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Revised Explanation of the pH Oscillations in the Iodate−Thiosulfate−Sulfite System

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A revised four-step model based on the reinvestigation of the kinetics of the subsystems is suggested for the description of the dynamics of the iodate−sulfite−thiosulfate reaction. It is shown that the rate equation of the iodate−sulfite reaction contains an undiscovered term that depends on the square of the concentration of the hydrogen ion as an autocatalyst making the reaction "supercatalytic". In contrast to earlier studies but already supposed by a more recent one, the parallel oxidation of thiosulfate by iodate into tetrathionate and sulfite has also been established experimentally as well as the rate coefficients of the parallel pathways. Combining these kinetic studies yields a new model that does not include the cross-catalytic effect of thiosulfate and the inhibitory effect of sulfite supposed hypothetically by Rábai and Beck to describe the dynamics of the combined system. In fact, the supercatalytic effect of the hydrogen ion on the sulfite−iodate reaction and the H^+ dependence of the thiosulfate−iodate reaction along with the parallel formation of sulfite and tetrathionate are sufficient for perfect reflection of all the most important characteristics of the pH−time curves of the composite system. Nevertheless, the revised model significantly decreases the number of the kinetic parameters necessary to simulate the experimental results.

Introduction

Batch chemical oscillations can rarely be found in the literature, and the number of different chemical systems exhibiting this characteristics can easily be counted on the fingers of our hands. The first clear demonstration of the existence of this phenomenon has been published by Bray in the early 1920s after recognizing the periodic appearance and disappearance of iodine in the reacting solution of the iodate−hydrogen peroxide system.[1] Later this reaction was reinvestigated by Liebhafsky,[2] and since then, this system has usually been referred to as the Bray−Liebhafsky reaction. In the early 1950s Belousov also found periodic color change in the cerium−bromate−citric acid reaction,[3] but oscillations in closed systems were then falsely believed to contradict the second law of thermodynamics; therefore, his discovery has fallen into oblivion. A decade later Zhabotinsky reinvestigated this reaction[4] and pointed out that the phenomena found by Belousov was not an artifact but the inherent feature of the system. Soon after Belousov's discovery had been reinforced, Field et al.[5] suggested the general core of the kinetic model that is capable of explaining the oscillating behavior of the system. Today, the BZ reaction is the most common example of the oscillating reactions mentioned in any physical chemistry textbooks. Though several variants of the original BZ reaction were also found to exhibit oscillations,[6] they cannot be treated as completely different chemical systems. In the early 90s the chlorite−iodide−malonic acid reaction was also shown to oscillate[7] in batch and soon it was clearly demonstrated that the chlorine dioxide−iodine−malonic acid reaction is responsible[8,9] for the origin of the oscillatory behavior. Recently, oscillatory decomposition of tetrationate has been observed in thermodynamically closed system driven by the light-beam of a diode-array spectrophotometer.[10]

The last two decades have witnessed considerable efforts to search real chemical systems that exhibit pH oscillation in closed system and by that time there had been only three reported cases.[11−13] In each case, however, the pH changes hardly exceeded the experimental error. The first system that is capable of large amplitude pH oscillation in closed conditions was discovered by Rábai and Beck in the iodate−thiosulfate−sulfite reaction.[14] This phenomenon was explained by the following simple three-step model (RB) having rather complicated rate equations:

$$IO_3^- + 3HSO_3^- \rightarrow I^- + 3SO_4^{2-} + 3H^+ \qquad (1)$$

$$v_1 = [IO_3^-][HSO_3^-](k_1[H^+] + k_1'[HSO_3^-] + k_c[S_2O_3^{2-}][H^+]^2 + k_c'[S_2O_3^{2-}][H^+]^3)$$

$$IO_3^- + 6S_2O_3^{2-} + 6H^+ \rightarrow I^- + 3S_4O_6^{2-} + 3H_2O \qquad (2)$$

$$v_2 = \frac{k_2[IO_3^-][S_2O_3^{2-}]^2[H^+]^2}{1 + k_i[HSO_3^-]}$$

$$2IO_3^- + 3S_2O_3^{2-} + 3H_2O \rightarrow 2I^- + 6HSO_3^- \qquad (3)$$

$$v_3 = \frac{k_3[IO_3^-][S_2O_3^{2-}][H^+]}{1 + k_i[HSO_3^-] + k_i'[S_2O_3^{2-}][H^+]}$$

For the interpretation of the pH-oscillation and the extraordinary drop of pH in a closed system, they assumed the catalytic effect of thiosulfate in eq 1 and the inhibitory effect of HSO_3^- in eqs 2 and 3. Shortly after that paper, Luo and Epstein published an article about a general model for pH oscillators,[15] in which they do not question the plausibility of eq 3 along with its rate equation but strongly suggest that an appropriate choice of k_3

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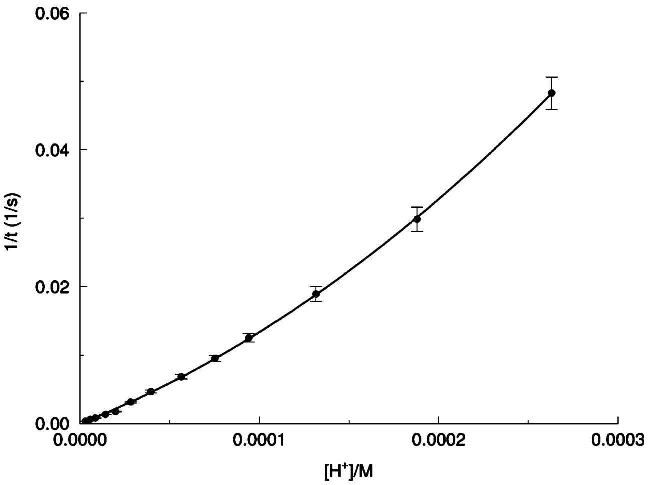

Figure 1. Measured (dots) reciprocal induction time of the appearance of triiodide as a function of hydrogen ion concentration. The solid line shows the second-order polynomial best fit having zero intercept ($y = ax^2 + bx$). Conditions: $[\mathrm{IO_3^-}]_0 = 0.01$ M; $[\mathrm{SO_3^{2-}}]_0 + [\mathrm{HSO_3^-}]_0 = 0.006$ M; $T = 25.0 \pm 0.3$ °C. a and b were found to be $(7.28 \pm 0.07) \times 10^5$ and 37 ± 3, respectively. Error bars indicate the standard deviation of the reciprocal of the Landolt time determined from parallel experiments.

without the inhibitory effect of hydrogen sulfite might explain the nonmonotonic batch behavior.

The aim of this paper is to explain at least semiquantitatively the oscillatory behavior observed by Rábai and Beck[14] by a chemical model obtained from independent kinetic studies of the composite systems.

Experimental Section

Reagents and Apparatus. Reagent grade chemicals were used without further purification. Stock solutions of $\mathrm{KIO_3}$, $\mathrm{Na_2S_2O_3}$, $\mathrm{Na_2SO_3}$, and the buffer solutions were prepared with deoxygenated four times distilled water. The concentrations of thiosulfate and sulfite were checked by standard iodometric titration. The kinetic runs of the thiosulfate−iodate and the sulfite−iodate reactions were conducted in acetic acid−acetate buffer ($\mathrm{p}K_\mathrm{a} = 4.55$). The sodium-acetate concentration was held constant 0.1 M in each kinetic run. The necessary amount of acetic acid was then added to reach the desired pH of the reacting solution. In the case of the thiosulfate−iodate reaction the ionic strength was adjusted to 0.5 M by adding the necessary amount of sodium perchlorate. The temperature was kept at 25.0 ± 0.1 °C in both cases. The composition of the kinetic runs of both systems can be seen in Table 1.

Methods and Instrumentation. Both reactions were followed by a Zeiss S10 diode-array spectrophotometer within the 260−450 nm wavelength range. Thiosulfate, iodate, and especially the product tetrathionate absorb the light intensively in the UV region; therefore, the thiosulfate−iodate reaction can easily be followed in this region. Although the spectra of these species are highly overlapping, we have clearly demonstrated in a number of other cases that meaningful results can be obtained by simultaneous curve fitting method of the kinetic curves using the absorbance−time traces at several wavelengths.[16−19] Thus the final fitting procedure has been executed at five different wavelengths such as, 260, 265, 270, 275, and 280 nm.

TABLE 1: Initial Composition of the Kinetic Runs

no.	$[\mathrm{S_2O_3^{2-}}]_0$ (mM)	$[\mathrm{IO_3^-}]_0$ (mM)	pH
1−5	1.2	0.2, 0.4, 0.6, 0.8, 1.2	4.75
6−9	1.2	1.4, 1.6, 2.0, 2.4	4.75
10−13	0.8	0.6	4.75, 4.57, 4.27, 4.05

no.	$[\mathrm{SO_3^{2-}}]_0$ (mM)	$[\mathrm{IO_3^-}]_0$ (mM)	pH
1−5	6	10	5.55, 5.27, 5.05, 4.85, 4.71
6−9	6	10	4.55, 4.40, 4.25, 4.12,
11−13	6	10	4.03, 3.83, 3.73, 3.58

Because sulfite hardly absorbs the light within the range studied, we have followed the sulfite−iodate reaction by measuring the Landolt[20] induction period by the appearance of the strong absorption band of triiodide at 350 nm. The rate coefficient of the supercatalytic pathway was determined in the following way. Assuming that the term containing k_1' in eq 6 (see later) is negligible compared to the other ones, straightforward derivation leads to the following integrated rate expression

$$\frac{1}{t} = k_1 G[\mathrm{H^+}] + k_1'' G[\mathrm{H^+}]^2 \tag{4}$$

where t is the Landolt induction time, G is defined as

$$G = \frac{T_0 - 3[\mathrm{IO_3^-}]_0}{\ln\left(\dfrac{3T}{3[\mathrm{IO_3^-}]_0 - T_0^2/[\mathrm{IO_3^-}]_0 + TT_0/[\mathrm{IO_3^-}]_0}\right)}$$

and T corresponds to the total sulfite concentration (sum of the concentration sulfite and hydrogen sulfite) at t time.

The kinetic traces were evaluated by ZiTa,[21] a comprehensive program package for simultaneous evaluation of kinetic data in the case of the thiosulfate−iodate reaction.

Results and Discussion

Kinetics of the Iodate−Sulfite Reaction. Landolt's discovery,[20] the sudden appearance of iodine in a well-defined time lag, is a popular lecture demonstration of clock reactions. The autocatalytic feature of the reaction was already characterized by Eggert and Scharnow,[22] and the most comprehensive kinetic study of the system was accomplished by Skrabal and Zahorka.[23] They have found that kinetics of the iodate−sulfite reaction (eq 1) can be best described by the following rate equation:

$$-\frac{\mathrm{d}[\mathrm{IO_3^-}]}{\mathrm{d}t} = k_1[\mathrm{IO_3^-}][\mathrm{HSO_3^-}][\mathrm{H^+}] + k_1'[\mathrm{IO_3^-}][\mathrm{HSO_3^-}]^2 \tag{5}$$

with $k_1 = 8800$ $\mathrm{M^{-2}\,s^{-1}}$ and $k_1' = 11$ $\mathrm{M^{-2}\,s^{-1}}$. Later Rábai and Beck have shown that this rate equation is not sufficient to take the experimental fact, the extremely sharp pH drop in the iodate−sulfite−thiosulfate system, qualitatively into consideration.[24] Therefore, a third term of the rate equation was suggested in which the catalytic effect of thiosulfate was considered. This feature, however, has never been supported by any direct experiments. Figure 1 shows the reciprocal of the induction time of the appearance of triiodide as a function of the hydrogen concentration kept constant by acetic acid−acetate buffer. On the basis of Figure 1 it is clear that the rate equation must contain a term that depends on the square of $[\mathrm{H^+}]$. Therefore, we suggest that the rate equation of eq 1 (oxidation of sulfite by iodate) is best described as

$$v_1 = k_1[\mathrm{HSO_3^-}][\mathrm{IO_3^-}][\mathrm{H^+}] + k_1'[\mathrm{HSO_3^-}]^2[\mathrm{IO_3^-}] + k_1''[\mathrm{HSO_3^-}][\mathrm{IO_3^-}][\mathrm{H^+}]^2 \tag{6}$$

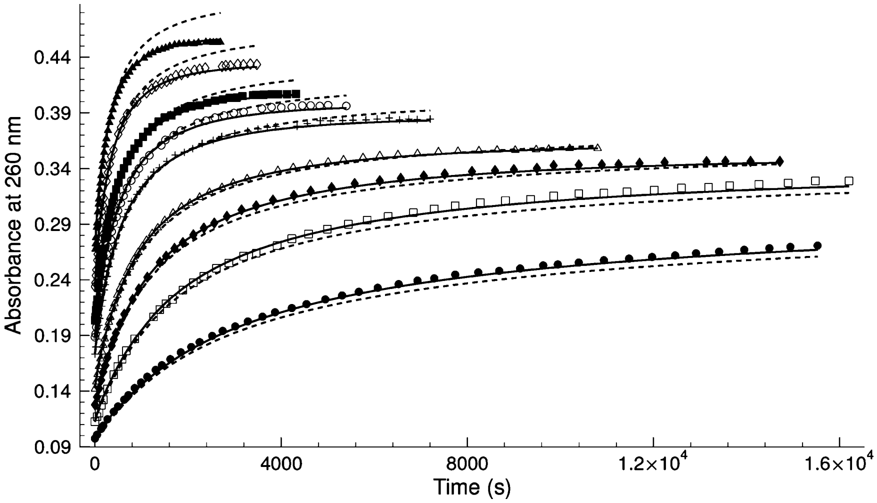

Figure 2. Measured (symbols) and calculated absorbance at 260 nm with (solid line) and without (dashed line) supposing eq 8. Conditions: $[S_2O_3^{2-}]_0 = 1.2$ mM; pH = 4.75; $[IO_3^-]_0$/mM = 0.2 (●), 0.4 (□), 0.6 (♦), 0.8 (△), 1.2 (+), 1.4 (○), 1.6 (■), 2.0 (◇), 2.4 (▲). Molar absorbances (M^{-1} cm^{-1}) at 260 nm used for thiosulfate, iodate, and tetrathionate are 68.56, 75.83, and 541.79, respectively.

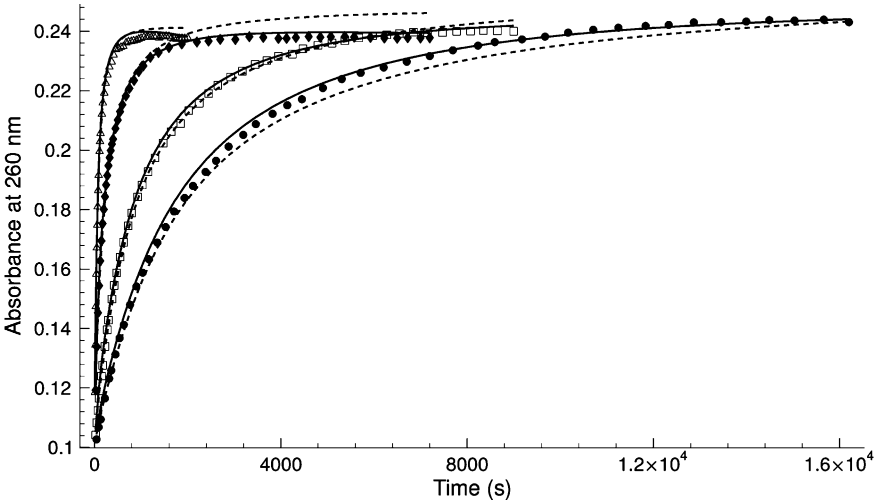

Figure 3. Measured (symbols) and calculated absorbance at 260 nm with (solid line) and without (dashed line) supposing eq 8. Molar absorbances (M^{-1} cm^{-1}) at 260 nm used for thiosulfate, iodate, and tetrathionate are 68.56, 75.83, and 541.79, respectively. Conditions: $[S_2O_3^{2-}]_0 = 0.8$ mM; $[IO_3^-]_0 = 0.6$ mM; pH = 4.75 (●), 4.57 (□), 4.27 (♦), 4.05 (△).

The second-order polynomial fit (see Figure 1) gives the value of the parameters as $a = (7.28 \pm 0.07) \times 10^5$ and $b = 37 \pm 3$, where a and b correspond to the transformed kinetic parameters of k_1'' and k_1, respectively, according to eq 4. Having known $k_1 = 8800$ M^{-2} s^{-1}, one can easily derive the value for k_1'' as $k_1'' = a\,k_1/b = (1.7 \pm 0.2) \times 10^8$ M^{-3} s^{-1}.

Kinetics of the Iodate−Thiosulfate Reaction. The kinetics of the iodate−thiosulfate reaction was first studied by Rieder.[25] The only sulfur-containing compound among the products was believed to be tetrathionate; therefore, the experiments were evaluated by the assumption of the stoichiometry represented by eq 2. The rate equation was determined to be second order with respect to both the thiosulfate and the hydrogen ion concentrations and first order with that of the iodate. For the sake of completeness it should be mentioned that the rate coefficient was falsely given as 5×10^8 M^{-4} s^{-1} in the original paper. As it was already pointed out by Rábai and Beck,[24] the correct evaluation would have yielded 2.7×10^{12} M^{-1} s^{-1}, which is in good agreement with the one determined later by Indelli.[26] Rábai and Beck have, however, found[14] large amplitude strongly damped pH oscillation in the mixed sulfite−thiosulfite−iodate system, the phenomenon that can only be explained by invoking partial oxidation of thiosulfate into sulfite. Therefore, we have tried to seek experimental evidence, in contrast to earlier studies,[25,26] for the parallel formation of tetrathionate and sulfite. Figures 2 and 3 show the final results of the simultaneous curve fitting procedure to the preliminary experiments of the system. The difference between the models can easily be seen: one of them that contains the parallel oxidation fits perfectly the experiments (see solid line of Figures 2 and 3), and the other, which misses that pathway, contains unacceptable systematic errors (see dashed lines of Figures 2 and 3). Therefore, we concluded that Rábai and Beck's assumption about the parallel oxidation of thiosulfate into tetrathionate and sulfite by iodate is correct and can clearly be supported by experiments. Moreover, our fitting procedure has indicated that the rate equations of eqs 2 and 3 are

$$v_2' = k_2'[S_2O_3^{2-}]^2[IO_3^-][H^+]^2 \tag{7}$$

and

$$v_3' = k_3'[S_2O_3^{2-}][IO_3^-]^2[H^+] \tag{8}$$

where $k_2' = (1.3 \pm 0.2) \times 10^{12}$ M^{-4} s^{-1} and $k_3' = (4.6 \pm 0.8) \times 10^6$ M^{-3} s^{-1}.

Overall Kinetic Model. As a result of the kinetic studies of the independent subsystems of the iodate−sulfite−thiosulfate reaction, the following kinetic model is suggested:

$$\mathrm{H} + \mathrm{A} \rightleftharpoons \mathrm{HA} \tag{M1}$$

$$3\mathrm{HA} + \mathrm{B} \rightarrow 3\mathrm{H} + \mathrm{P}_1 \tag{M2}$$

$$6\mathrm{C} + \mathrm{B} + 6\mathrm{H} \rightarrow \mathrm{P}_2 \tag{M3}$$

$$3\mathrm{C} + 2\mathrm{B} \rightarrow 6\mathrm{HA} \tag{M4}$$

where A, B, C, and H stand for sulfite, iodate, thiosulfate and hydrogen ions and P_1 and P_2 correspond to sulfate and tetrathionate, respectively. As a starting point of modeling the behavior of the composite iodate−sulfite−thiosulfate system, the following rate equations were considered on the basis of the independent kinetic studies of the subsystems:

$$v_{\mathrm{M1}} = k_{\mathrm{M1}}[\mathrm{H}][\mathrm{A}] \qquad v_{-\mathrm{M1}} = k_{-\mathrm{M1}}[\mathrm{HA}] \tag{9}$$

$$v_{\mathrm{M2}} = k_{\mathrm{M2}}[\mathrm{HA}]^2[\mathrm{B}] + k'_{\mathrm{M2}}[\mathrm{HA}][\mathrm{B}][\mathrm{H}]^2 + k''_{\mathrm{M2}}[\mathrm{HA}][\mathrm{B}][\mathrm{H}] \tag{10}$$

$$v_{\mathrm{M3}} = k_{\mathrm{M3}}[\mathrm{C}]^2[\mathrm{B}][\mathrm{H}]^2 \tag{11}$$

$$v_{\mathrm{M4}} = k_{\mathrm{M4}}[\mathrm{C}][\mathrm{B}]^2[\mathrm{H}] \tag{12}$$

It should be emphasized that all the steps of the model along with their rate equations are either well-documented in the literature or determined by the present work. As one may also notice, the cross-catalytic effect of thiosulfate and hydrogen sulfite is completely missing from the model, instead of the supercatalytic effect of H^+ being inserted. Later we shall see that the cross-catalytic and inhibitory effect is not a necessary condition of the kinetic model to explain all the important experimental observations, such as the batch oscillations and the extraordinarily sharp drop of pH.

Choice of the Rate Coefficients. Both the forward ($k_{\mathrm{M1}} = 10^{11}$ M^{-1} s^{-1}) and the reverse ($k_{-\mathrm{M1}} = 10^4$ s^{-1}) processes of M1 are considered to be rapid reactions and $K_{\mathrm{M1}} = k_{\mathrm{M1}}/k_{-\mathrm{M1}} = 10^7$ M^{-1} is the protonation constant of SO_3^{2-}. The value of k_{M2} has slightly been modified if we compare it to the one determined by Skrabal and Zahorka.[23] We used $k_{\mathrm{M2}} = 20$ M^{-2} s^{-1} in the final simulation, the value that resulted in the best quantitative agreement of the simulated kinetic curves compared to the measured ones reported by Rábai and Beck.[14,24] We believe that the less than 2-fold difference may easily be interpreted by the different experimental conditions used in the early work of Skrabal[23] compared to that of Rábai's paper.[14,24] The value of $k''_{\mathrm{M2}} = 8800$ M^{-2} s^{-1} was directly adopted,[23] but the simulation has revealed that $k'_{\mathrm{M2}} = 1.7 \times 10^8$ M^{-3} s^{-1} determined from the Landolt induction time is significantly lower than 4.7×10^{10} M^{-3} s^{-1}, the value above which the extraordinarily sharp drop of pH is manifested in the simulated curves. Because the value of k'_{M2} was derived from that of k''_{M2}, part of the 2 orders of magnitude difference might be explained by the different experimental circumstances, but it seems more likely that the Landolt reaction is a bit more complicated than one would assume. An easily conceivable explanation of this difference might be the rate equation contains another term that depends on the cube of the hydrogen concentration. But because no direct experimental evidence has been obtained so far that proves such a high-order autocatalysis with respect to H^+ in the Landolt reaction—although a faint allusion might already be found in the literature[14]—we did not consider it in the revised model. It should also be mentioned that eq 4 is only an approximation to determine the value of k'_{M2} that might explain part of the difference between the value of k'_{M2} determined experimentally and that of used in the simulation. As a result we used $k'_{\mathrm{M2}} = 4.7 \times 10^{10}$ M^{-3} s^{-1} in the final calculations to simulate Rábai's experiments, but certainly more research is required to explore fully the kinetics of the pH dependence of the Landolt reaction. The values of k_{M3} and k_{M4} were 1.3×10^{12} and 4.6×10^6 M^{-3} s^{-1}, respectively, as determined in this work.

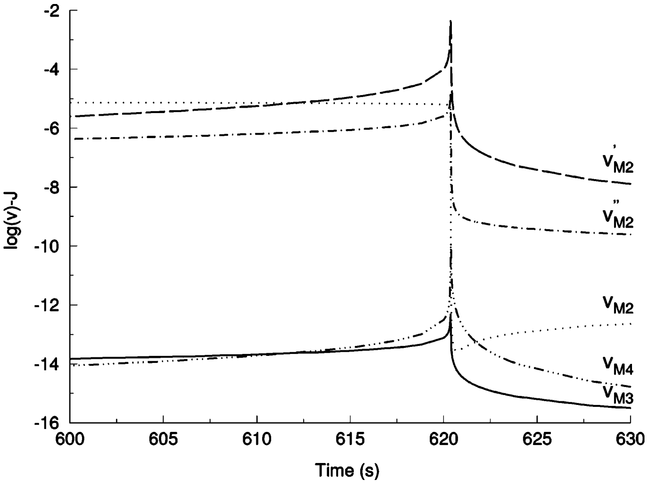

Figure 4. Logarithm of the calculated rates of the component reactions M2−M4. Conditions: $[S_2O_3^{2-}]_0 = 0.011$ M; $[IO_3^-]_0 = 0.0115$ M; $[HSO_3^-]_0 + [SO_3^{2-}]_0 = 0.0245$ M; $[H^+]_0 = 0.007$ M. Key: v_{M2} (dotted line); v'_{M2} (long dashed line); v''_{M2} (dot-dashed line); v_{M3} (solid line); v_{M4} (dot−dot dashed line). Note that $J = 0$ except for $\log(v_{\mathrm{M3}})$ and $\log(v_{\mathrm{M4}})$ values where $J = 8$ to see the trends better.

Figure 4 shows the logarithm of the calculated rates of the component reactions at a usual composition of the system. It clearly indicates that though k''_{M2} is well-supported by the individual experiments,[23] it plays only a very minor role among the parallel steps of M2 in determining the nonmonotonic behavior of the system. As a result, k''_{M2} is considered to be zero in further calculations.

Characteristics of the Batch System. ***Sharp pH Minimum.*** Rábai and Beck have discovered[24] an extraordinarily sharp drop of pH at given compositions of the iodate−sulfite−thiosulfate mixed system. The pH change was so rapid and the amplitude of pH was so high that the potential of the glass electrode could not follow it. This phenomenon can be visualized if a drop of a methyl-orange indicator is added to the reacting solution. The color of the solution turns completely red just for a moment, indicating that the pH clearly falls below 3. This characteristics was explained by the cross-catalytic and inhibitory effect of the substrates thiosulfate and sulfite. In fact, they considered that thiosulfate catalyzes the iodate−sulfite reaction and sulfite inhibits the thiosulfate−iodate system, as seen in eqs 1−3.[24] Figure 5, however, clearly shows that our model is also capable of providing a good description of this well-reproducible phenomenon without including the cross-catalytic and inhibitory effect of the substrates. The reason for the sharp drop of pH can easily be understood on the basis of Figure 5. At the beginning of the reaction, the pH is around 7 because of the strong buffering effect of hydrogen sulfite/sulfite system. As M2 proceeds, the pH is continuously shifted to lower values and the buffer simultaneously loses its capacity. The first relatively long stage lasts until the buffer capacity is exhausted. During this period as the pH falls, k'_{M2} gradually overwhelms

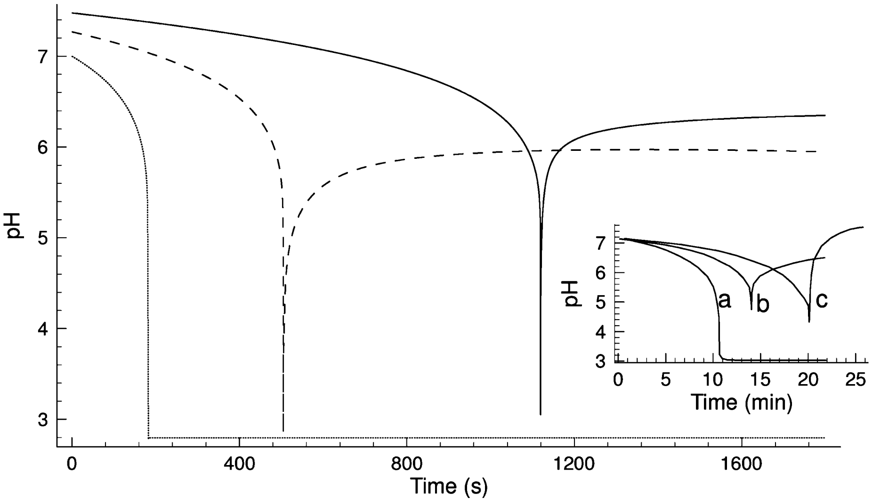

Figure 5. Calculated pH−time curves on the basis of model (M1)−(M4) in batch condition. Conditions: $[S_2O_3^{2-}]_0 = 0.01$ M; $[IO_3^-]_0 = 0.01$ M; $[HSO_3^-]_0 + [SO_3^{2-}]_0 = 0.02$ M; $[H^+]_0/M = 0.005$ (solid line), 0.007 (dashed line), 0.01 (dotted line). The inset, which was taken from a part of Figure 1 of the original Rábai and Beck paper,[24] shows the measured pH−time curves as $[H^+]_0$ changes.

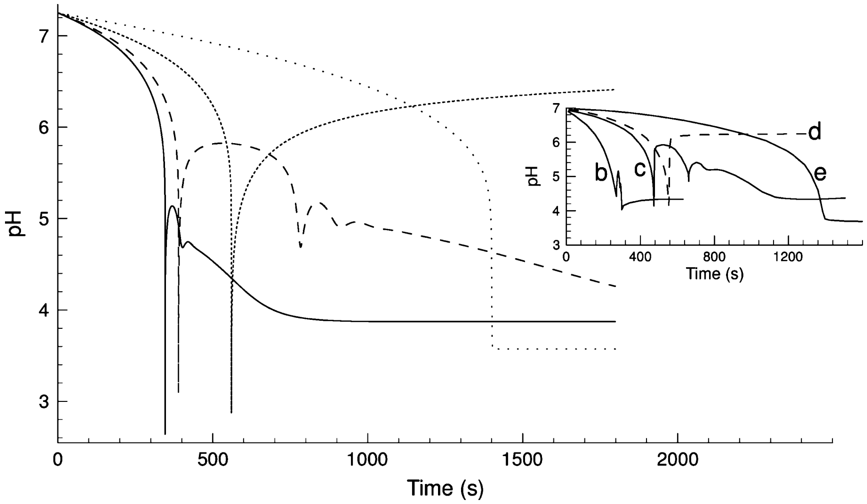

Figure 6. Calculated pH−time curves on the basis of model (M1)−(M4) in batch condition. Conditions: $[S_2O_3^{2-}]_0 = 0.011$ M; $[HSO_3^-]_0 + [SO_3^{2-}]_0 = 0.0195$ M; $[H^+]_0 = 0.007$ M; $[IO_3^-]_0/M = 0.0125$ (solid line), 0.0115 (long dashed line), 0.009 (short dashed line), 0.0055 (dotted line). The inset, which was taken from a part of Figure 1 of the original Rábai and Beck paper,[14] shows the measured pH−time curves as the iodate concentration changes.

the significance of k_{M2}. As can be clearly seen, the route where k'_{M2} governs is autocatalytic with respect to H^+. In fact, the formal kinetic order of the catalyst is 2, meaning that this reaction is supercatalytic.[27] Therefore, below pH = 5.0, the strong autocatalytic feature of k_{M2} ignites the immediate consumption of hydrogen sulfite and also results in the sharp drop of pH. At the point where the substrate sulfite is consumed, and therefore the “supercatalysis” stops, the oxidation of thiosulfate by iodate starts to give rise to the consumption of hydrogen ion according to step M3. The consumption of H^+ also results in deceleration of the given step. If the concentration of thiosulfate is high enough to suppress M4, then the product tetrathionate forms, preventing the buildup of HA (HSO_3^-). Thus the rapid rise of pH after the instantaneous drop is the consequence of the second-order dependence of M3 on the H^+ concentration.

Batch Oscillations. Rábai and Beck have successfully pointed out in their experiments the existence of high amplitude damped pH oscillation in a rather narrow range of the reactants.[14] To take this characteristic into account, a parallel oxidation step of thiosulfate by iodate has been invoked in which sulfite is regenerated besides the formation of tetrathionate. With the help of the rather complicated rate equations of eqs 1−3, they were able to reproduce semiqualitatively the observed batch oscillation. Later Luo and Epstein have predicted[15] that eq 3 along with a simple straightforward rate equation (depending only on the concentration of the reactants, thiosulfate, iodate and hydrogen ion) and with an appropriate choice of the rate constant should result in oscillation without having any complicated rate law. In fact, as Figures 6−8 clearly show, the values of k_{M3} and k_{M4} determined in this work are sufficient for the perfect explanation of both the existence of pH oscillations and the relatively narrow range, where the phenomenon is observable. The chemistry behind the batch oscillation can also be understood with the help of eqs M1−M4. The explanation of the first stage (reaching the extraordinarily sharp pH drop) is the same as was already enlightened before. After that, however, parallel formation of tetrathionate and hydrogen sulfite occurs, meaning that part of the hydrogen ion is preserved in a form (HSO_3^-) that can release the hydrogen ion again in the next period. Meanwhile, the oxidation of thiosulfate by iodate takes place, the pH increases, which decelerates the rate of steps M3 and M4 and simultaneously opens up the route for step M2 with regeneration of HA in step M4, and the oscillation cycle

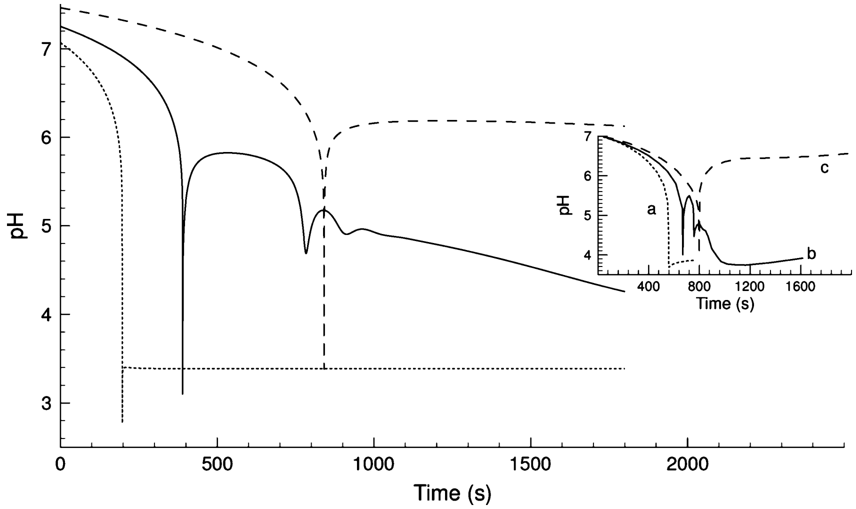

Figure 7. Calculated pH−time curves on the basis of model (M1)−(M4) in batch condition. Conditions: $[S_2O_3^{2-}]_0 = 0.011$ M; $[HSO_3^-]_0 + [SO_3^{2-}]_0 = 0.0195$ M; $[IO_3^-]_0 = 0.0115$ M; $[H^+]_0/M = 0.009$ (dotted line), 0.007 (solid line), 0.005 (dashed line). The inset, which was taken from a part of Figure 2 of the original Rábai and Beck paper,[14] shows the measured pH−time curves as $[H^+]_0$ changes.

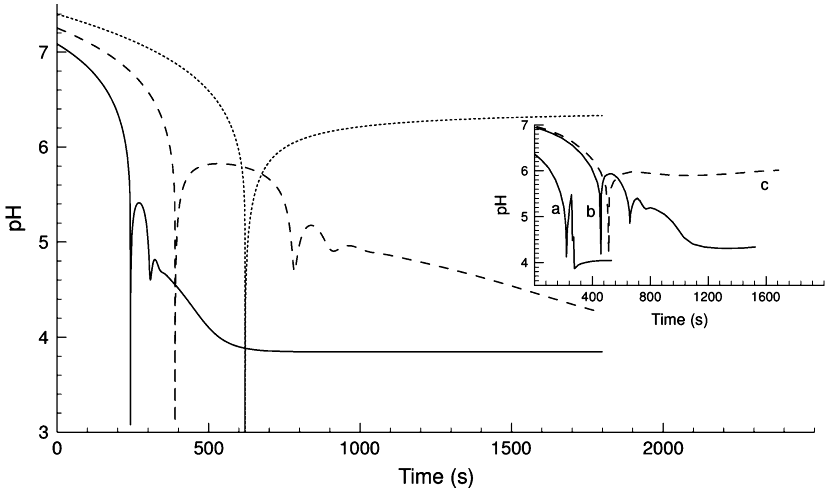

Figure 8. Calculated pH−time curves on the basis of model (M1)−(M4) in batch condition. Conditions: $[S_2O_3^{2-}]_0 = 0.011$ M; $[IO_3^-]_0 = 0.0115$ M; $[H^+]_0 = 0.007$ M; $[HSO_3^-]_0 + [SO_3^{2-}]_0/M = 0.0155$ (solid line), 0.0195 (dashed line), 0.0245 (dotted line). The inset, which was taken from a part of Figure 3 of the original Rábai and Beck paper,[14] shows the measured pH−time curves as the total sulfite concentration changes.

starts again. To keep the oscillation alive for two or even three periods, the concentration of the reactants has to be in a certain well-defined narrow range. As seen in Figures 6−8, the simulated pH−time traces reproduce well the shape of the measured curves as a function of the initial concentration of the reactants.

Characteristics of the CSTR System. Finally, it is also shown that the model along with its chemical parameters is also capable of explaining the sustained oscillation in CSTR system (Figure 9). The model, which can oscillate in batch, with an appropriate choice of the flow rate should exhibit sustained oscillation. Unfortunately, we are not yet able to explain the extreme sensitivity of the period length of the oscillation[24] to the temperature, because it would require the extended investigation of the temperature dependence of the kinetics of the subsystems themselves.

Comparison of the RB Model and Its Revised Version. Obviously, the basic core of the models is the same, but two important differences should clearly be emphasized. On the one hand, the revised model operates with four kinetic parameters (apart from the common preequilibrium of HSO_3^-), and the RB model uses eight of them. Thus, the revised model successfully reduced the number of kinetic parameters without losing any significant characteristics of the system. On the other hand, the revised model does not contain any cross-catalytic or inhibitory effect of the substrates, and all the rate equations can be supported by direct experimental evidence. It is, however, worthwhile to examine the connection between the key kinetic parameters of the two models. The values of k_c and k_c' in the RB model, responsible for the catalytic effect of thiosulfate, are closely related to that of our k_{M2}' if one assumes that the concentration of thiosulfate is approximately unchanged before the pH of the system reaches its extraordinarily sharp minimum. This assumption is, however, definitely valid in the case of the RB model because the thiosulfate−iodate reaction is considered to be completely inhibited by hydrogen sulfite. As a result, the sudden drop of pH is rather the consequence of the supercatalytic effect of hydrogen ion on the hydrogen sulfite−iodate reaction than that of the catalytic effect of thiosulfate. This statement is further supported by the fact that if the third and fourth terms are eliminated from the rate equation of eq 1 then the extraordinarily sharp drop of pH cannot be simulated even if the remaining terms contain the concentration of thiosulfate.

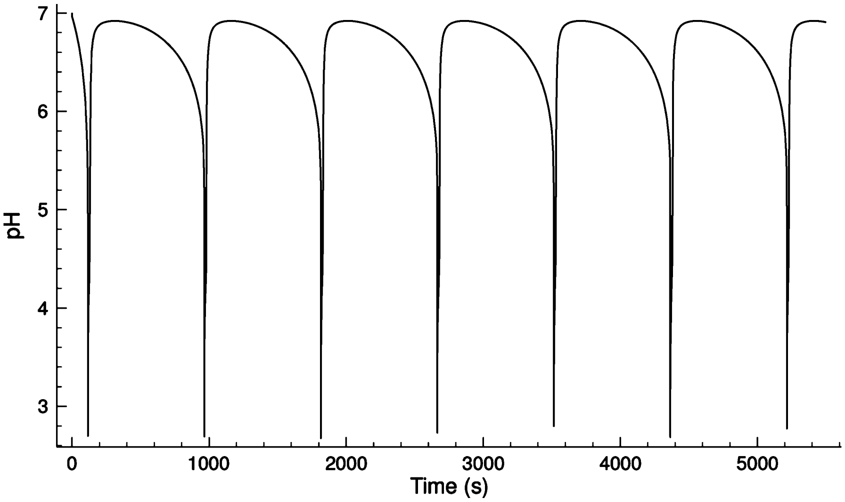

Figure 9. Calculated pH−time curves on the basis of model (M1)−(M4) in CSTR. Conditions: $[S_2O_3^{2-}]_0 = 0.017$ M; $[IO_3^-]_0 = 0.0125$ M; $[H^+]_0 = 0.013$ M; $[HSO_3^-]_0 + [SO_3^{2-}]_0 = 0.025$ M; $k_0 = 1.3 \times 10^{-3}$ s^{-1}.

As a result, the thiosulfate catalysis can be eliminated from the rate law of the hydrogen sulfite−iodate reaction.

The considerations outlined above may be extended for the comparison of k_2 of the RB model and our k_{M3} value. After the sudden drop of pH, i.e., after the hydrogen sulfite−iodate reaction is completed, the intense rise of pH is the consequence of the pH dependence of eq 2 alone. The inhibitory effect of sulfite can therefore play an important role only in the pH-fall stage, as it provides the necessary rate difference between the autocatalytic release of H^+ by eq 1 and the consumption of H^+ by eq 2 resulting in the sharp drop of pH. Certainly, if k_2 is increased in the original RB model, then the significance of the inhibitory effect of hydrogen sulfite would gradually be lost. Thus beyond a well-defined limit value of k_2, the inhibitory effect of HSO_3^- is no longer needed to give rise to the extraordinarily sharp drop of pH in the RB model. The main difference between the RB model and the revised model is, therefore, how the necessary rate difference of eqs 1 and 2 is maintained to preserve the main characteristics of the system, i.e., the extraordinarily sharp drop of pH. The RB model operates with the hydrogen sulfite inhibition and the revised model simply keeps the k'_{M2} at sufficiently high level. Further discussions about the inhibition of HSO_3^- will be detailed below.

As was already pointed out by Rábai and Beck,[14] eq 3 is necessary to produce batch oscillation by the regeneration of HSO_3^- in the combined system. Comparison of k_3 and k_{M4} reveals striking difference, i.e., the RB model contains—besides hydrogen sulfite inhibition—a further self-inhibitory effect of thiosulfate on the thiosulfate−iodate reaction, whereas the revised model operates with a straightforward rate equation. Although the inhibitory effect of HSO_3^- cannot be unambiguously ruled out, it is certainly not the case with thiosulfate. Rábai and Beck have argued[14] for the existence of the self-inhibitory effect of thiosulfate, because, on the one hand, without that, the RB model exhibits oscillatory behavior even if there is no initial sulfite present in the system and, on the other hand, no sulfite formation is allowed at thiosulfate excess. The latter argument is, however, only the question of the ratio of k_2 and k_3 or in the revised model the question of ratio of k_{M3} and k_{M4}. Nevertheless, our preliminary experiments have provided experimental evidence of hydrogen sulfite formation besides tetrathionate; therefore we concluded that the self-inhibitory effect of thiosulfate is unlikely to occur. It, however, indirectly questions the inhibitory effect of HSO_3^- because, without it, according to Rábai and Beck's argument, the RB model shows oscillations even in the absence of hydrogen sulfite with the given k_2, k_3 and k_i values. In favor of the inhibitory effect of HSO_3^-, however, it should be mentioned that there might exist a certain parameter set of k_2, k_3 and k_i, where the model does not show oscillation in absence of hydrogen sulfite but still preserves the most important experimental findings of the system.

As a summary of these arguments, we are convinced that the revised model is at the same time a significant improvement and simplification of the RB model in describing the dynamics of the combined iodate−sulfite−thiosulfate system. The most remarkable fact is that the revised model properly takes into account the dynamical behavior of the system as a function of the reactant concentrations (see Figures 5−9). No such evidence has been presented so far for the original RB model. For the sake of completeness, it should also be mentioned that the region of the batch oscillation in the revised model is somewhat shifted in the concentration space than found in the experiments. It, however, may be the consequence of the error of the determination of the individual rate coefficients or the different experimental conditions (ionic strength, buffer, temperature), or the fact that the intermediates of the individual reactions might slightly be involved in the overall dynamics.

Conclusion

In this paper it is demonstrated that the reinvestigation of the kinetics of the subsystems of the iodate−sulfite−thiosulfate system made it necessary to revise the kinetic model of the composite system on which the explanation of "exotic" phenomena is based. The new model, which was constructed on the basis of the kinetics of the individual subsystems, perfectly explains all the important dynamical behavior of the composite system. It is shown that the rate equation of the iodate−sulfite system contains a new term that depends on the square of the hydrogen ion concentration. In contrast to earlier studies,[25,26] where the oxidation of thiosulfate by iodate supposes exclusive formation of tetrathionate, the assumption[14] that thiosulfate oxidation by iodate occurs in parallel pathways yielding tetrathionate and sulfite has been experimentally justified. On the basis of the kinetics of the two subsystems a new kinetic model has been suggested in which the dynamics in both batch and flow experiments is explained without using the cross-catalytic and inhibitory effect of the substrates thiosulfate and sulfite. In fact, the sharp minimum in pH and the batch oscillation are the consequences of the supercatalytic term (with respect to the hydrogen ion) of the sulfite−iodate reaction and the pH dependence of the parallel formation of tetrathionate and sulfite during the oxidation of thiosulfate by iodate.

It should be emphasized that the revised model is definitely an oversimplification of the kinetics of the combined iodate−sulfite−thiosulfate system. Evidently, more research is in need to understand the behavior of the combined system fully. Besides the simplification, however, it is already remarkable that the revised model properly takes all the most attractive kinetic behavior of the system into consideration. Certainly, clarification of more intimate details of the dynamics of the iodate−sulfite−thiosulfate reaction must await for comprehensive kinetic studies of its subsystems, but it is strongly believed that the revised model may serve as a solid starting point to such investigations.

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References and Notes

(1) Bray, W. C. *J. Am. Chem. Sos.* **1921**, *43*, 1262.
(2) Bray, W. C.; Liebhafsky, H. A. *J. Am. Chem. Soc.* **1931**, *53*, 38.
(3) Belousov, B. P. *Ref. Radiats. Med. 1958, Medgiz, Moscow*, 1959, 145.
(4) Zhabotinsky, A. M. *Biofizika* **1964**, *9*, 306.
(5) Field, R. J.; Körös, E.; Noyes, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 8649.
(6) Körös, E.; Orbán, M. *Nature* **1978**, *273*, 371.
(7) Noszticzius, Z.; Ouyang, Q.; McCormick, W. D.; Swinney, H. L. *J. Am. Chem. Soc.* **1992**, *114*, 4290.
(8) Lengyel, I.; Rábai, Gy.; Epstein, I. R. *J. Am. Chem. Soc.* **1990**, *112*, 4607.
(9) Rábai, Gy. *J. Phys. Chem.* **1994**, *98*, 5920.
(10) Horváth, A. K.; Nagypál, I.; Epstein, I. R. *J. Am. Chem. Soc.* **2002**, *124*, 10956.
(11) Rinker, R. G.; Lynn, S.; Mason, D. M.; Corcoran, W. H. *Ind. Eng. Chem. Fundam.* **1965**, *4*, 282.
(12) Matsuzaki, I.; Woodson, J. H.; Liebhafsky, H. A. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3317.
(13) Tsukada, M. *Chem. Lett.* **1987**, 1707.
(14) Rábai, Gy.; Beck, M. T. *J. Phys. Chem.* **1988**, *92*, 4831.
(15) Luo, Y.; Epstein, I. R. *J. Am. Chem. Soc.* **1991**, *113*, 1518.
(16) Horváth, A. K.; Nagypál, I. *Int. J. Chem. Kinet.* **2000**, *32*, 395.
(17) Horváth, A. K.; Nagypál, I.; Peintler, G.; Epstein, I. R.; Kustin, K. *J. Phys. Chem. A* **2003**, *107*, 6966.
(18) Varga, D.; Horváth, A. K.; Nagypál, I. *J. Phys. Chem. B* **2006**, *110*, 2467.
(19) Horváth, A. K. *J. Phys. Chem. A* **2007**, *111*, 890.
(20) Landolt, H. *Ber. Dtsch. Chem. Ges.* **1886**, *19*, 1317.
(21) Peintler, G. *ZiTa, Version 5.0, a Comprehensive Program Package for Fitting Parameters of Chemical Reaction Mechanism*. József Attila Tudományegyetem, Szeged, Hungary, 1990−1998. (The program can freely be downloaded from the following website: http://www.staff.u-szeged.hu/~peintler/download/chemmech/zitainst.zip).
(22) Eggert, J.; Scharnow, B. *Z. Electrochem. Angew. Phys. Chem.* **1921**, *27*, 455.
(23) Skrabal, A.; Zahorka, A. *Z. Electrochem. Angew. Phys. Chem.* **1927**, *33*, 42.
(24) Rábai, Gy.; Beck, M. T. *J. Phys. Chem.* **1988**, *92*, 2804.
(25) Rieder, R. *J. Phys. Chem.* **1930**, *34*, 2111.
(26) Indelli, A. *J. Phys. Chem.* **1961**, *65*, 240.
(27) Horváth, A. K.; Nagypál, I.; Peintler, G.; Epstein, I. R. *J. Am. Chem. Soc.* **2004**, *126*, 6246.