to solve the mystery of the pH dependence of the rate of the periodate−iodide reaction. In addition, the title reaction may also play a significant role in the oscillatory behavior of the thiosulfate−periodate reaction.[6] To date, neither systematic investigation on the stoichiometry nor a complete mechanism is available for the title reaction.

## Experimental Section

**Materials.** All the commercially available reagents (potassium periodate, potassium iodide, sodium acetate, acetic acid, perchloric acid), except for sodium perchlorate, were of the highest purity and were used without further purification. The commercially available sodium perchlorate (Sigma-Aldrich) has been purified by recrystallization. Four times distilled water was used to prepare all the stock solutions. The periodate stock solution was protected from light during the storage.

In series 1, acetic acid−acetate buffer was used to maintain the pH between 4.55 and 5.55. The acetate concentration was kept constant at 0.3 M and the desired amount of acetic acid was added to adjust the pH taking the p$K_a$ of acetic acid as 4.55. The ionic strength was adjusted to 0.5 M with 0.2 M sodium perchlorate solution. In series 2, we have checked the possibility of general acid catalysis, keeping the acetate−acetic acid concentration ratio constant at 2.5 (pH = 4.95) and varying the acetate concentration from $1.667 \times 10^{-2}$ to 0.4 M. The ionic strength was also adjusted to 0.5 M in these experiments by adding the necessary amount of sodium perchlorate. Finally, in series 3, the initial pH was adjusted by perchloric acid and the ionic strength was kept constant at 0.5 M adjusted by sodium perchlorate.

**Methods.** The kinetic measurements were carried out in a standard 1 cm quartz cuvette equipped with a Teflon cap and a

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magnetic stirrer. The cuvette was carefully sealed with Parafilm at the Teflon cap to minimize the loss of iodine. The reaction was followed with a Zeiss Specord S10 diode array spectrophotometer within the 290−500 nm wavelength range. Separate experiments have shown that the light source of spectrophotometer does not have significant influence on either the periodate or the iodine solutions within the acquisition time for following the reaction.

After the reaction was complete, the final spectra of the solutions were analyzed for the composition to establish the stoichiometry of the reaction by taking the molar absorbances of the iodine-containing species into account.

## Data Treatment

**Stoichiometry.** In excess periodate, according to the laws of mass and oxidation number balance applied for the iodine containing species, the following equation may be derived to calculate the stoichiometric ratio (SR) of the consumed iodide and periodate ions

$$\mathrm{SR} = \frac{[\mathrm{I}^-]_0}{3[\mathrm{I}^-]_0 - 5[\mathrm{I}_2]_\infty} \tag{1}$$

if iodate, iodine and periodate are the only iodine-containing species that can be detected after the reaction was complete. With an excess of iodide the concentration of iodine and triiodide were determined from the spectra of the solutions at the end of the reaction. Having known the stability constant of the triiodide ion the equilibrium concentration of the iodide ion can easily be calculated, from which SR is given as

$$\mathrm{SR} = \frac{[\mathrm{I}^-]_0 - [\mathrm{I}^-]_\infty - [\mathrm{I}_3^-]_\infty}{[\mathrm{IO}_4^-]_0} \tag{2}$$

**Kinetics.** The experimental curves were analyzed with the program package ZiTa.[11] Five different wavelengths have been chosen for the evaluation procedure: 290, 320, 350, 468, 490 nm. The selection contains the two characteristic absorption maxima of triiodide (290, 350 nm), the isosbestic point of the triiodide−iodine system (468 nm). Only the absorbance up to 1.0 has been used for evaluation because above this value the relative error of absorbance measurement increases significantly. Altogether almost 15000 experimental points from 355 absorbance−time series (71 different compositions at 5 different wavelengths) were used for simultaneous fitting that contained both the buffered and the nonbuffered experiments. The sum of squares of the deviations between the measured and calculated absorbances was selected as the parameter to be minimized. Our quantitative criterion for an acceptable fit was that the average deviation for the absolute fit approach 0.004 absorbance unit, which is close to the uncertainty of the spectrophotometer.

## Results

**Equilibrium Study.** The evaluation of the stoichiometric and kinetic measurements requires precise stability constant of triiodide ion and molar absorbances of both iodine and triiodide ion in the 290−500 nm wavelength range at the given experimental conditions. Table 1 contains the molar absorbances of iodine and triiodide ion calculated by PSEQUAD[12] at the wavelengths selected for the kinetic evaluation. The stability constant of triiodide ion was calculated to be 666 ± 19 $\mathrm{M}^{-1}$ with an average deviation of 0.0025 absorbance unit. The fitted stability constant and the molar absorbances of the absorbing species agree well with the data found in the literature.[13,14]

**TABLE 1: Molar Absorbances of the Absorbing Species at the Wavelengths Selected for Evaluation of the Stoichiometric and Kinetic Measurements**[a]

| $\lambda$ (nm) | $\epsilon(\mathrm{IO}_4^-)$ | $\epsilon(\mathrm{IO}_3^-)$ | $\epsilon(\mathrm{I}_2)$ | $\epsilon(\mathrm{I}_3^-)$ |
|---|---|---|---|---|
| 290 | 224.6 | 1.76 | 302.1 | 38431 |
| 320 | 37.7 | 0 | 72.47 | 14157 |
| 350 | 2.97 | 0 | 36.9 | 26035 |
| 468 | 0 | 0 | 754.2 | 747.1 |
| 490 | 0 | 0 | 605.0 | 323.0 |

[a] The molar absorbances are given in $\mathrm{M}^{-1}\ \mathrm{cm}^{-1}$.

**TABLE 2: Determination of the Stoichiometric Ratio (SR) in an Excess of Iodide**[a]

| $[\mathrm{I}^-]_0$ | $[\mathrm{IO}_4^-]_0$ | pH | $[\mathrm{I}_3^-]_\infty$ | $[\mathrm{I}^-]_\infty$ | SR |
|---|---|---|---|---|---|
| 3.0 | 0.4 | 5.55 | 0.2262 | 0.1706 | 1.96 |
| 1.0 | 0.14 | 5.55 | 0.0427 | 0.0946 | 2.00 |
| 1.4 | 0.4 | 5.55 | 0.1046 | 0.2911 | 1.89 |
| 1.0 | 0.3 | 5.03 | 0.0607 | 0.2329 | 1.83 |
| 1.4 | 0.4 | 5.03 | 0.1038 | 0.2900 | 1.90 |
| 2.0 | 0.4 | 5.03 | 0.1615 | 0.2353 | 2.02 |
| 1.0 | 0.1 | 4.55 | 0.0346 | 0.0687 | 2.09 |
| 1.0 | 0.2 | 4.55 | 0.0556 | 0.1497 | 1.93 |
| 1.4 | 0.4 | 4.55 | 0.0977 | 0.3054 | 2.05 |
| 1.0 | 0.01667 | 4.48 | 0.006829 | 0.9551 | 2.28 |
| 1.0 | 0.01667 | 4.30 | 0.007033 | 0.9542 | 2.32 |
| 1.0 | 0.01667 | 4.18 | 0.007017 | 0.9508 | 2.53 |
| 1.0 | 0.01667 | 4.08 | 0.007561 | 0.9460 | 2.78 |
| 1.0 | 0.01667 | 4.00 | 0.007780 | 0.9486 | 2.62 |
| 1.0 | 0.01667 | 3.93 | 0.007864 | 0.9449 | 2.83 |
| 1.0 | 0.01667 | 3.88 | 0.007787 | 0.9399 | 3.13 |
| 1.0 | 0.01667 | 3.78 | 0.008515 | 0.9419 | 2.97 |
| 1.0 | 0.01667 | 3.70 | 0.009025 | 0.9327 | 3.49 |
| 1.0 | 0.01667 | 3.63 | 0.009289 | 0.9343 | 3.38 |
| 1.0 | 0.01667 | 3.57 | 0.009964 | 0.9282 | 3.71 |
| 1.0 | 0.01667 | 3.52 | 0.01055 | 0.9248 | 3.87 |
| 1.0 | 0.01667 | 3.48 | 0.01097 | 0.9201 | 4.13 |
| 1.0 | 0.01667 | 3.13 | 0.01756 | 0.8871 | 5.72 |

[a] The concentrations are given in mM.

**TABLE 3: Determination of the Stoichiometric Ratio (SR) in an Excess of Periodate**[a]

|  |  | $[\mathrm{I}_2]_\infty$ (mM) |  |  | SR |  |  |
|---|---|---|---|---|---|---|---|
| $[\mathrm{I}^-]_0$ | $[\mathrm{IO}_4^-]_0$ | $\mathrm{pH}_1$ | $\mathrm{pH}_2$ | $\mathrm{pH}_3$ | $\mathrm{pH}_1$ | $\mathrm{pH}_2$ | $\mathrm{pH}_3$ |
| 0.1 | 0.4 | 0.0448 | 0.0439 | 0.0396 | 1.32 | 1.24 | 0.98 |
| 0.2 | 0.4 | 0.0928 | 0.0895 | 0.0848 | 1.47 | 1.31 | 1.14 |
| 0.3 | 0.4 | 0.1399 | 0.1313 | 0.1343 | 1.50 | 1.43 | 1.31 |
| 0.4 | 0.4 | 0.1892 | 0.1864 | 0.1799 | 1.58 | 1.49 | 1.33 |
| 0.5 | 0.4 | 0.2388 | 0.2341 | 0.2269 | 1.63 | 1.52 | 1.37 |
| 0.7 | 0.4 | 0.3452 | 0.3411 | 0.3407 | 1.87 | 1.77 | 1.76 |
| 1.0 | 1.0 | 0.4811 | 0.4803 | 0.4681 | 1.68 | 1.67 | 1.52 |
| 1.0 | 1.4 | 0.4819 | 0.4792 | 0.4649 | 1.69 | 1.66 | 1.48 |
| 1.0 | 2.0 | 0.4792 | 0.4772 | 0.4640 | 1.66 | 1.63 | 1.47 |

[a] The concentrations are given in mM. $\mathrm{pH}_1$, $\mathrm{pH}_2$ and $\mathrm{pH}_3$ stand for 5.55, 5.03 and 4.55, respectively.

**Stoichiometric Considerations.** The results of the stoichiometric studies are collected in Tables 2 and 3. Several authors have found,[3,5,9] without providing primary data in determining the stoichiometry, that iodine and iodate are the first product of the reaction according to the following equation:

$$\mathrm{IO}_4^- + 2\mathrm{I}^- + 2\mathrm{H}^+ \rightarrow \mathrm{IO}_3^- + \mathrm{I}_2 + \mathrm{H}_2\mathrm{O} \tag{3}$$

It is clearly seen from Table 2 that, with excess iodide and above pH = 4.55 within the experimental error, SR is 2.00, in

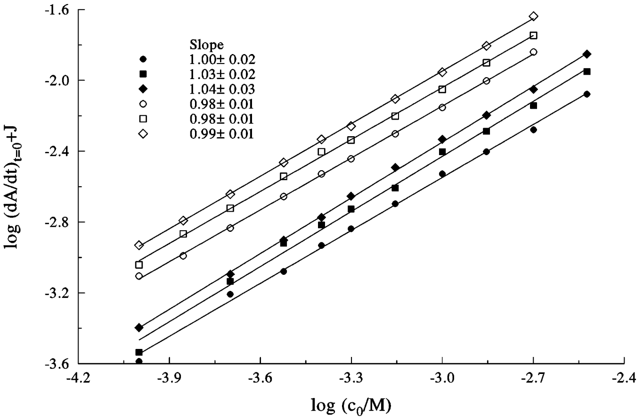

**Figure 1.** Kinetic orders of the reactants at different pHs. $[IO_4^-]_0 = 0.4$ mM and $[I^-]_0 = 1.0$ mM were kept constant for the filled and empty symbols, respectively. pH = 5.55 and $J = 0$ for (●) and (○), pH = 5.03 and $J = 0.1$ for (■) and (□), pH = 4.55 and $J = 0.2$ for (◇) and (◆). Note that some of the curves are shifted along the $Y$-axis to see the trends better.

agreement with the previous findings. If, however, the iodide excess is high enough and the pH falls below 4.5, the following equation

$$IO_4^- + 7I^- + 8H^+ \rightarrow 4I_2 + 4H_2O \tag{4}$$

occurs parallel to eq 3 and SR starts to increase, as seen in the lower part of Table 2. It is easily seen that, if these processes alone determined the stoichiometry of the reaction, then SR would definitely be higher than 2. Table 3, however, clearly shows that in excess periodate SR is significantly lower than 2, meaning that beside eqs 3 and 4 another process must be taken into consideration. Later, we shall see that

$$I^- + 3IO_4^- \rightarrow 4IO_3^- \tag{5}$$

also plays a significant role in determining the stoichiometry of the reaction. It should be mentioned that the effect of this process has already been tentatively realized by Abel and Fürth,[3] but later it somehow escaped the investigators' attention.

**Kinetics in Acetate Buffer.** The initial rate study has revealed that the reaction of periodate with iodide is perfectly first order with respect to both species, independently of pH (see Figure 1) as was found in previous works.[3−5] The second-order rate coefficients determined from the individual fit of the absorbance−time curves at 468 nm (isosbestic point of triiodide−iodine system) with the strict 2:1 stoichiometry shown in eq 3 were found to be 12.17 ± 0.91, 12.13 ± 0.71 and 12.05 ± 0.62 $M^{-1}$ $s^{-1}$ at pH = 5.55, 5.03 and 4.55, respectively, indicating that no pH dependence could be observed, in agreement with some earlier investigations.[3,9] Furthermore, the buffer concentration does not have any effect on the rate of the reaction (see Figure 2) within the acetate concentration range studied, indicating the lack of buffer assistance that frequently accompanies the reactions[15−17] of oxyhalogen species. This result also agrees well with the previous work done by Abel and Fürth.[3] It was considered to be important to strengthen this early result because the lack of pH dependence found by Marques and Hasty[9] was argued by Ferranti and Indelli[10] that it is due to a possible unrecognized influence of undissociated acetic acid.

**Kinetics without Acetate Buffer.** Because the reaction between periodate and iodide ion consumes $H^+$ according to eq 3 and application of no buffer at the concentration range

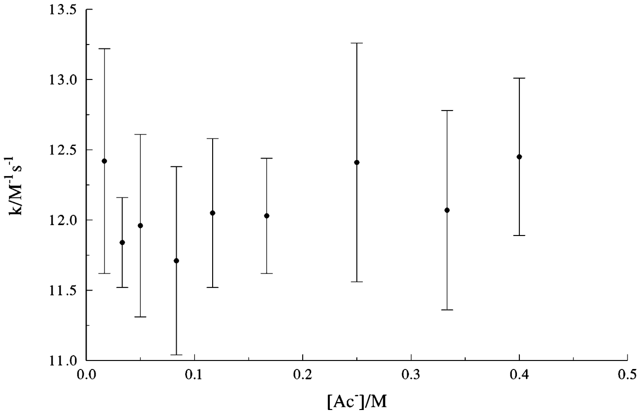

**Figure 2.** Effect of buffer concentration on the rate of the periodate−iodide reaction at $I = 0.5$ M ionic strength adjusted by sodium perchlorate. $[IO_4^-]_0 = 0.25$ mM, $[I^-]_0 = 1.5$ mM, [HAc]/[Ac$^-$] = 0.4.

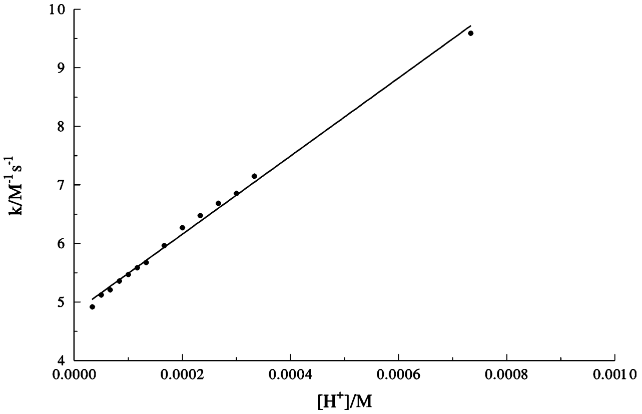

**Figure 3.** Apparent dependence of the second-order rate coefficient determined from the initial rate study on pH. $[I^-]_0 = 1.0$ mM, $[IO_4^-]_0 = 0.01667$ mM, $I = 0.5$ M adjusted by sodium perchlorate.

used in our experiments may lead to a relatively huge change in pH during the course of the reaction, especially at low perchloric acid concentrations, the rate coefficients have been determined from initial rate studies in accordance with Ferranti and Indelli.[10] Our results are illustrated in Figure 3 and are in perfect harmony with Ferranti and Indelli's findings. The fit has yielded a 4.82 ± 0.13 $M^{-1}$ $s^{-1}$ value for the pH-independent part of the periodate−iodide reaction and 6680 ± 420 $M^{-2}$ $s^{-1}$ value for the pH-dependent term of the rate equation. Although the slope is somewhat greater than it was previously found to be, 1420 ± 40 and 2730 ± 240 $M^{-2}$ $s^{-1}$ by the above-mentioned authors,[5,10] the intercept is surprisingly good compared to 4.72 ± 0.03 and 4.78 ± 0.06 $M^{-1}$ $s^{-1}$, even though the experimental circumstances were quite different in these studies. Nevertheless, it also means that there is an apparent contradiction between the results obtained from the presence and absence of acetate buffer, because on the one hand the reaction is independent of both the pH and the buffer concentration in the presence of the acetate/acetic acid buffer and on the other hand its rate law contains a $[H^+]$-dependent path besides the $[H^+]$-independent term in the absence of buffer! Later, we shall see that this apparent contradiction can entirely be resolved by an appropriately suggested mechanism in which the rate determining step is pH-independent but the stoichiometry of the reaction strongly depends on pH.

**Proposed Mechanism.** As a starting point, to build up the mechanism, we have chosen the following set of species that are very likely to participate in the final kinetic model. This set consists of the reactants $I^-$ and $IO_4^-$, the products $I_2$, $I_3^-$ and

$IO_3^-$, some intermediates such as HOI, $HIO_2$, $I_2O_4^{2-}$ and the species $H^+$, $H_2O$, $OH^-$ that are always present in aqueous medium. After that all the possible mono- and bimolecular steps of these species were considered along with their $H^+$- and $OH^-$-catalyzed pathways. This method has been successfully applied in several cases of our previous work.[18−20] After long but straightforward systematic reduction, the following model has emerged.

$$H^+ + OH^- \rightleftharpoons H_2O \tag{P1}$$

$$Ac^- + H^+ \rightleftharpoons HAc \tag{P2}$$

$$I^- + IO_4^- \rightarrow I_2O_4^{2-} \tag{R1}$$

$$I_2O_4^{2-} + H^+ + H_2O \rightarrow 2HIO_2 + OH^- \tag{R2}$$

$$I_2O_4^{2-} + I^- + H_2O \rightarrow I_2 + IO_3^- + 2OH^- \tag{R3}$$

$$HIO_2 + I^- + H^+ \rightarrow 2HOI \tag{R4}$$

$$HIO_2 + IO_4^- \rightarrow 2IO_3^- + H^+ \tag{R5}$$

$$I_2 + H_2O \rightleftharpoons HOI + I^- + H^+ \tag{R6}$$

$$I_2 + I^- \rightleftharpoons I_3^- \tag{R7}$$

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O \tag{R8}$$

## Discussion

The fast protonation and deprotonation processes (equilibria P1 and P2) were taken into consideration with the well-known equilibrium constants to adjust the pH in buffered solution and to follow the pH change during the course of the reaction in unbuffered solution. They are regarded as auxiliary processes, necessary for the calculations, but they are not part of the proposed model.

Step R1 is the initial elementary reaction of our model in which the adduct $I_2O_4^{2-}$ is formed. As we shall see, this is the rate-limiting step and the second-order rate coefficient was found to be $12.3 \pm 0.3$ $M^{-1}$ $s^{-1}$ at $I = 0.5$ M ionic strength. From Marques and Hasty's data[9] one can estimate a 12.6 $M^{-1}$ $s^{-1}$ value at $I = 0.5$ M, which perfectly agrees with the value determined from this work. Nevertheless, Abel and Fürth have estimated[3] a 11.8 $M^{-1}$ $s^{-1}$ value at an ionic strength of $I = 0.4$ M adjusted by sodium acetate that also indicates perfect agreement with our work. It has to be mentioned for the sake of correctness that in his early paper a 707 $M^{-1}$ $s^{-1}$ value was given, but it seems likely that it is a typographical error and the unit of this value is properly $M^{-1}$ $min^{-1}$, which can be converted to 11.8 $M^{-1}$ $s^{-1}$. It should also be noted that four species are present[21] in the aqueous periodate solution, $H_5IO_6$, $H_4IO_6^-$, $IO_4^-$ and $H_3IO_6^{2-}$. Those are, however, rapidly equilibrated with each other and the periodate is mainly in univalent form (either $H_4IO_6^-$ or $IO_4^-$) in the pH range studied. Because there is a rapid pH-independent equilibrium[22] between $H_4IO_6^-$ and $IO_4^-$ and the ratio of $[IO_4^-]/[H_4IO_6^-]$ is 29.5, it looks reasonable to suppose that the reactive species is $IO_4^-$ despite the fact that our measurements do not provide solid basis to establish the kinetically active form of periodate.

Steps R2 and R3 are further reactions of $I_2O_4^{2-}$. The individual rate coefficients $k_2$ and $k_3$ cannot be determined independently; they are in total correlation with each other. We therefore fixed $k_3 = 10^5$ $M^{-1}$ $s^{-1}$ and calculated $k_2$ to be $(8.3 \pm 0.9) \times 10^4$ $M^{-1}$ $s^{-1}$. At low $H^+$ and high iodide concentration the adduct formed in step R1 reacts almost exclusively with iodide, yielding iodine and iodate in a 1:1 molar ratio, giving back the stoichiometry indicated by eq 3. At low pH and iodide concentrations, however, the reaction is shifted to the formation of iodous acid.

Iodous acid, however, quickly reacts further with either iodide or periodate in steps R4 and R5. Both reactions are fast, only their ratio can be calculated from our experiment. Because $k_4 = 10^9$ $M^{-2}$ $s^{-1}$ was determined independently by Lengyel and his co-workers,[23] we have fixed it during the calculations. The fitting procedure has yielded a reasonable value for $k_5 = (1.23 \pm 0.34) \times 10^5$ $M^{-1}$ $s^{-1}$. In excess periodate, step R5 drives the reaction; thus the stoichiometry is shifted toward eq 5; however, at low periodate concentration, step R4 yields hypoiodous acid almost instantaneously. As one may notice, if step R4 dominates (along with the iodine hydrolysis), then the stoichiometry of the reaction is shifted toward eq 4, whereas prevalence of step R5 leads to the stoichiometry indicated by eq 5. Several other reactions of iodous acid were also considered, including the well-known and easily conceivable disproportionation

$$2HIO_2 \rightarrow IO_3^- + HOI + H^+ \tag{6}$$

but none of them improved the quality of fit. The rate coefficient of this process was determined[23,24] to be between 25 and 50 $M^{-1}$ $s^{-1}$, which is too slow to compete with either step R4 or step R5 in our experimental circumstances.

Step R6 is the well-known hydrolysis of iodine studied by several authors.[25,26] All the rate coefficients, including the hydroxide-driven hydrolysis of iodine determined previously, were implanted in our final model without any change. This process together with their rate coefficients provides a sufficiently low level of hypoiodous acid ($<10^{-5}$ M) that does not have significant absorbance contribution in the wavelength range used in our experiments. Moreover, it also implies that the well-known back-reaction of step R4 cannot have a significant effect with a rate coefficient being[23,27,28] between 5 and 22 $M^{-1}$ $s^{-1}$; therefore it is not included in the proposed model. It should also be mentioned that the following

$$HOI + IO_4^- \rightarrow HIO_2 + IO_3^- \tag{7}$$

reaction was also considered but it turned out to be unnecessary for describing the kinetics of the title reaction.

Step R7 is the well-known fast formation of triiodide ion. For the values of $k_7$ and $k_{-7}$ $6.66 \times 10^8$ $M^{-1}$ $s^{-1}$ and $10^6$ $s^{-1}$ have been used, respectively, which gives the formation constant of triiodide to be 666 $M^{-1}$ determined independently from equilibrium studies.

Step R8 is the well-known Dushman reaction that starts to rise only at lower pH.[29] From his early paper one can estimate a value of $8.0 \times 10^8$ $M^{-4}$ $s^{-1}$ for $k_8$ at an ionic strength between 0.0015 and 0.003 M. Our fitted value $k_8 = (2.35 \pm 0.71) \times 10^9$ $M^{-4}$ $s^{-1}$ at $I = 0.5$ M is therefore in reasonable agreement with his measurements. To show that this reaction plays only a minor role, additional fitting has been carried out with three fitted kinetic parameters ($k_1$, $k_2/k_3$ and $k_5$ without $k_8$) on those experimental curves where the pH was higher than 3.6. This fitting procedure has led to a bit lower average deviation (0.0035 absorbance unit), meanwhile the values of the three fitted parameters remained basically the same within their standard deviation given in Table 4.

**TABLE 4: Fitted and Fixed Rate Coefficients Used in the Fitting Procedure**[a]

| step | rate equation | parameter | ref |
|---|---|---|---|
| (R1) | $k_1[I^-][IO_4^-]$ | $12.3 \pm 0.3$ M$^{-1}$ s$^{-1}$ | this work |
| (R2) | $k_2[I_2O_4^{2-}][H^+]$ | | |
| (R3) | $k_3[I_2O_4^{2-}][I^-]$ | $k_2/k_3 = 0.83 \pm 0.09$ | this work |
| (R4) | $k_4[HIO_2][I^-][H^+]$ | $10^9$ M$^{-2}$ s$^{-1}$ | 22 |
| (R5) | $k_5[HIO_2][IO_4^-]$ | $(1.23 \pm 0.34) \times 10^5$ M$^{-1}$ s$^{-1}$ | this work |
| (R6) | $k_6[I_2]$ | 0.0552 s$^{-1}$ | 22 |
| | $k_{-6}[HOI][I^-][H^+]$ | $1.023 \times 10^{11}$ M$^{-2}$ s$^{-1}$ | 22 |
| | $k_6'[I_2]/[H^+]$ | $1.98 \times 10^{-3}$ M s$^{-1}$ | 22 |
| | $k_{-6}'[HOI][I^-]$ | $3.67 \times 10^9$ M$^{-1}$ s$^{-1}$ | 22 |
| (R7) | $k_7[I_2][I^-]$ | | |
| | $k_{-7}[I_3^-]$ | $k_7/k_{-7} = 666$ M$^{-1}$ | 14 |
| (R8) | $k_8[IO_3^-][I^-]^2[H^+]^2$ | $(2.35 \pm 0.71) \times 10^9$ M$^{-4}$ s$^{-1}$ | this work |

[a] No error indicates that the value in question was fixed during the fitting procedure. Note that the actual calculations yielded $k_2/k_3$, $k_4/k_5$.

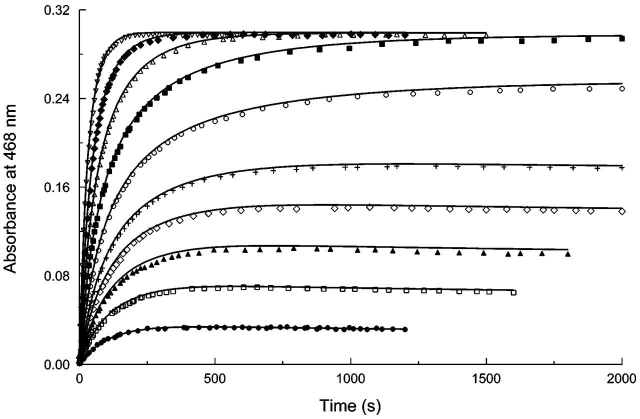

**Figure 4.** Measured (symbols) and calculated (solid lines) kinetic curves at pH = 5.55 and $[IO_4^-]_0$ = 0.4 mM in acetate buffer. $[I^-]_0$ (mM) = 0.1 (●), 0.2 (□), 0.3 (▲), 0.4 (◇), 0.5 (+), 0.7 (○), 1.0 (■), 1.4 (△), 2.0 (◆), 3.0 (▽).

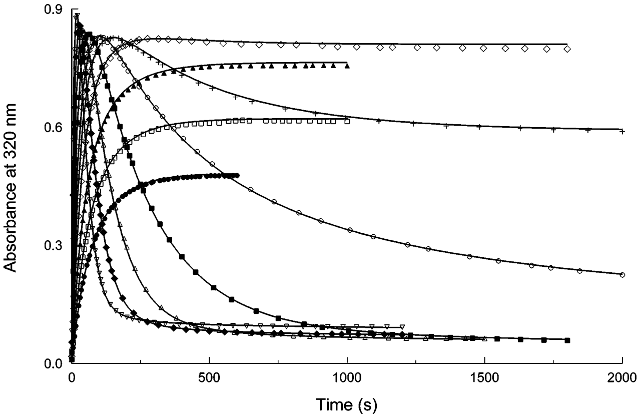

**Figure 5.** Measured (symbols) and calculated (solid lines) kinetic curves at pH = 5.55 and $[I^-]_0$ = 1.0 mM in acetate buffer. $[IO_4^-]_0$ (mM) = 0.1 (●), 0.14 (□), 0.2 (▲), 0.3 (◇), 0.4 (+), 0.5 (○), 0.7 (■), 1.0 (△), 1.4 (◆), 2.0 (▽).

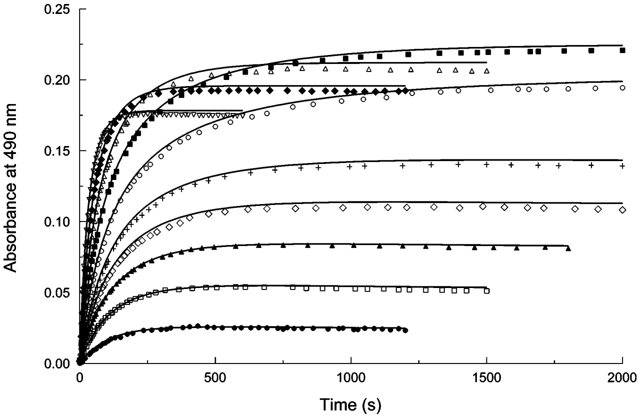

**Figure 6.** Measured (symbols) and calculated (solid lines) kinetic curves at pH = 5.03 and $[IO_4^-]_0$ = 0.4 mM in acetate buffer. $[I^-]_0$ (mM) = 0.1 (●), 0.2 (□), 0.3 (▲), 0.4 (◇), 0.5 (+), 0.7 (○), 1.0 (■), 1.4 (△), 2.0 (◆), 3.0 (▽).

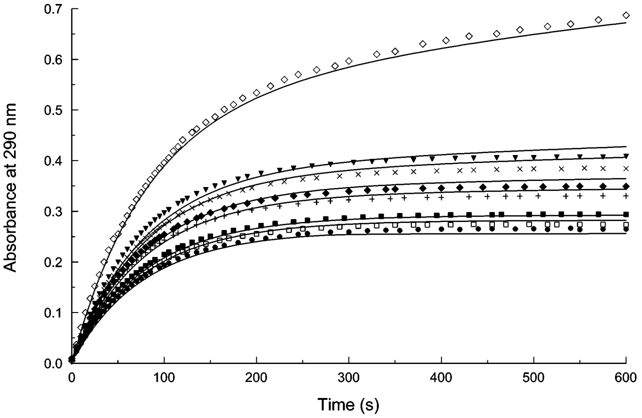

**Figure 7.** Measured (symbols) and calculated (solid lines) kinetic curves at $[I^-]_0$ = 1.0 mM and $[IO_4^-]_0$ = 0.016667 mM without acetate buffer. pH = 4.48 (●), 4.18 (□), 4.08 (■), 3.78 (+), 3.70 (◆), 3.57 (×), 3.52 (▼), 3.13 (◇).

It should also be mentioned that any trial to include the easily conceivable direct reaction between iodine and periodate

$$I_2 + IO_4^- + H_2O \rightarrow 2HOI + IO_3^- \tag{8}$$

was unsuccessful; therefore we concluded that this reaction is not necessary for describing the kinetics and mechanism of the iodide−periodate reaction.

Table 4 summarizes the fixed and fitted rate coefficients in the fitting procedure. Figures 4−9 demonstrate that the model is capable of good description of the absorbance change during the reaction in a wide concentration range of the reactants at the selected wavelengths. The average deviation was found to be 0.0037 absorbance unit, which is close to the experimentally achievable limit of error of the spectrophotometer. The proposed model perfectly fits all the experimental data because, besides the low average deviation, all the most important characteristics of the experimental kinetic curves are reflected in the fitted curves. Among them, four important characteristics have to be emphasized:

•Figures 4−6 clearly demonstrate that at high pH and high iodide concentration eq 3 rules the stoichiometry of the reaction. If, however, periodate is in molar excess over the iodide ion, then less iodine is formed that can be expected from eq 3, meaning that the stoichiometry is slightly shifted toward eq 5.

•Figure 7 clearly indicates that the reaction cannot be interpreted by a single stoichiometry. As the pH decreases, more and more iodine (triiodide) is formed than could be expected from eq 3 even at those pHs where the Dushman reaction[29] is extremely slow. It clearly indicates the continuously growing effect of eq 4 on the stoichiometry of the reaction.

•Figure 8 shows that there is no difference in the early stage of the kinetic curves as a function of pH in buffered solution in the pH range 4.55−5.55, meaning no pH dependence in the

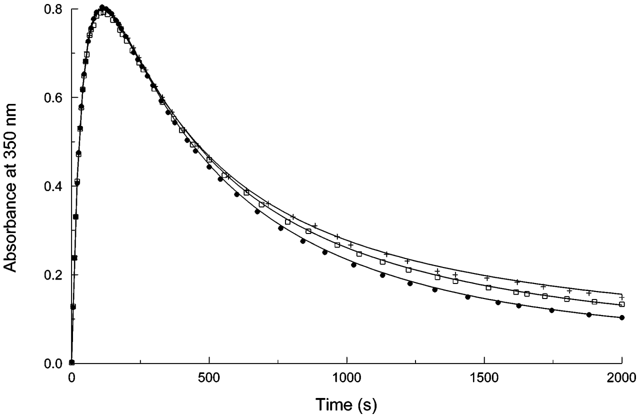

**Figure 8.** Measured (symbols) and calculated (solid lines) kinetic curves at $[I^-]_0 = 0.7$ mM and $[IO_4^-]_0 = 0.4$ mM in acetate buffer. pH = 5.55 (●), 5.03 (□), 4.55 (+).

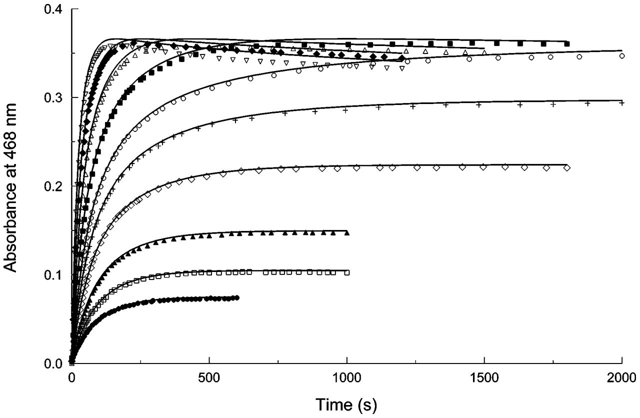

**Figure 9.** Measured (symbols) and calculated (solid lines) kinetic curves at pH = 5.55 and $[I^-]_0 = 1.0$ mM in acetate buffer. $[IO_4^-]_0$ (mM) = 0.1 (●), 0.14 (□), 0.2 (▲), 0.3 (◇), 0.4 (+), 0.5 (○), 0.7 (■), 1.0 (△), 1.4 (◆), 2.0 (▽).

rate-limiting step. Later a slight difference appears, indicating a stoichiometric shift as the pH decreases.

•Figure 9 shows that in high periodate excess the total iodine concentration gradually decreases after it reaches its maximum, though the direct reaction between iodine and periodate is not included in the proposed kinetic model. The decrease can also be explained by the fact that the iodine hydrolysis is a considerable iodide source—especially at higher pH—that can serve as further breeding ground for the iodide–periodate reaction.

Finally, we shall point out how the apparent contradiction obtained from the two different approaches of the evaluation should be resolved. The rate-determining step of the proposed model is step R1, the rate equation of which is pH-independent. The influence of pH, however, is that it shifts the stoichiometry of the reaction from the strict 2:1 iodide–periodate ratio beyond the stoichiometry that can be represented by the linear combination of eqs 3 and 4. It means that the ratio of the concentration of the formed total iodine ($[I_2] + [I_3^-]$) and the consumed periodate increases. If the reaction was only followed up to 10% conversion, the concentration of total iodine formed in a time unit would increase as a function of $[H^+]$. Therefore it can also be interpreted or more accurately misinterpreted as if the rate equation contains a pH-dependent term. To be more convincing, we have determined the individual rate coefficients of the kinetic curves measured in unbuffered solution in the same way as they had been done in the case of buffered solutions. A value of $13.5 \pm 1.2$ $M^{-1}$ $s^{-1}$ for the rate coefficient of eq 3 has been found in unbuffered medium, which is slightly higher than the value of $12.1 \pm 0.7$ $M^{-1}$ $s^{-1}$ in the case of the buffered solutions. The 10% difference between these values can easily be explained by the dissimilar characteristics of the background salts of sodium acetate and sodium perchlorate.

## Conclusions

It is clearly demonstrated in this paper that the rate of periodate–iodide reaction is independent of pH in the pH range 3.1–5.55, in agreement with Marques and Hasty's study.[9] The stoichiometry of the reaction, however, is strongly affected by pH. The lower the pH is, the higher the ratio of the formed total iodine and consumed periodate is. A simple kinetic model is suggested that is able to explain not only all the most important characteristics of the kinetic curves but also the origin of the completely different interpretation of pH dependence on the rate of the title reaction. Four of the suggested eight kinetic steps are well-known from the literature with well-determined rate equations. Step R1 turned out to be the rate-limiting step, the rate equation of which is independent of pH. The fate of the adduct formed in this step, however, strongly depends on the pH that results in branching stoichiometries. The higher the acidity is, the more iodine can form in a time unit. The increasing amount of iodine in a time unit as a function of pH, however, might be defectively interpreted as if the rate coefficient, obtained from initial rate study assuming a strict stoichiometry, has an apparent pH dependence.

This work, however, has a more serious consequence than the refinement of the kinetics and stoichiometry of the title reaction itself. The tool with which the information of the experimental curves is extracted to draw the final conclusion must be chosen with special circumspection. A badly chosen evaluation method might unavoidably lead to a complete misinterpretation of the results. Therefore even the seemingly simple reactions can be handled with special care and be evaluated by the recently available computational techniques in chemical kinetics, because any simplification might carry in itself the possibility of potential misinterpretation of the kinetic data. The simultaneous fitting of all the measured kinetic curves without any data transformation is therefore strongly recommended if a feasible kinetic model is intended to be proposed.

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**Supporting Information Available:** File containing the derivation of eq 1 and the measured and calculated absorbances for all the kinetic curves (takes up 19 pages) are available free of charge via the Internet at http://pubs.acs.org.

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