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Simultaneous Investigation of the Landolt and Dushman Reactions

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The Dushman reaction taking place after the abrupt change of the absorbance in the Landolt reaction was followed by monitoring the concentration of triiodide spectrophotometrically in buffered solutions. The joint evaluation of the experimental data on the kinetic system (Landolt) and subsystem (Dushman) has revealed that the inverse of the Landolt induction time (t_i) is proportional to the combination of the concentration and the square of the concentration of both the iodide and hydrogen ions, while the inverse of t_i is linearly proportional to the iodate concentration. The hydrogen sulfite dependence, however, is found to be more complex; the Landolt induction time goes through a minimum as a function of hydrogen sulfite concentration; the phenomenon that has not been reported yet. A kinetic model is suggested in which the rate law of both the Landolt and Dushman reactions is supplemented to take all the characteristics of the measured curves into account. It is demonstrated that the supercatalytic term of the Landolt reaction with respect to hydrogen ion discovered recently and the rate term of the Dushman reaction being first order with respect to iodide ion play an important role in explaining the dependencies of the Landolt induction period.

Introduction

The abrupt appearance of the $I_2 + I^- \rightleftharpoons I_3^-$ equilibrium after a well-defined time lag as long as the stoichiometric constraint $3[IO_3^-]_0 > [HSO_3^-]_0$ is held has long been known in the acidic hydrogen sulfite−iodate reaction.[1,2] Ever since this feature of the reaction has been used extensively as a popular lecture demonstration of the reaction rate and has often been referred to as the "iodine clock reaction" or simply the "Landolt reaction". The qualitative picture of the reaction has long been accepted:[3] the reaction starts with slow oxidation of hydrogen sulfite by iodate yielding iodide

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

followed by the well-known Dushman reaction[4]

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

but no color change appears unless the reactant hydrogen sulfite is entirely consumed due to the fast oxidation of hydrogen sulfite by iodine

$$HSO_3^- + I_2 + H_2O \rightarrow SO_4^{2-} + 2I^- + 3H^+ \qquad (3)$$

Since the rate constant of eq 3 is near to the diffusion control limit and the kinetics of eqs 1 and 2 can easily be studied independently, the fate of the reactants is unambiguously determined. Therefore one would expect that the dependencies of the Landolt induction period on the reactants have already been established unambiguously. The survey of the literature, however, has revealed perceptible discrepancies in the dependencies of the time lag as a function of the reactant concentrations. In 1917 Eggert[3] showed that the Landolt time is independent of the concentration of hydrogen sulfite and inversely proportional to the square of both the concentrations of iodate and hydrogen ions over a fixed range of concentrations. Moreover it was also demonstrated that iodide ion decreases the Landolt induction time. Later Skrabal[5] showed that if all the concentrations were chosen large with respect to that of hydrogen sulfite then the Landolt induction time must be proportional to the concentration of hydrogen sulfite and inversely proportional to that of iodate and to square of the concentration of both iodide and hydrogen ions. In case of eq 1 the following rate law has been deduced

$$v_1 = k_1^s[SO_3^{2-}][IO_3^-][H^+] \qquad (4)$$

that was shown to accompany eq 2 with the rate law ($v_2 = k_2^d[IO_3^-][I^-]^2[H^+]^2$) determined by Dushman.[4] Later Skrabal and Zahorka[6] have reinvestigated the hydrogen sulfite iodate reaction in a wider concentration range and found a different rate law for eq 1

$$v_1 = k_1^z[H^+][HSO_3^-][IO_3^-] + k_1^{z'}[HSO_3^-]^2[IO_3^-] \qquad (5)$$

In 1968 Church and Dreskin[7] established a simple relationship between the Landolt induction period and the concentration of the reactants

$$P = \frac{0.0037M^2s}{[IO_3^-][HSO_3^-]} \qquad (6)$$

that seems to contradict the early study of Eggert's,[3] in which the independence of the induction period with respect to hydrogen sulfite was emphasized.

The extensive studies on the oscillatory behavior has nowadays renewed the interest on the Landolt reaction. Large amplitude pH oscillations were observed in the Landolt reaction with ferrocyanide in CSTR[8] and soon after its detailed mechanism was published by two independent research groups[9,10] in which the rate equation (eq 4) published originally by Skrabal[5] was used to interpret the dynamical behavior of the system. Shortly after that Rábai and Beck[11,12] discovered large amplitude batch oscillation in the Landolt reaction perturbed by thiosulfate. An empirical rate law was also suggested to explain the batch

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oscillation in which a complicated rate equation was used for the Landolt reaction

$$v_1^r = [IO_3^-][HSO_3^-](k_1^r[H^+] + k_1^{r\prime}[HSO_3^-] + k_c[S_2O_3^{2-}][H^+]^2 + k_c'[S_2O_3^{2-}][H^+]^3) \quad (7)$$

Our recent study has, however, just revealed that it is not necessary to complicate the rate equation of the Landolt reaction to such an extent; simple supercatalytic effect of hydrogen ion is sufficient to take all the major experimental facts quantitatively into account.[13] So far no direct experimental evidence has been obtained to support the supercatalytic effect of hydrogen ion on the Landolt reaction other than our recent preliminary study.[13] It is clear that precise knowledge of the kinetics of the Landolt reaction should harmonize the distinctive reports on the dependencies of the Landolt induction time. As we shall see later the Landolt induction time does not depend exclusively on the rate of Landolt reaction, but there is a continuously growing contributory effect of the Dushman reaction with increasing iodide concentration that eventually stems from the increase of $[HSO_3^-]$. Therefore it seems quite reasonable to study simultaneously both reactions to unravel the apparent contradiction of the dependencies of the Landolt induction time as a function of the concentration of the reactants.

The story of the iodate−iodide reaction has been started by Dushman's original study more than a century ago.[4] It was found that the reaction is second order with respect to both iodide and hydrogen ions and first order with that of iodate in moderate acidic solution. At more acidic solution, however, the kinetic order of iodide ion significantly falls below 2 as was noticed by several independent researchers.[14–16] Less than a decade ago Schmitz provided[17] experimental evidence for the coexistence of the first and second order term of iodide in the rate equation of the Dushman reaction.

The kinetics of the Dushman reaction seems to be settled but there is a considerable disagreement with regard to that of the Landolt reaction. We therefore decided to reinvestigate the kinetics of both reactions simultaneously. Recent renewed interest of the spatiotemporal behavior of the iodate−sulfite systems also justifies this reinvestigation.[18–22]

Experimental Section

Reagents and Apparatus. All the chemicals were of the highest purity commercially available (sodium hydrogen sulfite, potassium iodate, potassium iodide, sodium hydroxide, chloroacetic acid, sodium nitrate) and were used without further purification. Four-times distilled water was used to prepare all the stock solutions.

Chloroacetic acid−chloroacetate buffer was used to maintain the pH between 2.45 and 3.90 (taking the pK_a of chloroacetic acid 2.90).[23] The chloroacetate concentration was kept constant at 0.28 M. The ionic strength was adjusted to 0.5 M with sodium nitrate. The initial concentrations and the concentration ranges of the reactants in the samples studied are collected in Table 1. The molar absorbance and the formation constant of triiodide was determined from the data collected for the Dushman reaction (last row in Table 1).

Methods

The kinetic measurements were carried out in a standard 1 cm quartz cuvette equipped with a Teflon cap and a magnetic stirrer. The temperature was kept constant at 25.0 ± 0.1 °C in a thermostatted cell holder. The buffer solution was introduced first into the cuvette followed by the iodate solution. The reaction was started with addition of the hydrogen sulfite solution from a fast delivery pipet. In case of the iodide dependence the sulfite and iodide solutions were introduced simultaneously to initiate the reaction. After starting the reaction the cuvette was carefully sealed with parafilm at the Teflon cap in order to minimize the loss of iodine. The reaction was followed by a Zeiss Specord S200 double beam spectrophotometer at 350 nm, where the triiodide ion has an absorbance maximum. The kinetics of the Landolt and the Dushman reactions was determined by the appearance of triiodide ion since neither HSO_3^- nor IO_3^- has significant absorbance above 260 nm. The huge molar absorbance of triiodide ion ($\varepsilon = 25660\ M^{-1}\ cm^{-1}$) makes it possible to follow the reaction conveniently in the Dushman range with sufficient sensitivity.

TABLE 1: Initial Concentrations and Concentration Ranges of the Solutions Studied

$[HSO_3^-]_0$ (mM)	$[IO_3^-]_0$ (mM)	$[H^+]$ (mM)	$[I^-]_0$ (mM)	no. experiments
0.6−10	4.0	0.25	0	16
0.6−10	4.0	0.63	0	16
3.5	1.5−10.0	0.5	0	6
4	1.5−10	0.2	0	6
4	4.0	0.4	0.7−5	7
4	4.0	0.13	0.7−5	7
4	4.0	0.2−2.5	0	8
0	0.02	0.5−2	0.2−2	14

Data Treatment. The experimental curves were analyzed with the program package ZiTa.[24] Only the absorbance up to 1.8 was used for the data evaluation because above this value the relative error of absorbance measurement increases significantly. Altogether 3523 experimental points from 80 absorbance−time series were used for simultaneous fitting. Orthogonal fitting, meaning that the experimental error in the time and absorbance data are also taken into consideration, was used to minimize the sum of squares of the deviations between the measured and calculated absorbance. In case of the orthogonal fitting every experimental absorbance−time series is transformed into a $0 \le x,y \le 1$ "box" and that the square sum of the perpendicular deviation in this box is minimized. The main reason for choosing the orthogonal fitting of the experimental absorbance−time curves was the fact that the absorbance starts to rise abruptly after the induction time resulting in a huge change in the first derivative of the experimental curves near the Landolt time. For such a type of experimental curves the orthogonal fitting method provides the most precise prediction of the rate constants in question. Our quantitative criterion for an acceptable fit was that the average deviation for the orthogonal fit decrease below 0.01, which is close to the experimentally achievable limit of error.

Results

Kinetics of the Dushman Reaction. For the evaluation of the triiodide concentration−time series it is essential to know the molar absorbance and the formation constant of triiodide at exactly the same experimental circumstances. Therefore, in most of our experiments, we followed the reaction between iodide and iodate in chloroacetic acid/chloroacetate buffer up to reaching the equilibrium state of triiodide/iodine system. This way the molar absorbance, the formation constant as well as the kinetic parameter(s) can be calculated independently, without significant correlation between them. The experimental data illustrating the iodide dependence of the measured absorbance−time series along with the fitted curves are shown in Figure 1. The

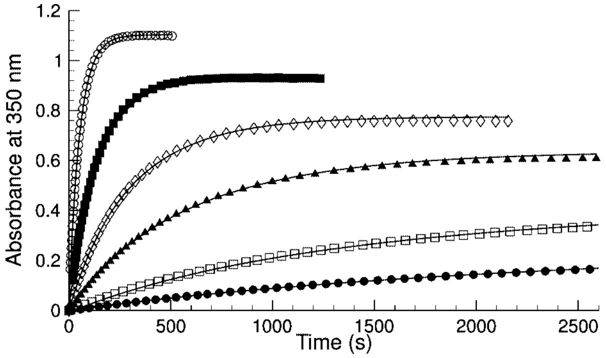

Figure 1. Measured (symbols) and calculated (solid lines) absorbance−time series in the Dushman reaction at pH = 3.12 and $[IO_3^-]_0 = 2 \times 10^{-5}$ M at different iodide concentrations. $[I^-]_0$/mM = 0.484 (●), 0.722 (□), 1.19 (▲), 1.66 (6), 2.43(◇), 3.95(○).

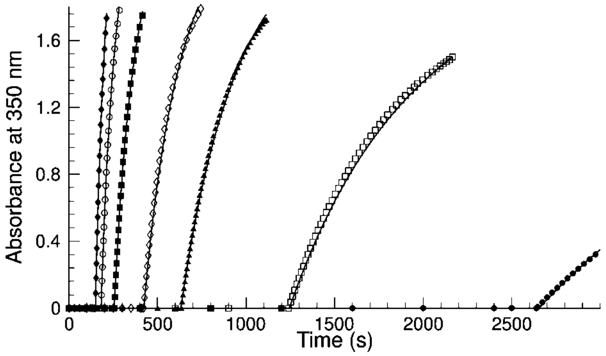

Figure 2. Measured (symbols) and calculated (solid lines) absorbance−time series in the Landolt reaction at pH = 3.73, $[HSO_3^-]_0$ = 4.0 mM and $[I^-]_0$ = 0 mM at different iodate concentrations. $[IO_3^-]_0$ (mM) = 1.41 (●), 1.88 (□), 2.82 (▲), 3.76 (◇), 5.64 (■), 7.52(○), 8.84 (♦).

calculation has revealed that three parameters: the molar absorbance, the formation constant, and the k_2 rate constant of the rate law suggested by Dushman[4] ($v_2 = k_2[IO_3^-][I^-]^2[H^+]^2$) is sufficient to describe the kinetics and the equilibrium state reached. It provided 664 ± 22 M^{-1} and 25660 ± 230 M^{-1} cm^{-1} for the value of the formation constant and molar absorbance (at 350 nm) of triiodide and $(2.21 \pm 0.20) \times 10^{9}$ M^{-4} s^{-1} for k_2. These data were fixed in the evaluation of the Landolt reaction. The data are in good agreement with the ones determined previously under similar experimental conditions.[25,26]

It should be mentioned, however, that under these experimental circumstances there was no possibility to confirm the first-order dependence of iodide ion that may dominate the kinetics of the Dushman reaction at low ($[I^-] \leq 10^{-5}$ M) initial iodide concentration. However, as we shall see later, by the help of measuring the Landolt reaction, it was possible to confirm the kinetic role of a first-order pathway when the sulfite concentration was low resulting in sufficiently small concentration of iodide.

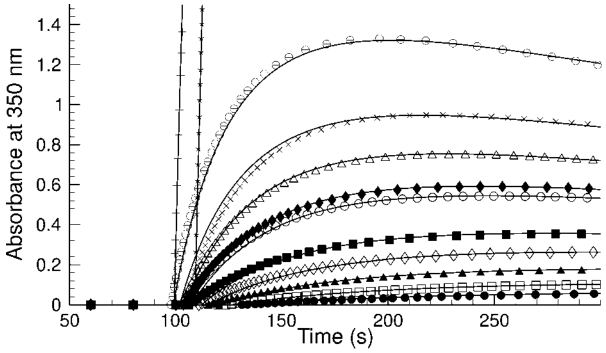

Figure 3. Measured (symbols) and calculated (solid lines) absorbance−time series in the Landolt reaction at pH = 3.20, $[IO_3^-]_0$ = 4.0 mM and $[I^-]_0$ = 0 mM at different hydrogen sulfite concentrations. $[HSO_3^-]_0$ (mM) = 0.58 (●), 0.72 (□), 0.98 (▲), 1.23 (◇), 1.47 (■), 1.88 (○), 1.97 (♦), 2.22 (▲), 2.47 (×), 3.00 (⊖), 6.88 (+), 8.86 (★).

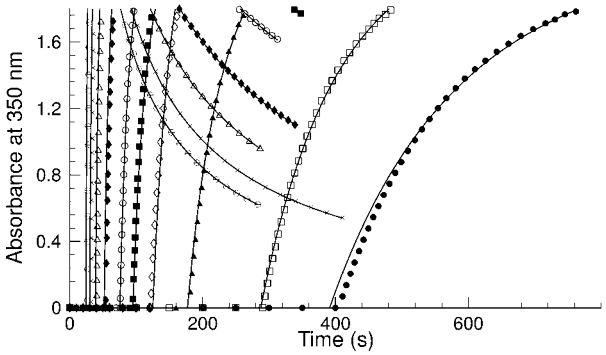

Figure 4. Measured (symbols) and calculated (solid lines) absorbance−time series in the Landolt reaction at $[HSO_3^-]_0$ = 4.0 mM, $[IO_3^-]_0$ = 4.0 mM and $[I^-]_0$ = 0 mM at different pHs. pH = 3.73 (●), 3.61 (□), 3.42 (▲), 3.30 (◇), 3.20 (■), 3.12 (○), 3.00 (♦), 2.90 (△), 2.82 (×), 2.75 (★). Note that the measured and calculated curves are cut at 1.8 absorbance unit since above this value the relative error of the absorbance measurement increases significantly.

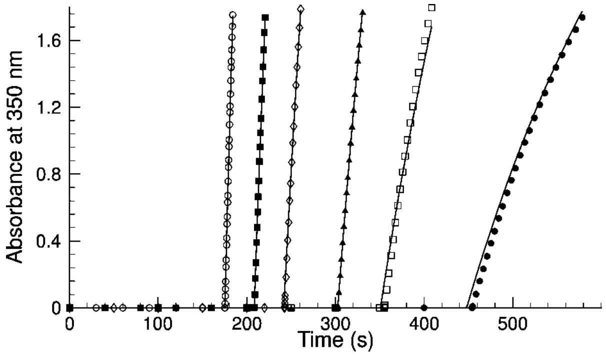

Figure 5. Measured (symbols) and calculated (solid lines) absorbance−time series in the Landolt reaction at $[HSO_3^-]_0$ = 4.0 mM, $[IO_3^-]_0$ = 4.0 mM, pH = 3.90 mM at different iodide concentrations. $[I^-]_0$ (mM) = 0.67 (●), 1.33 (□), 2.00 (▲), 2.67 (◇), 3.34 (■), 4.00 (○).

Characteristics of the Induction Period of the Landolt Reaction. Figures 2–5 show some characteristic experimental and fitted curves on the dependence of the absorbance-time series on the initial concentration of the four reactants (HSO_3^-, IO_3^-, H^+, and I^-). Figure 6 shows the dependence of the Landolt induction period on the hydrogen sulfite concentration. It clearly indicates that the induction time is more or less independent of the hydrogen sulfite concentration in a relatively wide concentration range, but both above and below that range it starts to increase significantly. This result is in complete contradiction with the early findings of Eggert,[3] who emphasized the independence of the Landolt time on the hydrogen sulfite concentration. No experimental demonstration of the complex hydrogen sulfite dependence of the Landolt induction time has been reported so far in the literature at buffered medium.

Figure 7 indicates the dependence of the inverse of the Landolt induction time on the iodate concentration. In agreement with Skrabal's or Church and Dreskin's results[5,7] we found that the Landolt time was inversely proportional to rather the iodate concentration than the square of the iodate concentration as suggested by Eggert.[3]

Figure 8 displays the hydrogen ion concentration dependence of the inverse of the Landolt induction period. The dashed line

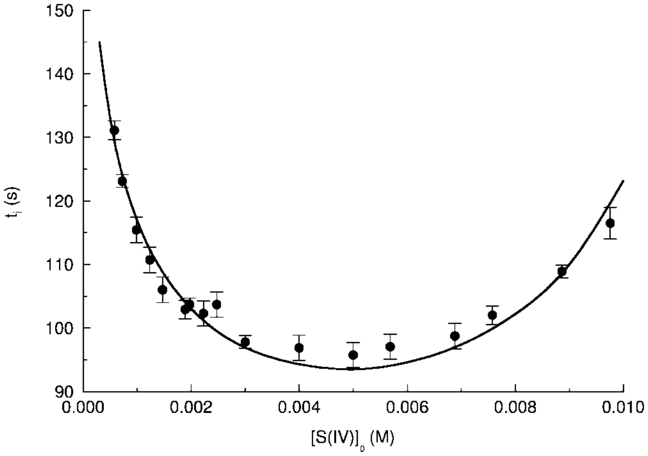

Figure 6. Measured (●) and calculated (solid lines) Landolt time as a function of the total sulfite concentration. $[IO_3^-]_0 = 0.004$ M, pH = 3.20, $[I^-]_0 = 0$ M.

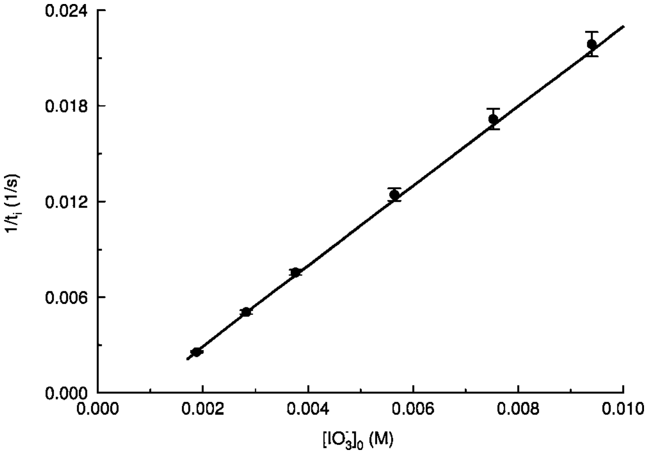

Figure 7. Reciprocals of the measured (●) and calculated (solid lines) Landolt time as a function of the iodate concentration. $[S(IV)]_0 = 0.00345$ M, pH = 3.30, $[I^-]_0 = 0$ M.

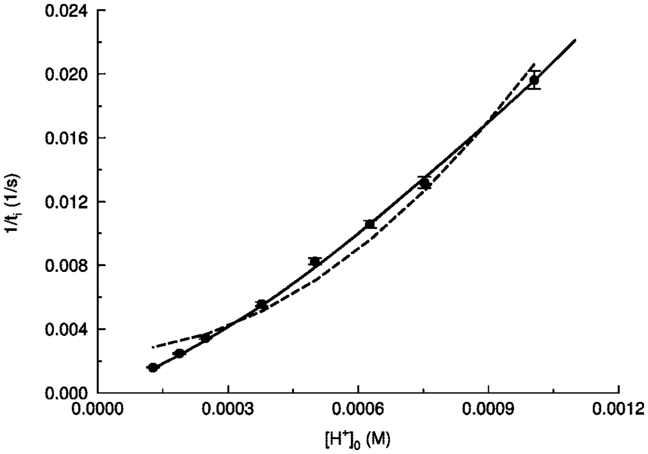

Figure 8. Reciprocals of the measured (●) and calculated (solid lines) Landolt time as a function of the hydrogen ion concentration. $[S(IV)]_0 = 0.00395$ M, $[IO_3^-]_0 = 0.004$ M, $[I^-]_0 = 0$ M. The dashed line shows the result of the least-squares fit of the $y = a + bx^2$ function.

of Figure 8 displays the result of the least-squares fit of the measured points calculated by only a quadratic hydrogen ion dependence. From this result one can easily conclude that, within the pH range studied, both first- and second-order dependence of the inverse of the Landolt induction time on the hydrogen ion concentration appear. This finding is in contrast to Eggert's[3] and Skrabal's[5] studies who established pure second-order dependence and also to Church and Dreskin's result[7] indicating no pH dependence at all. Thorough survey of the literature has revealed that no clear experimental evidence has been presented so far that shows the central role of the first-order dependence of the Landolt time on the hydrogen ion concentration other than our paper published recently.[13]

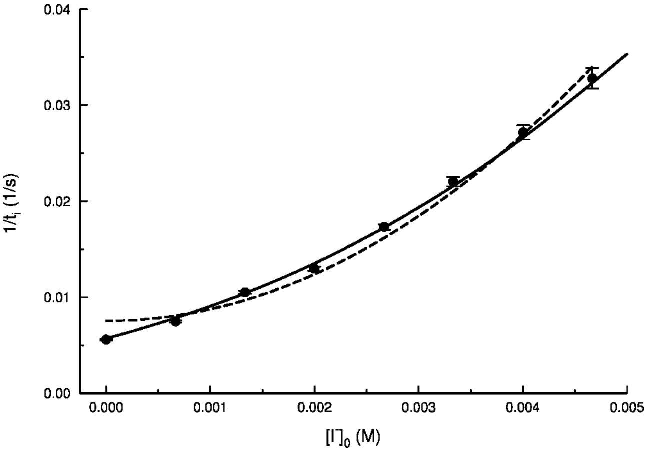

Figure 9. Reciprocals of the measured (●) and calculated (solid lines) Landolt time as a function of the initial iodide concentration. $[S(IV)]_0 = 0.00396$ M, $[IO_3^-]_0 = 0.004$ M, pH = 3.42. The dashed line shows the result of the least-squares fit of the $y = a + bx^2$ function.

Figure 9 shows the iodide dependence of the inverse of the Landolt induction time clearly indicating that $1/t_i$ depends on both the concentration and the square of the concentration of iodide ion. Note that the dashed line of Figure 9 shows the least-squares fit of the measured points calculated by only a quadratic iodide concentration dependence. This result just partially agrees with Skrabal's early findings[5] who showed that the inverse of the Landolt induction time depends purely on the square of the iodide concentration.

Proposed Kinetic Model. The basic chemistry of the Landolt reaction has long been accepted, and no further experimental evidence has been presented to modify it. Therefore our primary interest was focused only on the rate laws of the key governing steps in eqs 1 and 2. The rate equation of the fast hydrogen sulfite−iodine reaction is well-established, and its rate constant ($k_3 = 1.7 \times 10^{9}$ M^{-1} s^{-1}) was used as determined by Yiin and Margerum.[27] Of course these steps must be augmented with the well-known formation equilibrium of triiodide

$$I^- + I_2 \rightleftharpoons I_3^- \qquad (8)$$

since the reaction was followed at 350 nm, where I_3^- has a strong absorbance maximum. As a starting point of the fitting procedure all the rate laws published for eqs 1 and 2 along with many other conceivable ones were considered. At the end of each calculation procedure the insensitive parameter(s) was/were omitted step by step prior to the new start. As a result of this long but straightforward calculation procedure, that was already successfully applied in our previous studies,[28–30] the rate laws indicated in Table 2 were found to be necessary for perfect simultaneous description of the measured absorbance−time curves. The average orthogonal deviation between the measured and calculated absorbances is 7.3×10^{-3}.

Discussion. The upper part of Table 2 contains the rate laws of the Landolt reaction required for fitting the experimental data. The first term, that is autocatalytic with respect to H^+ was already well-established by Skrabal and Zahorka[6] with $k_1^{\sim} = 8800$ M^{-2} s^{-1}. Our calculation has provided a somewhat lower value

TABLE 2: Rate Laws and Rate Constants for the Landolt and Dushman Reaction (References Noted)

		rate constant	
reaction	rate law	present work	ref
$3HSO_3^- + IO_3^- \rightarrow 3SO_4^{2-} + I^- + 3H^+$	$k_1[H^+][HSO_3^-][IO_3^-]$	3970 ± 480	8800[6]
	$k_1'[HSO_3^-][IO_3^-]$	0.146 ± 0.022	
	$k_1''[H^+]^2[HSO_3^-][IO_3^-]$	$(3.02 \pm 0.59) \times 10^5$	
	$k_1^{z'}[HSO_3^-]^2[IO_3^-]$		11[6]
$5I^- + IO_3^- + 6H^+ \rightarrow 3I_2 + 3H_2O$	$k_2[H^+]^2[I^-]^2[IO_3^-]$	$(2.21 \pm 0.20) \times 10^9$	2.36×10^9 [26]
	$k_2^s[H^+]^2[I^-][IO_3^-]$		1200[17]
	$k_2'[H^+][I^-][IO_3^-]$	24.9 ± 4.2	

$k_1 = (3.97 \pm 0.48) \times 10^3$ M^{-2} s^{-1}, but the difference between them may easily be explained by the different conditions used in the experiments (e.g., buffer components, inert salts by what the ionic strength is adjusted, etc.). Skrabal and Zahorka have also found[6] an additional rate term of the Landolt reaction that does not depend directly on $[H^+]$ but contains a second-order dependence on $[HSO_3^-]$ along with a first-order dependence on the iodate concentration. Our measurements do not support the second-order dependence with respect to $[HSO_3^-]$ but revealed indeed the necessity of a term that depends only on the first power of the concentration of both reactants. The rate coefficent k_1' was found to be $(1.46 \pm 0.22) \times 10^{-1}$ M^{-1} s^{-1} . Besides, the third term of the Landolt reaction is also established that depends on the square of the hydrogen ion concentration taking it as a "supercatalytic" reaction. This feature makes it possible to explain the batch pH oscillation in the combined iodate−thiosulfate−sulfite system[13] without unnecessary cross-catalytic and cross-inhibitory complications of the rate equations of the sulfite−iodate and thiosulfate−iodate reactions suggested before.[12] Our fitting has provided $(3.02 \pm 0.59) \times 10^5$ M^{-3} s^{-1} value for k_1''. If any of the three rate terms indicated above is neglected then not only the average deviation would increase to an unacceptable high value but also systematic difference between the measured and calculated data would appear. Therefore we concluded that all these rate terms for the Landolt reaction are necessary to describe the most important characteristics of the kinetic curves.

The lower part of Table 2 contains the rate laws of the Dushman reaction necessary for perfect description of the experimental curves. The rate law of the iodate-iodide reaction originally established by Dushman[4] is reinforced by our measurements. The corresponding rate constant $k_2 = (2.21 \pm 0.20) \times 10^9$ M^{-4} s^{-1} is in good agreement with the values found in the literature for this reaction.[4,17] However good description of our measurements requires an additional term for the Dushman reaction at lower iodide concentrations. The role of this term becomes more pronounced at lower initial hydrogen sulfite concentrations that eventually results in lower iodide concentrations. Schmitz[17] has recently provided experimental evidence for an additional rate term of the Dushman reaction that is first order with respect to iodide. We confirmed this term but also found that the agreement between the measured and calculated kinetic curves is even better by approximately 20% if this term is first order with respect to the iodide, iodate, and the hydrogen concentration. Therefore we rather suggest first order hydrogen ion dependence in the additional term having a rate constant to be $k_2' = 24.9 \pm 4.2$ M^{-2} s^{-1} . This suggestion is further supported by the following fact. Systematic deviations, appearing between the measured and calculated curves when using the rate term suggested by Schmitz,[17] may be eliminated if the molar absorbance of triiodide is increased to 27500 M^{-1} cm^{-1} that is over the acceptable limit for this value. Of course the rest of the fitted parameters remained within their standard deviations meaning that the rate term depending on the first power of iodide concentration suggested by Schmitz depends rather on the concentration of hydrogen ion than the square of that. Omitting k_2' from the final kinetic model would lead to not only significantly higher average deviations but also to systematic deviations; therefore we concluded that both terms of the Dushman reaction are necessary to describe quantitatively the measured kinetic curves.

The solid lines of Figures 6–9 show how the proposed model predicts the dependencies of the Landolt induction period on the concentration of the reactants. It clearly indicates that the steps along with their rate equations perfectly reflect all the most important characteristics of the measured quantities. Finally, we shall point out how the complex dependence of the Landolt induction period (t_i) on the concentration of the reactants follows from the proposed kinetic model. As shown in Figure 6 t_i goes through a minimum as a function of hydrogen sulfite concentration. The reason of the minimum can be understood as follows. The removal of hydrogen sulfite takes place simultaneously by the Landolt reaction and by iodine formed in the Dushman reaction. At low hydrogen sulfite concentration t_i decreases with increasing hydrogen sulfite concentration since iodine removes hydrogen sulfite much faster than iodate does indicating the growing effect of the Dushman reaction determining the Landolt induction period. At higher hydrogen sulfite concentrations, however, most of the iodate is consumed resulting in a slower formation of iodine from the Dushman reaction. In other words the decreasing effect of the Dushman reaction on the Landolt induction period becomes less important if the rate of the Dushman reaction is decreased by shifting the iodate−iodide ratio with addition of more hydrogen sulfite. Thus t_i becomes almost independent of $[HSO_3^-]_0$ within a certain hydrogen sulfite concentration range. Since this concentration range is relatively wide, the Landolt induction time would easily be misinterpreted as if it was independent of the hydrogen sulfite concentration. Further increase of $[HSO_3^-]_0$ consumes almost all the iodate within the Landolt induction time (t_i) that results in slower removal of hydrogen sulfite. Therefore t_i starts to increase again beyond a certain hydrogen sulfite concentration. The dependence of t_i on the iodate concentration is straightforward since the rate of both the Landolt and the Dushman reactions is proportional to the iodate concentration resulting in the linear dependence of the inverse of t_i as a function of iodate concentration. The dependence of the inverse of t_i as a function of pH is also well-understandable since the rate of both the Landolt and the Dushman reactions is increased by decreasing pH. Since the Landolt reaction is first and second order with respect to $[H^+]$, it is not surprising at all that the inverse of t_i is proportional to both the hydrogen concentration and the square of it. The iodide dependence of t_i is also straightforward since initial addition of iodide simply removes hydrogen sulfite faster than the iodate throughout iodine formed in the Dushman reaction.

Summary and Conclusion

In this paper the dependencies of the Landolt induction period on the concentration of hydrogen sulfite, iodate, iodide, and hydrogen ions have been clarified. For the first time it is shown that t_i goes through a minimum as a function of hydrogen sulfite concentration providing therefore a relatively wide range of HSO_3^- concentration, where the Landolt induction period becomes almost independent of $[HSO_3^-]_0$ within the experimental error thus misleading the early researchers. It is also justified that the inverse of the Landolt induction period is proportional to the concentration and the square of the concentration of hydrogen ion as well as that of the iodide ion. To our best knowledge the governing role of the linear proportionality of the inverse of the Landolt induction time on the concentration of hydrogen and iodide ions has not been shown so far. Our experiments clearly indicated the fact that $1/t_i$ is rather proportional to the concentration iodate than to the square of it as was suggested by Eggert.[3] As demonstrated above the kinetic model in which the "supercatalytic" effect of hydrogen ion in the hydrogen sulfite-iodate reaction and the original rate law of the Dushman reaction enhanced by a first-order dependence on iodide ion suggested recently[17] both play important role in determining the Landolt induction period.

We also believe that the refinement of the kinetic model of the Landolt reaction may also contribute to a better understanding of the interpretation of the spatiotemporal structures observed recently.[22]

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