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Compatible Mechanism for a Simultaneous Description of the Roebuck, Dushman, and Iodate–Arsenous Acid Reactions in an Acidic Medium

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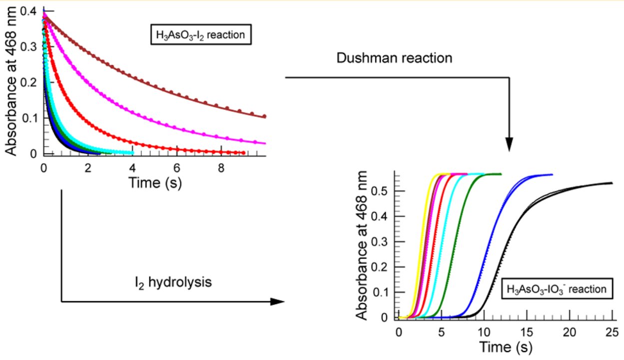
ABSTRACT: The iodine–arsenous acid (Roebuck), iodide–iodate (Dushman), and iodate–arsenous acid reactions have been studied simultaneously by a stopped-flow technique by monitoring the absorbance–time profiles at the isosbestic point of the I_2/I_3^- system (468 nm). Using the well-accepted rate coefficients of iodine hydrolysis, we have proven that iodine is the kinetically active species of the iodine–arsenous acid reaction. Strong iodide inhibition of this system is explained by a rapidly established equilibrium between iodine and arsenous acid to produce an iodide ion, a hydrogen ion, and a short-lived intermediate H_2AsO_3I, which is shifted far to the left. Taking into consideration the generally accepted kinetic model of the Dushman reaction where I_2O_2 plays a key role to account for all of the most important observations in this subsystem and a sequence of simple formal oxygen-transfer reactions between arsenous acid and iodic acid as well as iodous acid and hypoiodous acid, we propose a 13-step comprehensive kinetic model, including seven rapidly established equilibria with only six fitted parameters, that is able to explain all of the most important characteristics of the kinetic curves of all of the title systems both individually and simultaneously.



■ INTRODUCTION

The iodate–arsenous acid reaction has been frequently used as a tool to study buoyancy-driven convection,[1,2] Marangoni instability,[3] convective dynamics in a modulated gravity field,[4] and other spatiotemporal phenomena connected to its clock feature and front propagation.[5−8] The kinetic model is simple because it starts with a slow direct overall reaction between the reactants to produce an iodide ion[9]

$$3H_3AsO_3 + IO_3^- \rightarrow 3H_3AsO_4 + I^- \qquad (1)$$

followed by the iodide–iodate process often referred to as the Dushman reaction.[10]

$$5I^- + IO_3^- + 6H^+ \rightarrow 3I_2 + 3H_2O \qquad (2)$$

Iodine produced in this way is, however, removed by the iodine–arsenous acid reaction, as discovered by Roebuck,[11] to reestablish an iodide ion that eventually closes the autocatalytic cycle.

$$H_3AsO_3 + I_2 + H_2O \rightarrow H_3AsO_4 + 2I^- + 2H^+ \qquad (3)$$

Even though this kinetic model seems to be relatively simple and all of these individual reactions are long known, it is interesting to note that the quantitative pictures of the component reactions are still in dispute. For example, up to now, it was a general belief that there is no direct reaction between iodate and arsenous acid, and the reaction is supposedly initiated by the iodide impurity of an iodate ion.[12,13] Our very recent study[9] has just provided experimental evidence that, although stock iodate solutions are usually not free from iodide contamination, mainly the direct process is responsible for initiation of the reaction, in agreement with an earlier study by Eggert and Scharnow.[14] Furthermore, Roebuck,[11] in his pioneering work on the kinetics of the iodine–arsenous acid reaction, proposed that the reactive species in the aqueous iodine solution is HOI. This assumption was strongly challenged by Liebhafsky, who interpreted his results in terms of the hydrates of iodine.[15,16] Later Pendlebury and Smith[17] found that indeed iodine is the kinetically active species that attacks arsenous acid, and this was later confirmed by Patil and Rewatkar.[18] It is generally well-known that an equilibrium between iodine and hypoiodous acid is established relatively rapidly; therefore, it is not straightforward at all which of these species is kinetically more active to react with arsenous acid. In principle, both possibilities are kinetically conceivable. Therefore, the kinetics of iodine hydrolysis appears to be a crucial process in comprehensively describing the temporal behavior of the title systems. The hydrolysis constant of iodine has been thoroughly studied by several independent research groups for more than a century and was established to be (2–6) × 10^{-13} M^2.[19−23] The kinetics of iodine hydrolysis was investigated by two independent research groups by means of

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temperature-jump studies.[24,25] Later Furrow[26] established the rate law $d[I_2]/dt = 0.0018[I_2]/[H^+] - 3.6 \times 10^9[HOI][I^-]$, which was confirmed indirectly by Schmitz.[27] All of these studies clearly support the equilibrium constant of iodine hydrolysis to be 5.4×10^{-13} M^2, but for the sake of completeness, it should also be mentioned that some earlier works reported a significantly higher, but seemingly unreliable, value.[28,29] We shall see that, of course, the value of the equilibrium constant of iodine has a substantial impact whether iodine or hypoiodous acid is the kinetically active species in the more complicated iodate−arsenous acid reaction as well. Our aim here is to establish a comprehensive kinetic model to be able to describe quantitatively the measured absorbance−time profiles of the iodine−arsenous acid, iodide−iodate, and iodate−arsenous acid reactions simultaneously.

■ EXPERIMENTAL SECTION

Methods and Materials. All of the reagents—arsenic(III) oxide (Reanal), anhydrous sodium sulfate (Reanal), perchloric acid (Germed), iodine (Reanal), sodium iodide (Reanal), sodium iodate (Reanal), sodium hydrogen carbonate (Reanal), methyl red (Reanal), and absolute ethanol (Merck)—were of the highest purity available commercially and were used without further purification. Stock solutions were made by dissolving the necessary amount of the target compound (except for an arsenous acid stock solution detailed below). Water was twice ion-exchanged and then distilled twice to remove ionic exchange resin residues and dissolved gases. All of the solutions were deoxygenated by bubbling oxygen-free argon for at least 10 min. All of the experiments were performed at temperature-controlled conditions (25.0 ± 0.1 °C) and at a constant ionic strength set to 0.68 M using sodium sulfate, sodium perchlorate, or both. The initial iodine, hydrogen ion, arsenous acid, and iodide concentrations were varied in the ranges of $(1-5) \times 10^{-4}$, 0.1−0.6, 0.0050−0.07, and 0−0.05 M, respectively. The concentration of a perchloric acid stock solution was determined by a standard titration method by applying sodium hydrogen carbonate and a methyl red indicator. All of the iodine solutions were prepared by dissolving excess iodine in a solution containing the necessary amount of perchloric acid and sodium sulfate and stirred at least for 1 night. These solutions were kept in the dark to avoid any photocatalyzed reaction. In the case of the iodide−iodate reaction, the initial concentrations of iodide, iodate, and hydrogen ion were varied in the ranges of 16−87.5 μM, 0.5−2.0 mM, and 0.05−0.5 M, respectively. The ionic strength was adjusted by the necessary amount of sodium perchlorate.

An arsenous acid stock solution was prepared by dissolving an excess of arsenic(III) oxide in boiling water by continuous stirring. The solution was then left to cool under persistent stirring. This procedure was repeated one more time. After the solution reached room temperature, the residues of undissolved arsenic(III) oxide were removed by filtration. An arsenous acid stock solution obtained in this way was completely free from carbonate impurities. The concentration of the stock solution was checked by spectrophotometry. In an excess of sodium iodate and perchloric acid, arsenous acid was delivered into a quartz cuvette having a Teflon stopper and was left to stand for at least 20 min. The absorption spectrum was recorded by UV−vis spectrophotometer, and according to the equation

$$2IO_3^- + 5H_3AsO_3 + 2H^+ \rightarrow I_2 + 5H_3AsO_4 + H_2O \qquad (4)$$

the concentration of an arsenous acid stock solution could be calculated. (An absorbance at 468 nm was used, where $\varepsilon_{I2} = \varepsilon_{I3^-} = 747$ M^{-1} cm^{-1}.) The reproducibility of the method was found to be better than 1%. The stock solution prepared was stable at room temperature; no crystal formation or any decomposition was visible, and the concentration was constant for over 1 month. In the case of the iodate−arsenous acid reaction, the initial concentrations of iodate, arsenous acid, and hydrogen perchlorate were varied in the ranges of 1.65−13 mM, 0.285−4.7 mM, and 0.14−1.0 M, respectively. In this case, the ionic strength was controlled by the addition of sodium perchlorate.

Instrumentation. Spectrophotometric measurements were carried out by a Zeiss S600 diode-array spectrophotometer equipped with a thermostated cell holder. The kinetic curves were recorded by a SX20 diode-array stopped-flow spectrophotometer manufactured by Applied Photophysics. As we shall see later, the kinetic runs last for several seconds, so a dead-time correction (found to be less than 1.0 ms) did not need to be applied.

Data Treatment. The absorbance−time profiles were evaluated simultaneously by the program package ZiTa/Chemmech.[30] The orthogonal fitting procedure was applied meaning that all of the kinetic curves were transformed into a $0 \leq x, y \leq 1$ box and the sum of the perpendicular deviation between the measured and calculated absorbances was minimized by kinetic parameter optimization. Our criterion was that the average deviation approaches 1.5%, which is the experimentally achievable limit of error under our experimental conditions.

■ RESULTS AND DISCUSSION

Kinetics of the Roebuck Reaction and Iodine Hydrolysis. The stoichiometry of the iodine−arsenous acid (Roebuck) reaction has long been accepted,[11] as indicated by eq 3. Despite the simplicity of this equation, the identity of the kinetically active iodine-containing species is still in question. Moreover, our very recent study[9] has just revealed that the rate equation of this reaction (see eq 5) is rather complex, and a factor (u) was introduced that may easily be interpreted as the iodide impurity of the stock iodate solution.

$$r = k\frac{[H_3AsO_3][I_2]}{[H^+]([I^-] + u)} \qquad (5)$$

To clarify, we have reinvestigated the reaction by a stopped-flow technique. Figure 1 depicts the effect of the arsenous acid concentration on the decay of the total amount of iodine. As is seen, these kinetic curves were measured in a high excess of arsenous acid, therefore one may expect that the absorbance−time profiles can easily be calculated by a single-exponential fit ($A = A_0 e^{-k_{obs}t}$) to obtain pseudo-first-order apparent rate coefficients at each condition individually if the formal kinetic

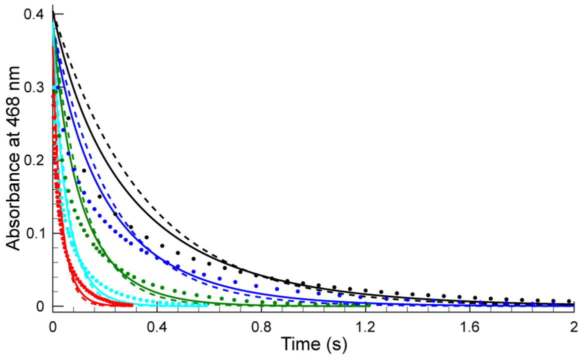

Figure 1. Individual fits in the iodine−arsenous acid (Roebuck) reaction at different arsenous acid concentrations in the absence of an initially added iodide ion. Conditions are as follows: $T^0_{I_2} = 0.5$ mM; $T_{SO_4^{2-}} = 0.2$ M; $[HClO_4] = 0.4$ M. $[H_3AsO_3]_0$/mM = 7.5 (black), 10.0 (blue), 20.0 (green), 40.0 (cyan), and 60.0 (red). Color dots correspond to experimental values. Dashed lines indicate the result of an individual single-exponential curve fit in each case. Solid lines represent the result of the individual curve fit by eq 3 with a specific second-order rate coefficient (k_r) along with taking into account the rapid equilibrium formation of a triiodide ion.

order of iodine is 1. The results are illustrated in Figure 1 by dashed lines: Although the average deviation of these curves was found to be 2.8%, evidently systematic deviations may be found between the experimental and calculated absorbance. At the initial stage of each curve, experiments indicate a much faster drop of the absorbance than that of the calculated one, while at the final stages, this trend is reversed. As a result, we concluded that, although arsenous acid is applied in a high excess, the kinetic curves cannot be described by a single-exponential fit. A conceivable explanation of this fact is that the iodide ion produced during the course of the reaction continuously transforms iodine into the kinetically less reactive triiodide ion. Therefore, as a next step, we tried to describe our kinetic data by considering eq 3 having law-of-mass-action kinetics ($r_3 = k_r[H_3AsO_3][I_2]$) along with the well-known rapid equilibrium formation of a triiodide ion ($I_2 + I^- \rightleftharpoons I_3^-$) by fitting only rate coefficient k_r. These fitting procedures were also carried out individually experiment by experiment. The results can also be seen in Figure 1 and represented by solid lines. As is visualized, a slight improvement is achieved—the average deviation decreased to 2.14%—but inspection of the results still indicates notable systematic deviations, from which we concluded that the iodide ion has a significantly more complex contribution to the kinetics of the reaction than just the simple triiodide formation. This result contradicts the main message reported by Patil and Rewatkar,[18] who showed that the kinetics of the Roebuck reaction can be described by a specific second-order rate coefficient that depends on the pH but not on the concentration of the iodide ion. To further prove experimentally that the reaction is more complex and cannot be described by a single specific rate coefficient, we present below the results of the initial rate studies. Figure 2 shows the log–log plots indicating that the formal kinetic orders of both arsenous acid and iodine (where T_{I2} id defined as $[I_2] + [I_3^-]$) are strictly 1, while that of the hydrogen ion is −1. However, the logarithm of the initial rate against the logarithm of the initial iodide concentration is clearly not linear, suggesting the fact that iodide dependence of the rate should be considered as a complex issue. It also indirectly supports that fact that the effect of the initially added iodide ion cannot be taken into consideration simply by supposing the formation of a triiodide ion. One thing is, however, straightforward; the reaction is autoinhibitory with respect to the iodide ion because formation of the product iodide inhibits the initial rate of consumption of iodine.

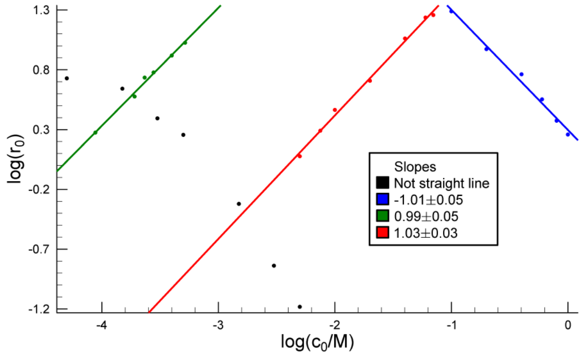

Figure 2. Initial rate studies to determine the formal kinetic orders of the reactants in the iodine–arsenous acid (Roebuck) reaction. Conditions are as follows: (black) $[H_3AsO_3]_0$ = 10 mM, $T^0_{I_2}$ = 0.54 mM, $[HClO_4]_0$ = 0.4 M, and c_0 corresponds to $[I^-]_0$; (blue) $[H_3AsO_3]_0$ = 10 mM, $T^0_{I_2}$ = 0.65 mM, $[I^-]_0$ = 0 mM, and c_0 corresponds to $[HClO_4]$; (green) $[H_3AsO_3]_0$ = 10 mM, $[HClO_4]$ = 0.4 M, $[I^-]_0$ = 0 mM, and c_0 corresponds to $T^0_{I_2}$; (red) $T^0_{I_2}$ = 0.4 mM, $[I^-]_0$ = 0 mM, $[HClO_4]$ = 0.4 M, and c_0 corresponds to $[H_3AsO_3]$. $T_{SO_4^{2-}}$ = 0.2 M was kept constant in all of these experiments.

Because this observation is very reminiscent of what we have recently reported in the case of the polythionate–iodine reactions,[31] as a next step, we considered the following kinetic model to provide a reasonable description of the kinetic runs. Below this point, the term “fitting” refers to the simultaneous evaluation of the kinetic curves.

$$HSO_4^- \rightleftharpoons SO_4^{2-} + H^+ \tag{E1}$$

$$I_2 + I^- \xrightleftharpoons{k_{R1},\, k_{-R1}} I_3^- \tag{R1}$$

$$I_2 + H_2O \xrightleftharpoons{k_{R2},\, k_{R2}',\, k_{-R2},\, k_{-R2}'} HOI + I^- + H^+ \tag{R2}$$

$$H_2OI^+ \xrightleftharpoons{k_{R3},\, k_{-R3}} HOI + H^+ \tag{R3}$$

$$H_3AsO_3 + HOI \xrightarrow{k_{R4}} H_3AsO_4 + I^- + H^+ \tag{R4}$$

$$H_3AsO_3 + H_2OI^+ \xrightarrow{k_{R5}} H_3AsO_4 + I^- + 2H^+ \tag{R5}$$

Step E1 is an auxiliary process, only necessary to take the slight pH change correctly into account during the course of the reaction. The rate coefficients of the forward and reverse reactions were set to the fixed values of $k_{E1} = 5.75 \times 10^8\ s^{-1}$ and $k_{-E1} = 10^{10}\ M^{-1}\ s^{-1}$ to give the pK_a of HSO_4^- as 1.24.[32] The rate coefficients of the forward and backward reactions of step R1 were also fixed as determined previously ($k_{R1} = 5.6 \times 10^9\ M^{-1}\ s^{-1}$ and $k_{-R1} = 8.5 \times 10^6\ s^{-1}$).[33,34]

The mechanism of iodine hydrolysis was proposed to proceed via multiple equilibrium steps[24] involving species like H_2OI^+ and I_2OH^-, but later it was shown that the role of I_2OH^- can be neglected at a strongly acidic solution;[35] hence, the rate equation of step R2 can be established as

$$r_{R2} = k_{R2}\frac{[I_2]}{[H^+]} - k_{-R2}[HOI][I^-] \tag{6}$$

where $k_{R2} = 1.98 \times 10^{-3}\ M\ s^{-1}$ and $k_{-R2} = 3.67 \times 10^9\ M^{-1}\ s^{-1}$, which give us an equilibrium constant of iodine of $5.4 \times 10^{-13}\ M^2$.[26,35] The acidic dissociation constant of H_2OI^+ was determined to be 2 M under our experimental conditions;[35] therefore, we set $k_{R3} = 2 \times 10^9\ s^{-1}$ and $k_{-R3} = 10^9\ M^{-1}\ s^{-1}$. Because these values appeared to be well-established, consequently the only parameters that remained to be fitted were k_{R4} and/or k_{R5} if both hypoiodous acid and H_2OI^+ are kinetically active species.

The result of the fit was found to be completely unacceptable, having an average deviation of 91%, with values of k_{R4} and k_{R5} being orders of magnitude higher than the diffusion control limit for second-order processes in aqueous solution! From this result, we concluded that indeed the direct reaction between arsenous acid and iodine has to be taken into consideration, which agrees well with the main message of the most recent reports;[17,18] i.e., the kinetically active species is iodine. As a result, steps E1 and R1–R5 were supplemented by two new processes to describe our kinetic data as follows:

$$H_3AsO_3 + I_2 \xrightleftharpoons{k_{R6},\, k_{-R6}} H_2AsO_3I + I^- + H^+ \tag{R6}$$

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$$H_2AsO_3I + H_2O \xrightarrow{k_{R7}} H_3AsO_4 + H^+ + I^- \qquad (R7)$$

We first fixed $k_{R4} = k_{R5} = 10^9\ M^{-1}\ s^{-1}$ to enlarge the role of a hypoiodous acid driven route as much as possible compared to the iodine-driven pathway. Because the rate coefficients k_{R6}, k_{-R6}, and k_{R7} cannot be determined individually because of a strong correlation between the kinetic parameters (this observation will be discussed later in the Validation of the Kinetic Model and Rate Coefficients section), we set $k_{-R6} = 1 \times 10^9\ M^{-2}\ s^{-1}$ and fitted k_{R6} and k_{R7}. It should be emphasized that any value higher than $10^9\ M^{-2}\ s^{-1}$ would lead to the same average deviation; therefore, we chose the lower limit of k_{-R6}. The final result indicated a perfect description of the kinetic data of an average deviation of 0.92% when the values of 9040 ± 100 $M^{-1}\ s^{-1}$ and 8980 ± 80 s^{-1} were obtained for k_{R6} and k_{R7}, respectively. It should, however, be noted that the values of k_{R7} and k_{-R6} were found to be in total correlation with each other, meaning that we could actually determine $k_{R7}/k_{-R6} = 8.98 \times 10^{-6}\ M^2$. In addition to that, a strong (correlation coefficient of 0.96), but not total, correlation was also observed between k_{R6} and k_{R7}, from which we concluded that we actually could determine $k_{R6}k_{R7}/k_{-R6} = 0.081 \pm 0.002\ M\ s^{-1}$ from our measurements, which is consistent with the value determined indirectly from our previous measurements.[9] Furthermore, the final result was completely insensitive for the highest possible values of k_{R4} and k_{R5}, from which we concluded that the role of the hypoiodous acid route is negligible in the case of the Roebuck reaction. As a result, the astonishingly perfect fit illustrated in Figures 3–6 may also be obtained by setting k_{R4} and k_{R5} to be zero, but actually these figures were generated by using $k_{R4} = 0$ and $k_{R5} = 7.4 \times 10^8\ M^{-1}\ s^{-1}$, which was determined with the help of the kinetic curves measured in the iodate–arsenous acid system (see later).

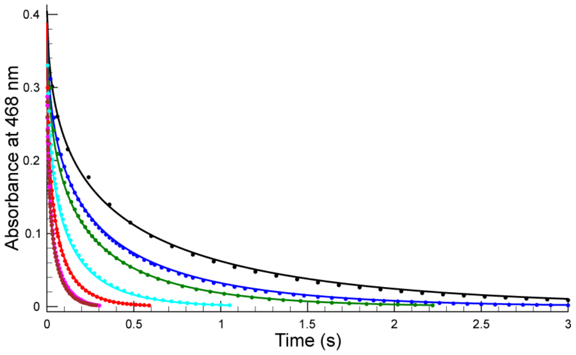

Figure 3. Measured (dots) and calculated (solid lines) absorbance–time curves in the absence of an initially added iodide ion in the case of the iodine–arsenous acid (Roebuck) reaction. The initial conditions are as follows: $T^0_{I_2}$ = 0.5 mM; $T_{SO_4^{2-}}$ = 0.2 M; $[HClO_4]_0$ = 0.4 M; $[H_3AsO_3]_0$/mM = 5.0 (black), 7.5 (blue), 10.0 (green), 20.0 (cyan), 40.0 (red), 60.0 (magenta), and 70.0 (brown).

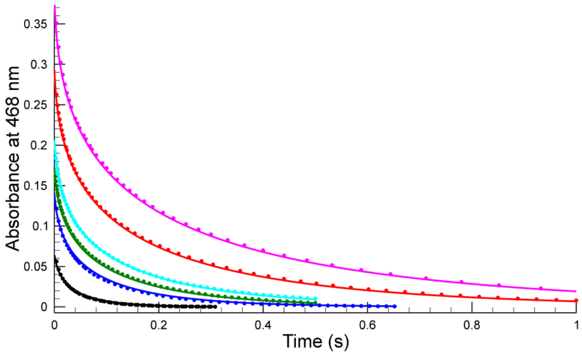

Figure 4. Measured (dots) and calculated (solid lines) absorbance–time curves in the absence of an initially added iodide ion in the case of the iodine–arsenous acid (Roebuck) reaction. The initial conditions are as follows: $[H_3AsO_3]_0$ = 10 mM; $T_{SO_4^{2-}}$ = 0.2 M; $[HClO_4]_0$ = 0.4 M; $T^0_{I_2}$/mM = 0.088 (black), 0.19 (blue), 0.23 (green), 0.28 (cyan), 0.4 (red), and 0.52 (magenta).

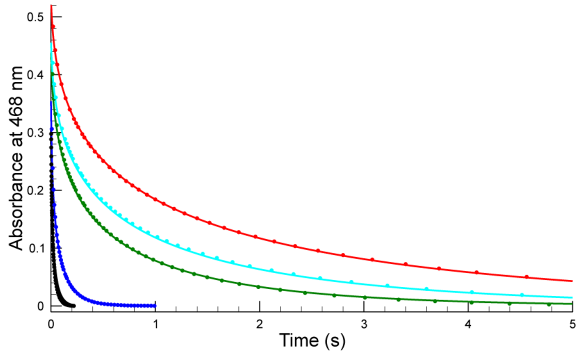

Figure 5. Measured (dots) and calculated (solid lines) absorbance–time curves in the absence of an initially added iodide ion in the case of the iodine–arsenous acid (Roebuck) reaction. $[H_3AsO_3]_0$ = 10 mM and $T_{SO_4^{2-}}$ = 0.2 M for all of the curves. $[HClO_4]_0$ = 0.1 M and $T^0_{I_2}$/mM = 0.41 (black); $[HClO_4]_0$ = 0.2 M and $T^0_{I_2}$/mM = 0.50 (blue); $[HClO_4]_0$ = 0.6 M and $T^0_{I_2}$/mM = 0.62 (green); $[HClO_4]_0$ = 0.8 M and $T^0_{I_2}$/mM = 0.64 (cyan); $[HClO_4]_0$ = 1.0 M and $T^0_{I_2}$/mM = 0.74 (red).

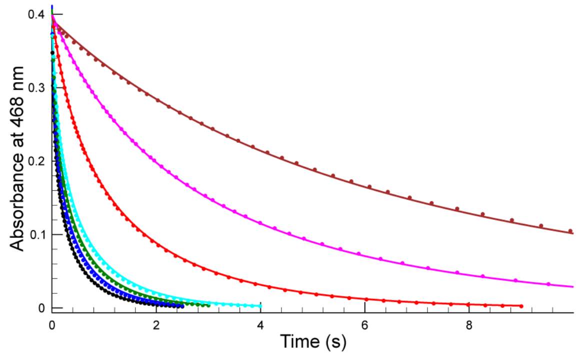

Figure 6. Measured (dots) and calculated (solid lines) absorbance–time curves in the presence of an initially added iodide ion in the case of the iodine–arsenous acid (Roebuck) reaction. The initial conditions are as follows: $T^0_{I_2}$ = 0.54 mM; $T_{SO_4}{}^{2-}$ = 0.2 M; $[HClO_4]_0$ = 0.4 M; $[H_3AsO_3]_0$/mM = 10.0. $[I^-]_0$/mM = 0.05 (black), 0.15 (blue), 0.3 (green), 0.5 (cyan), 1.5 (red), 3.0 (magenta), and 5.0 (brown).

Kinetics of the Dushman Reaction. The kinetics of the Dushman reaction has been well-established since 2000.[36,37] In 1999, Schmitz correctly pointed out that in acidic conditions, pH < 3, one should consider the rapid protonation equilibrium of iodate to form iodic acid by taking the different reactivities of iodate ion and iodic acid into consideration. The acid dissociation constant of iodic acid is accepted as 0.156 ± 0.002 M, determined independently by Ramette and Palmer[38] as well as by Strong and Pethybridge[39] at zero ionic strength. Taking into account that at I = 0.68 M, the activity coefficient $\gamma_\pm \approx 0.7$ K_{R8} was set to 0.32 using sufficiently high values for

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k_{R8} and k_{-R8} to establish this protonation equilibrium instantaneously.

$$HIO_3 \xrightleftharpoons{k_{R8},\, k_{-R8}} IO_3^- + H^+ \tag{R8}$$

It is also well-known that the Dushman reaction starts with the following process to form the reactive intermediate I_2O_2 in an equilibrium:[36,37,40]

$$I^- + HIO_3 + H^+ \xrightleftharpoons{k_{R9},\, k_{-R9}} I_2O_2 + H_2O \tag{R9}$$

This reaction is established rapidly but shifting far to the left to provide a low concentration level of I_2O_2.[41,42] The steady-state intermediate I_2O_2 either then further reacts with an iodide ion or hydrolyzes to give iodous and hypoiodous acid:

$$I^- + I_2O_2 + H^+ \xrightarrow{k_{R10}} I_2 + HIO_2 \tag{R10}$$

$$I_2O_2 + H_2O \xrightarrow{k_{R11}} HIO_2 + HOI \tag{R11}$$

Iodous acid then comproportionates with an iodide ion to give hypoiodous acid in a rapid reaction:[43]

$$HIO_2 + I^- + H^+ \xrightarrow{k_{R12}} 2HOI \tag{R12}$$

Along with steps R1 and R2, this mechanism gives us the overall stoichiometry of the Dushman reaction, as shown in eq 2. It is clear that, although hydrolysis of iodine is not necessary to interpret the kinetics of the Roebuck reaction, its backward reaction of hydrolysis is certainly obligatory to have the correct stoichiometry to produce iodine from HOI and I^- in the case of the Dushman reaction.

Step R9 is a rapidly established equilibrium, and its equilibrium constant was set to 0.1 M^{-2} to provide a sufficiently low concentration level of I_2O_2. What this means is that the overall rate coefficient of the Dushman reaction can be obtained by $K_{R9}k_{R10}$ and $K_{R9}k_{R11}$ (see later). Schmitz[36] also pointed out that the rate coefficients of both steps R10 and R11 depend on the buffer concentrations and on the nature of the medium applied. Evidently, this means that both of the rate coefficients (k_{R10} and k_{R11}) are subject to being fitted during the course of the reaction. One may also realize that in the case of step R11 $[H^+]$ is also involved in the rate equation (see Table 1). To support its role, we carried out an additional fitting procedure with elimination of the pH dependence from the rate law of step R11. This fitting procedure resulted in a 1.8% average deviation, which is almost twice as high as that in the original case. From this indirect support, we decided to keep $[H^+]$ in the rate equation of step R11. Step R12 is, however, a rapid reaction under the condition studied; therefore, its rate coefficient can be fixed to a sufficiently high value.[43] Actually, any value higher than 10^9 M^{-2} s^{-1} would give the same final result; therefore, we set $k_{R12} = 10^9$ M^{-2} s^{-1}. This lower value is in complete agreement with the one proposed by Lengyel et al.,[43] but it should also be mentioned that Furrow used[26] a significantly higher value (5×10^9 M^{-1} s^{-1}) with no $[H^+]$ dependence on the rate equation to explain the most important kinetic feature of the iodate−hydrogen peroxide reaction.

Furthermore, it should also be emphasized that step R10 can be completely substituted with the following reaction, and no unambiguous decision can be made about which pathway is more preferable to explain the second-order iodide dependence of the Dushman reaction:

$$I^- + I_2O_2 + H^+ + H_2O \xrightarrow{k_{R10}'} 3HOI \tag{R10a}$$

Table 1. Fitted and Fixed Rate Coefficients of the Proposed Kinetic Model

step	rate equation	parameter value	refs
R1	$k_{R1}[I_2][I^-]$	5.6×10^9 M^{-1} s^{-1}	28 and 29
−R1	$k_{-R1}[I_3^-]$	8.5×10^6 s^{-1}	28 and 29
R2	$k_{R2}[I_2]/[H^+]$	0.00198 M s^{-1}	39
−R2	$k_{-R2}[HOI][I^-]$	3.67×10^9 M^{-1} s^{-1}	39
R2′	$k_{R2}'[I_2]$	0.0552 s^{-1}	39
−R2′	$k_{-R2}'[HOI][H^+][I^-]$	1.023×10^{11} M^{-2} s^{-1}	39
R3	$k_{R3}[H_2OI^+]$	2×10^9 s^{-1}	31
−R3	$k_{-R3}[HOI][H^+]$	10^9 M^{-1} s^{-1}	31
R4	$k_{R4}[H_3AsO_3][HOI]$		not necessary[a]
R5	$k_{R5}[H_3AsO_3][H_2OI^+]$	$(7.4 \pm 0.3) \times 10^8$ M^{-1} s^{-1}	present work
R6	$k_{R6}[H_3AsO_3][I_2]$	10830 ± 70 M^{-1} s^{-1}	present work
−R6	$k_{-R6}[H_2AsO_3I][I^-][H^+]$	10^9 M^{-2} s^{-1}	fixed[b]
R7	$k_{R7}[H_2AsO_3I]$	7390 ± 50 s^{-1}	present work
R8	$k_{R8}[HIO_3]$	10^8 s^{-1}	34 and 35
−R8	$k_{-R8}[H^+][IO_3^-]$	3.125×10^8 M^{-1} s^{-1}	34 and 35
R9	$k_{R9}[H^+][I^-][HIO_3]$	$\geq 10^5$ M^{-2} s^{-1}	fixed[c]
−R9	$k_{-R9}[I_2O_2]$	$\geq 10^6$ s^{-1}	fixed[c]
R10	$k_{R10}[I^-][I_2O_2]$	$(1.02 \pm 0.01) \times 10^9$ M^{-1} s^{-1}	present work
R11	$k_{R11}[H^+][I_2O_2]$	$(3.2 \pm 0.1) \times 10^4$ M^{-1} s^{-1}	present work
R12	$k_{R12}[I^-][[H^+]HIO_2]$	$\geq 10^9$ M^{-2} s^{-1}	39
R13	$k_{R13}[H_3AsO_3][HIO_3][H^+]^2$	0.33 ± 0.01 M^{-3} s^{-1}	present work
R14	$k_{R14}[H_3AsO_3][HIO_2]$	$\geq 10^6$ M^{-1} s^{-1}	fixed[b]

[a] Either step R4 or R5 is necessary to describe the experiments. The description by step R4 is slightly worse (1.15%) compared to that by step R5. [b] Just a lower limit could be determined. [c] K_{R9} = 0.1 was chosen arbitrarily, and only $K_{R9}k_{R10}$ and $K_{R9}k_{R11}$ can be calculated.

Our choice, however, remains step R10, in agreement with Schmitz[37] and Agreda et al.[40]

Figures 7−9 demonstrate that steps R1−R3 along with steps R8−R12 are working properly to soundly describe the absorbance−time profiles measured in the iodide−iodate reaction.

Kinetics of the Arsenous Acid−Iodate Reaction. So far we considered the mechanism of the subsystems of the arsenous acid−iodate reaction. Certainly, in themselves, they

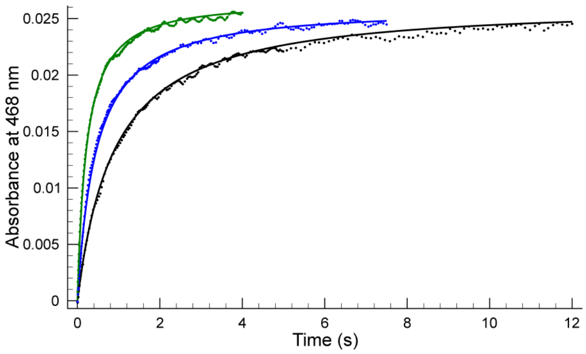

Figure 7. Measured (dots) and calculated (solid lines) absorbance−time curves in the case of the iodide−iodate (Dushman) reaction. The ionic strength is adjusted to 1.0 M by sodium perchlorate. The initial conditions are as follows: $[I^-]_0$ = 57 μM; $[HClO_4]_0$ = 0.2 M. $T_{IO_3^-}$/mM = 0.5 (black), 1.0 (blue), and 2.0 (green).

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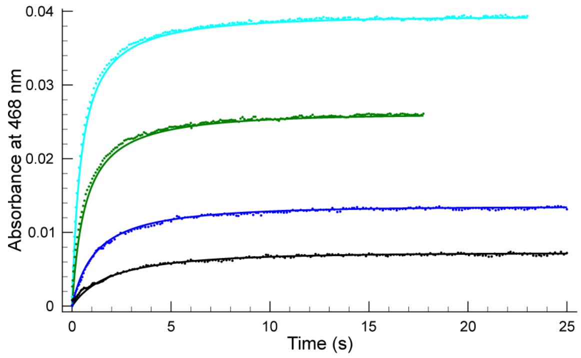

Figure 8. Measured (dots) and calculated (solid lines) absorbance−time curves in the case of the iodide−iodate (Dushman) reaction. The ionic strength is adjusted to 1.0 M by sodium perchlorate. The initial conditions are as follows: $T_{\mathrm{IO}_3^-}$ = 0.66 mM; $[\mathrm{HClO}_4]_0$ = 0.2 M. $[\mathrm{I}^-]_0/\mu\mathrm{M}$ = 16 (black), 30 (blue), 57 (green), and 87.5 (cyan).

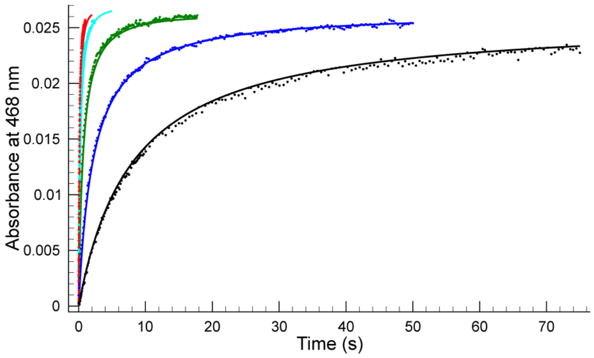

Figure 9. Measured (dots) and calculated (solid lines) absorbance−time curves in the case of the iodide−iodate (Dushman) reaction. The ionic strength is adjusted to 1.0 M by sodium perchlorate. The initial conditions are as follows: $[\mathrm{I}^-]_0$ = 57 μM; $T_{\mathrm{IO}_3^-}$ = 0.66 mM. $[\mathrm{HClO}_4]_0/\mathrm{mM}$ = 0.05 (black), 0.1 (blue), 0.2 (green), 0.35 (cyan), and 0.5 (red).

are able to describe the kinetics of all of the subsystems separately, meaning that they can conveniently be assembled to describe the kinetics of the overall arsenous acid−iodate reaction; meanwhile, the mechanisms of the subsystems preserve their most important original characteristics. In order to complete the mechanism of the title reaction, we have to consider formal oxygen-transfer reactions between iodic acid and arsenous acid as well as between iodous acid and arsenous acid. The necessity of the pH dependence of step R13 was thoroughly discussed recently;[9] therefore, we directly adopted this rate equation (see Table 1).

$$\mathrm{H_3AsO_3} + \mathrm{HIO_3} \xrightarrow{k_{\mathrm{R13}}} \mathrm{H_3AsO_4} + \mathrm{HIO_2} \qquad (\mathrm{R13})$$

$$\mathrm{H_3AsO_3} + \mathrm{HIO_2} \xrightarrow{k_{\mathrm{R14}}} \mathrm{H_3AsO_4} + \mathrm{HOI} \qquad (\mathrm{R14})$$

Therefore, combining these equations with steps R1−R12 should give the overall mechanism of the arsenous acid−iodate reaction. To determine the rate coefficients of the kinetic model mentioned above, we have fitted all of the experimental curves of the arsenous acid−iodine, iodide−iodate, and arsenous acid−iodate reactions simultaneously. With the help of six fitted rate coefficients along with the fixed rate coefficients (among them, eq 10 was directly taken from the literature, and in the case of the remaining fixed parameters, only a lower limit could be determined) indicated in Table 1, all of the measured 117 experimental curves containing 10300 experimental points can be described by 1.0% average deviation by means of the orthogonal fitting method, which indicates a perfect description of the kinetic curves. While k_{R13} and k_{R5} can evidently be determined from the absorbance−time traces of the iodate−arsenous acid reaction, k_{R10} and k_{R11} are sensitive enough to describe the kinetics feature of the Dushman reaction as well as that of the iodate−arsenous acid reaction. Evidently, step R5 is necessary to provide an iodide ion if the iodate−arsenous acid reaction is studied; therefore, this value can be obtained from the absorbance−time series of this system. A similar argument can also be made about the values of k_{R6} and k_{R7}: they are sensitive enough to determine the absorbance−time profiles of both the iodine−arsenous acid and iodate−arsenous acid reactions. The only difference is that if these parameters are determined simply from the Roebuck reaction, then a strong correlation is experienced between them. This correlation, however, decreases when the kinetic curves of both systems are evaluated simultaneously; hence, the individual rate coefficients can be obtained. It is likely to stem from the fact that, at the induction period of the iodate−arsenous acid reaction, the concentration of the iodide ion is so low that inhibition is not effective; hence, k_{R6} may be determined. It follows from the point that the denominator of eq 9 (see later) may be simplified as $r = k_{\mathrm{R6}}[\mathrm{H_3AsO_3}][\mathrm{I_2}]$. If this value is well-determined, then from the later stages of the reaction, $k_{\mathrm{R7}}/k_{-\mathrm{R6}}$ can also be obtained, so fixing $k_{-\mathrm{R6}}$ enables us to calculate k_{R7} as well. In the case of the iodine−arsenous acid reaction, however, hydrolysis of iodine easily produces an iodide ion to such an extent where iodide inhibition appears in the very beginning stage of the reaction; hence, there is no direct information to obtain k_{R6}. Typical measured and calculated curves in the arsenous acid−iodate reactions are indicated in Figures 10−12. At the same time, Figures 3−6 and 7−9 indicate the capability of the kinetic model in describing the kinetic curves in the case of the iodine−arsenous acid and iodide−iodate reactions, respectively.

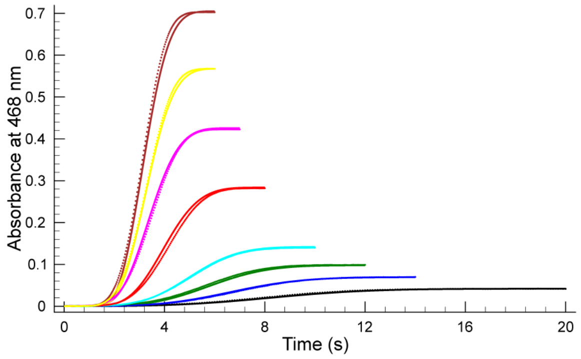

Figure 10. Measured (dots) and calculated (solid lines) absorbance−time curves in the case of the arsenous acid−iodate reaction. The initial conditions are as follows: $T^0_{\mathrm{IO}_3^-}$ = 10.0 mM; $[\mathrm{HClO}_4]_0$ = 0.4 M; $[\mathrm{H_3AsO_3}]_0/\mathrm{mM}$ = 0.29 (black), 0.48 (blue), 0.67 (green), 0.95 (cyan), 1.9 (red), 2.9 (magenta), 3.8 (yellow), and 4.7 (brown).

Validation of the Kinetic Model and Rate Coefficients.

Arsenous Acid−Iodine (Roebuck) Reaction. Steps R6 and R7 constitute the mechanism of the arsenous acid−iodine (Roebuck) reaction. At this point, reactions R1−R3 were not considered to obtain eq 9. A steady-state approximation may be applied for the short-lived $\mathrm{H_2AsO_3I}$ intermediate, from which one can easily obtain the following expression:

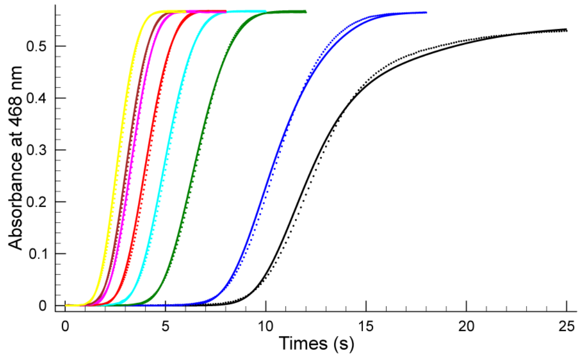

Figure 11. Measured (dots) and calculated (solid lines) absorbance−time curves in the case of the arsenous acid−iodate reaction. The initial conditions are as follows: $[H_3AsO_3]_0$ = 3.8 mM; $[HClO_4]_0$ = 0.4 M; $T^0_{IO_3^-}$/mM = 1.65 (black), 2.1 (blue), 3.5 (green), 5.0 (cyan), 7.0 (red), 9.0 (magenta), 10.0 (brown), and 13.0 (yellow).

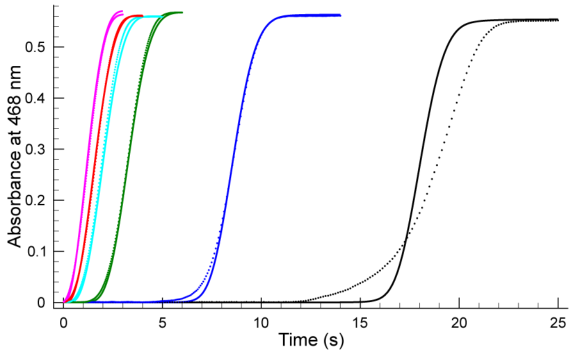

Figure 12. Measured (dots) and calculated (solid lines) absorbance−time curves in the case of the arsenous acid−iodate reaction. The initial conditions are as follows: $[H_3AsO_3]_0$ = 3.8 mM; $T^0_{IO_3^-}$ = 10.0 mM; $[HClO_4]_0$/M = 0.14 (black), 0.2 (blue), 0.4 (green), 0.6 (cyan), 0.8 (red), and 1.0 (magenta).

$$[H_2AsO_3I] = \frac{k_{R6}[H_3AsO_3][I_2]}{k_{-R6}[I^-][H^+] + k_{R7}} \tag{7}$$

Because consumption of arsenous acid (as well as that of the total amount of iodine according to eq 3) can be described by

$$-\frac{d[H_3AsO_3]}{dt} = -\frac{dT_{I_2}}{dt} = k_{R7}[H_2AsO_3I] \tag{8}$$

Substitution of eq 7 into eq 8 gives the following equation:

$$\begin{aligned} -\frac{d[H_3AsO_3]}{dt} &= -\frac{dT_{I_2}}{dt} \\ &= \frac{K_{R6}k_{R7}[H_3AsO_3][I_2]}{[H^+]\left([I^-] + \frac{k_{R7}}{k_{-R6}[H^+]}\right)} \\ &= k_{obs}\frac{[H_3AsO_3][I_2]}{[H^+]([I^-] + u)} \end{aligned} \tag{9}$$

Substituting the rate coefficients indicated in Table 1, one can easily obtain $K_{R6}k_{R7}$ = 0.083 M s^{-1}, which is in a good agreement with 0.094 M s^{-1} determined in our previous work.[9] It straightforwardly means that parameter u introduced in the rate equation of the Roebuck reaction is equal to $\frac{k_{R7}}{k_{-R6}[H^+]}$, meaning that there is no direct connection between parameter u and the iodide impurity.

It is also worth mentioning why the hypoiodous acid (or H_2OI^+) route of the Roebuck reaction is negligible compared to the pathway driven through iodine. Applying a steady-state approximation for species HOI, one can obtain

$$[HOI] = \frac{\left(\frac{k_{R2}}{[H^+]} + k_{R2}'\right)[I_2]}{(k_{-R2} + k_{-R2}'[H^+])[I^-] + k_{R4}[H_3AsO_3]} \tag{10}$$

In this case, consumption of arsenous acid can be written as follows:

$$-\frac{d[H_3AsO_3]}{dt} = -\frac{dT_{I_2}}{dt} = k_{R4}[H_3AsO_3][HOI] \tag{11}$$

Substituting eq 10 into eq 11 followed by some algebraic manipulation, we arrive at

$$\begin{aligned} -\frac{d[H_3AsO_3]}{dt} &= -\frac{dT_{I_2}}{dt} \\ &= \frac{\frac{k_{R2} + k_{R2}'[H^+]}{k_{-R2} + k_{-R2}'[H^+]}k_{R4}[H_3AsO_3][I_2]}{[H^+]\left([I^-] + \frac{k_{R4}[H_3AsO_3]}{k_{-R2} + k_{-R2}'[H^+]}\right)} \\ &= k_{obs}\frac{[H_3AsO][I_2]}{[H^+]([I^-] + u)} \end{aligned} \tag{12}$$

A comparison of eq 12 by eq 9 reveals a similar expression for the disappearance of iodine. However, substituting the well-known rate coefficients of iodine hydrolysis and the upper limit of k_{R4} (or k_{R5} in the case of H_2OI^+), we shall obtain $k_{obs} = 4 \times 10^{-4}$ M s^{-1}. This value is at least 200 times lower than the one determined directly from the measured absorbance−time series. Therefore, this route has no effective contribution to the overall kinetics of the Roebuck reaction as long as the well-known rate coefficients of iodine hydrolysis (see Table 1) are held to provide the hydrolysis constant of iodine to be about (2−6) × 10^{-13} M^2 at room temperature.[19,23,24] To clarify the role of these pathways, however, reinvestigation of the kinetics of iodine hydrolysis seems to be unavoidable because surprisingly values of approximately 2 orders of magnitude higher (around 10^{-11} M^2) have also been reported by independent research groups.[28,29] This means that the otherwise well-known iodine hydrolysis still leaves some unresolved problems for future studies.

Dushman Reaction. It is easily seen that the rate of the Dushman reaction is determined by steps R8−R12 along with steps R1−R3. Applying a steady-state approximation for species I_2O_2 and after some algebraic manipulation along with some simplifications ($k_{-R9} \gg k_{R10}[I^-]$ and $k_{-R9} \gg k_{R11}[H^+]$), one can arrive at the following equation:

$$\begin{aligned} r_d &= \left(\frac{k_{R9}k_{R10}[I^-]}{k_{-R9}} + \frac{k_{R9}k_{R11}[H^+]}{k_{-R9}}\right)[H^+][I^-][HIO_3] \\ &= \left(\frac{K_{R9}k_{R10}}{K_{R8} + [H^+]}[I^-] + \frac{K_{R9}k_{R11}[H^+]}{K_{R8} + [H^+]}\right)[H^+]^2[I^-]T_{IO_3^-} \end{aligned} \tag{13}$$

Substitution of the corresponding rate coefficients and pH range used during the experiments leads to the overall rate coefficients of (0.77−2.18) × 10^8 M^{-4} s^{-1} and 2230−2420 M^{-3} s^{-1} for the second-order and first-order pathways of the

Dushman reaction with respect to the iodide ion, respectively. These values are quite consistent with the ones reported by Schmitz,[36] giving therefore further support of the presented mechanism.

Direct Iodate–Arsenous Acid Reaction. Our present study provides here further support that the direct iodate–arsenous acid reaction exists and starts the overall process. Again considering no direct reaction at all between the reactants, the iodide impurity of the stock iodate solution is insufficient to describe simultaneously the measured absorbance–time series. This is consistent with our very recent result.[9] The obtained rate coefficients for k_{R5}, k_{R13}, and k_{R14} are also in sound agreement with the fact that the reactivity of oxoacids of iodine increases with the decreasing number of O atoms involved. This result also means that the direct reaction (along with steps R14 and R5) plays a significant role only during the induction phase of the arsenous acid–iodate reaction, and the decisive role is gradually shifted to the overall combined effect of the Roebuck and Dushman reactions.

A word is also in order here to mention that even a better description of the kinetic curves of the arsenous acid–iodate and arsenous acid–iodine reactions is possible if the rate coefficient of the forward reaction of iodine is also fitted. This fit (having an average deviation of 0.9%!) resulted a rate coefficient for k_{R2} of 1.54 ± 0.08 s^{-1}; meanwhile, k_{R6} decreased by approximately 15% to 8730 ± 90 M^{-1} s^{-1} and k_{R7} increased to 9100 ± 90 s^{-1}. The rest of the parameters did not change significantly. This means that arsenous acid is capable of being oxidized by both iodine and hypoiodous acid. This would, however, lead to the equilibrium constant of iodine K_{R2} being 1.51×10^{-11} M^2, which is almost 2 orders of magnitude higher than the most widely accepted 5×10^{-13} M^2. Although there are two relatively old but relevant literatures challenging this value,[28,29] at this moment we are inclined to use the generally accepted value for K_{R2}. At the same time, it provides a subsequent task to reinvestigate the kinetics of iodine hydrolysis to decide unambiguously whether the hypoiodous acid driven pathway plays a notable role in determining the kinetics of the Roebuck as well as the iodate–arsenous reaction.

■ CONCLUSION

In this work, we presented a 13-step kinetic model for a simultaneous description of the iodate–arsenous acid, Roebuck, and Dushman reactions. This model was gradually built up by subsequent extension of the kinetic models obtained from the subsystems of the iodate–arsenous reaction. Although the agreement between the experimental and calculated kinetic curves seems to be close to perfection, it does not necessarily mean that an unambiguous decision can be made with regard to even the kinetically important steps of the proposed kinetic model. Furthermore, the mathematically best average deviation achieved does not necessarily mean that the model is consistent chemically. In other words, in the present case, it is clear that a mathematically better description of the kinetic data exists if the equilibrium constant of iodine is considered to be more than 1 order of magnitude higher than generally accepted. This would, however, straightforwardly mean that kinetically both pathways of the Roebuck reaction (the iodine-driven and hypoiodous acid driven routes) have significant contributions to the overall kinetics. Although two independent but old reports[28,29] exist to support this value as well at this moment, it is impossible to decide unambiguously whether the equilibrium constant of iodine hydrolysis needs to be revised without a thorough reinvestigation.

Although the story of the iodate–arsenous acid reaction started more than a century ago by Roebuck's and Bray's pioneering kinetic studies, it certainly does not end up here. This work provides additional insight into how the application of simultaneous evaluation in chemical kinetics is used to obtain reliable models and mechanisms of an unknown or a well-studied reaction. At the same time, it appears to establish a strong warning flag that even a wide range of well-designed kinetic experiments along with the recently available computational techniques may not be sufficient to establish unambiguously the kinetically active species of a kinetic model.

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Notes

The authors declare no competing financial interest.

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