

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/23150462>

Theoretical Investigation on the Concentration Dependence of the Landolt Time

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY A · SEPTEMBER 2008

Impact Factor: 2.69 · DOI: 10.1021/jp803790e · Source: PubMed

CITATIONS

6

READS

30

3 AUTHORS:



Attila K Horváth

University of Pécs

54 PUBLICATIONS 536 CITATIONS

SEE PROFILE



István Nagypál

University of Szeged

86 PUBLICATIONS 1,447 CITATIONS

SEE PROFILE



Csekő György

China University of Mining Technology

15 PUBLICATIONS 66 CITATIONS

SEE PROFILE

Theoretical Investigation on the Concentration Dependence of the Landolt Time

Attila K. Horváth,* István Nagypál, and György Csekő

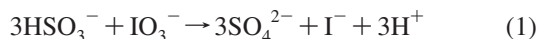
Department of Physical Chemistry, University of Szeged, Szeged, Hungary

Received: April 30, 2008; Revised Manuscript Received: July 1, 2008

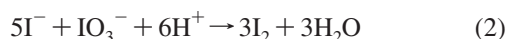
Based on the modified kinetic model of the Landolt and the Dushman reactions published recently, an exact expression has been derived for the concentration dependence of the Landolt time. It is also shown that all the apparently contradictory formulas, regarding the concentration dependence of the Landolt time, reported previously at quite different experimental circumstances can easily be reconciled from the simplification of the newly proposed equation. It also means that the formula derived may satisfactorily be applied to calculate the Landolt time basically with no restrictions for the concentration of the reactants.

Introduction

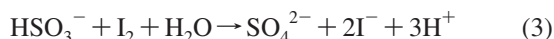
The hydrogen sulfite–iodate reaction or even better known as the Landolt reaction named after its discoverer, is probably one of the most familiar chemical reactions for any chemists all around the world.^{1,2} As long as the initial total sulfite concentration is held less than thrice the initial iodate concentration, blue color appears after a well-defined time lag in the presence of starch indicator due to formation of the starch triiodide complex. This feature of the reaction has been extensively used as a popular lecture demonstration to interpret the basic definitions of the reaction kinetics. The reaction is thought to be simple, started by the slow oxidation of hydrogen sulfite by iodate



Iodate can oxidize iodide by the well-known Dushman reaction³



but iodine is quickly removed⁴ by hydrogen sulfite



It is easily seen that, if the stoichiometric constraint $3[\text{IO}_3^-]_0 > [\text{HSO}_3^-]_0$ is fulfilled, then the iodine formed from the excess of iodate is no longer removed by hydrogen sulfite resulting in the appearance of the following equilibrium



The time necessary for the removal of all the hydrogen sulfite molecules is therefore unambiguously determined by the rate laws of the rate-determining steps (eqs 1 and 2) having much slower rate constants than that of eq 3, and is usually called as the Landolt time (t_i). This quantity has been thoroughly studied since Landolt's original discovery, but survey of the literature has revealed rather diverse concentration dependence of the Landolt time. In 1917, Eggert showed⁵ that t_i is independent of the concentration of sulfite ion, and inversely proportional to the square of the concentration of both the iodate and the hydrogen ions. Even an approximate formula was established

$$t_i = \frac{1}{(k_2 - k_1)} \ln\left(\frac{k_2}{k_1}\right) \quad (5)$$

where k_1 and k_2 are the rate constants assigned to the Landolt and Dushman reaction, respectively. It was also demonstrated

qualitatively that iodide ion decreases t_i , but no exact formula was derived indicating the dependence of t_i on the concentration of iodide. Half a decade later, Skrabal showed⁶ in both buffered and unbuffered media that if all the concentrations (iodide, iodate, and hydrogen ions) were chosen large with respect to hydrogen sulfite then t_i is linearly proportional to the concentration of hydrogen sulfite, but inversely proportional to the concentration of iodate and inversely proportional to the square of the concentration of both the iodide and the hydrogen ions

$$t_i = R \frac{[\text{HSO}_3^-]}{[\text{IO}_3^-][\text{I}^-]^2[\text{H}^+]^2} \quad (6)$$

where R is a constant. In 1968, Church and Dreskin established⁷ a simple relationship between t_i and the concentration of the reactants in unbuffered medium:

$$t_i = \frac{0.0037 \text{ M}^2 \text{ s}}{[\text{IO}_3^-][\text{HSO}_3^-]} \quad (7)$$

Our recent study⁸ has just revealed that though the inverse of t_i depends linearly on the concentration of iodate, $1/t_i$ is proportional to the combination of the concentration and the square of the concentration of both iodide and hydrogen ions in buffered medium. The hydrogen sulfite dependence, however, was found to be even more complex; the Landolt time went through a minimum as a function of hydrogen sulfite concentration.⁸ As easily seen, these observations on the concentration dependence of t_i or at least part of them apparently contradict to each other. Therefore, one would really expect that there must exist a general formula for the concentration dependence of the Landolt time based on which majority of these seemingly contradictory observations may be adequately explained. Derivation of such a complex formula, however, requires exact knowledge of the rate equations of the subsystems.

The apparent simplicity of the iodate–hydrogen sulfite reaction would suggest relatively simple rate equations for eqs 1 and 2, but survey of the literature has revealed several alternative recommendations for them. The rate law for eq 1 was first proposed independently by Eggert⁵ and Skrabal⁶ to be

$$v_1^{\text{es}} = k_1^{\text{es}}[\text{SO}_3^{2-}][\text{IO}_3^-][\text{H}^+] \quad (8)$$

Shortly later, it was slightly modified by Skrabal and Zahorka:⁹

* Corresponding author. E-mail: horvatha@chem.u-szeged.hu.

$$\nu_1^z = k_1^z[\text{HSO}_3^-][\text{IO}_3^-][\text{H}^+] + k_1''[\text{HSO}_3^-]^2[\text{IO}_3^-] \quad (9)$$

After a considerable period of inactivity, the extensive studies on the oscillating reactions have brought the Landolt reaction into the focus of interest. Large-amplitude pH oscillations were discovered¹⁰ in the Landolt reaction perturbed by ferrocyanide in continuously stirred tank reactor (CSTR) and soon after its detailed mechanism was published by two independent research groups^{11,12} in which the rate equation published originally by Skrabal⁶ was used to interpret the dynamical behavior of the system. Shortly after that, Rábai and Beck^{13,14} observed large-amplitude batch oscillations in the Landolt reaction in the presence of thiosulfate. An empirical rate law was also suggested to explain the batch oscillation in which a complicated rate equation was used for the Landolt reaction:

$$\nu_1^r = [\text{IO}_3^-][\text{HSO}_3^-](k_1^r[\text{H}^+] + k_1'^r[\text{HSO}_3^-] + k_c[\text{S}_2\text{O}_3^{2-}][\text{H}^+]^2 + k_c'[\text{S}_2\text{O}_3^{2-}][\text{H}^+]^3) \quad (10)$$

Our recent studies^{8,15} have, however, just revealed that simple supercatalytic effect of hydrogen ion is sufficient to take all the major experimental facts into account quantitatively. We suggested the following rate equations for the Landolt (eq 1) and Dushman (eq 2) reactions:¹⁵

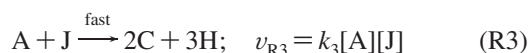
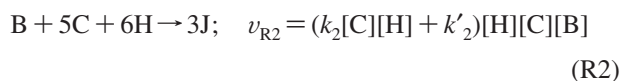
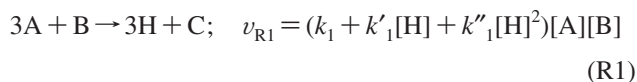
$$\nu_1^h = k_1[\text{HSO}_3^-][\text{IO}_3^-] + k_1'[\text{HSO}_3^-][\text{IO}_3^-][\text{H}^+] + k_1''[\text{HSO}_3^-][\text{IO}_3^-][\text{H}^+]^2 \quad (11)$$

$$\nu_2^h = k_2[\text{I}^-]^2[\text{IO}_3^-][\text{H}^+]^2 + k_2'[\text{I}^-][\text{IO}_3^-][\text{H}^+] \quad (12)$$

Having these rate equations in hand, numerical integration of our model has predicted all the concentration dependence of the Landolt time well.⁸ The question, however, still remained to be answered whether a general formula may be derived indicating the exact concentration dependence of the Landolt time. The aim of our paper is, therefore, to find an exact formula for t_i and to show how the earlier, apparently contradictory, observations may be explained and reconciled. Recent renewed interest of spatio-temporal behavior of the iodate–hydrogen sulfite system also justifies the efforts to understand the intimate details of the kinetics of the Landolt reaction.^{16–20}

Results

We have recently shown in our previous paper⁸ that the following kinetic model is capable of good description of the concentration dependence of the Landolt time:



where A, B, H, C, and J correspond to hydrogen sulfite, iodate, hydrogen ion, iodide ion, and iodine, respectively. Note that sulfate and water are not included for the sake of simplicity. The values of the rate constants were determined as follows: $k_1 = 0.146 \text{ M}^{-1} \text{ s}^{-1}$, $k_1' = 3970 \text{ M}^{-2} \text{ s}^{-1}$, $k_1'' = 3.02 \times 10^5 \text{ M}^{-3} \text{ s}^{-1}$, $k_2 = 2.21 \times 10^9 \text{ M}^{-4} \text{ s}^{-1}$ and $k_2' = 24.9 \text{ M}^{-2} \text{ s}^{-1}$. During the induction period steady-state approximation may be applied to species J:

$$k_3[\text{A}][\text{J}] = 3[\text{H}][\text{C}][\text{B}](k_2[\text{H}][\text{C}] + k_2') \quad (13)$$

According to steps R1–R3, the concentration of C (iodide) is governed by the following differential equation after substitution of eq 13:

$$\frac{d[\text{C}]}{dt} = \nu_{\text{R1}} - 5\nu_{\text{R2}} + 2\nu_{\text{R3}} = (k_1 + k_1'[\text{H}] + k_1''[\text{H}]^2)[\text{A}][\text{B}] + (k_2[\text{C}][\text{H}] + k_2')[\text{H}][\text{C}][\text{B}] \quad (14)$$

Two separate cases should be distinguished before solving the differential equation, namely the one in which [H] is kept constant (buffered solutions) and the other where [H] changes as the reaction proceeds (unbuffered solutions).

Buffered Medium. If [H] is kept constant, i.e., buffer is applied, then the following differential equation is valid:

$$\frac{dx}{dt} = K_1([\text{A}]_0 - 3x)([\text{B}]_0 - x) + ([\text{C}]_0 + x) \times ([\text{B}]_0 - x)(K_2([\text{C}]_0 + x) + K_3) \quad (15)$$

where x is the reaction coordinate, and subscript zero means the initial concentration of the given reactant. K_1 , K_2 , and K_3 are defined as follows:

$$K_1 = k_1 + k_1'[\text{H}]_0 + k_1''[\text{H}]_0^2; \quad K_2 = k_2[\text{H}]_0^2; \quad K_3 = k_2'[\text{H}]_0 \quad (16)$$

Taking into account that the appearance of the sudden color change takes place when x reaches $[\text{A}]_0/3$, and rearranging eq 15 followed by separation of the variables and integration leads to the following equation:

$$\int_0^{[\text{A}]_0/3} \frac{1}{([\text{B}]_0 - x)(K_2x^2 + Vx + K_1[\text{A}]_0 + W)} dx = \int_0^{t_i} dt \quad (17)$$

where

$$V = 2K_2[\text{C}]_0 + K_3 - 3K_1, \quad W = K_2[\text{C}]_0^2 + K_3[\text{C}]_0 \quad (18)$$

It should be kept in mind that the Landolt time can only be defined if the $3[\text{B}]_0 > [\text{A}]_0$ inequality is fulfilled that results in keeping A (hydrogen sulfite) as the limiting agent. By using the equality for the arctangent function below

$$\arctan(M) + \arctan(N) = \arctan\left(\frac{M+N}{1-M \cdot N}\right) \quad (19)$$

and solving eq 17 leads to the following expression:

$$t_i = \frac{1}{f_0} \ln \left(\frac{[\text{B}]_0}{3[\text{B}]_0 - [\text{A}]_0} \sqrt{\frac{K_2[\text{A}]_0^2 + 3V[\text{A}]_0 + 9(W + K_1[\text{A}]_0)}{W + K_1[\text{A}]_0}} \right) + \frac{V + 2K_2[\text{B}]_0}{f_0 \sqrt{4K_2(W + K_1[\text{A}]_0) - V^2}} \arctan \frac{\frac{2}{3}[\text{A}]_0 \sqrt{4K_2(W + K_1[\text{A}]_0) - V^2}}{4(W + K_1[\text{A}]_0) + \frac{2}{3}V[\text{A}]_0} \quad (20)$$

whereas

$$f_0 = f([\text{A}]_0, [\text{B}]_0, [\text{C}]_0, [\text{H}]_0) = K_2[\text{B}]_0^2 + V[\text{B}]_0 + W + K_1[\text{A}]_0 \quad (21)$$

To our best knowledge this is the most comprehensive exact formula for calculating the Landolt time (t_i) that involves all the concentration dependence (hydrogen sulfite, iodate, iodide,

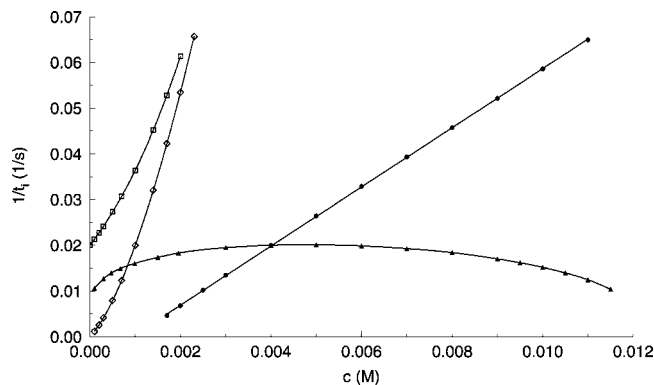


Figure 1. Reciprocals of the calculated (symbols and solid lines) Landolt time at different conditions in buffered media: (▲) $[A]_0$ changes $[B]_0 = 0.004$ M, $[C]_0 = 0.0$ M, $[H]_0 = 0.001$ M; (●) $[B]_0$ changes $[A]_0 = 0.004$ M, $[C]_0 = 0.0$ M, $[H]_0 = 0.001$ M; (□) $[C]_0$ changes $[A]_0 = 0.004$ M, $[B]_0 = 0.004$ M, $[H]_0 = 0.001$ M; (◇) $[H]_0$ changes $[A]_0 = 0.004$ M, $[B]_0 = 0.004$ M, $[C]_0 = 0.0$ M.

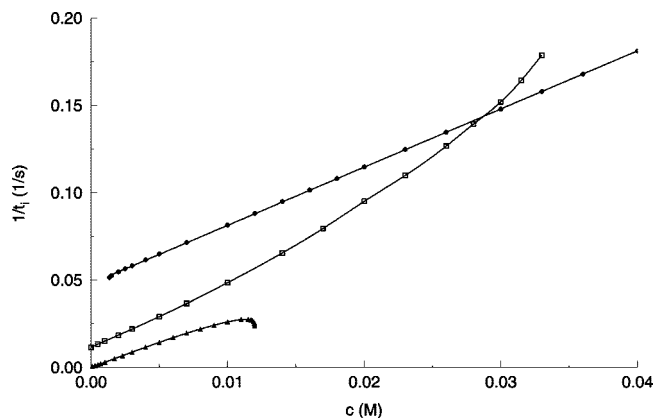


Figure 2. Reciprocals of the calculated (symbols and solid lines) Landolt time at different conditions in unbuffered media: (▲) $[A]_0$ changes $[B]_0 = 0.004$ M, $[C]_0 = 0.0$ M, $[H]_0 = 1 \times 10^{-5}$ M; (●) $[B]_0$ changes $[A]_0 = 0.004$ M, $[C]_0 = 0.0$ M, $[H]_0 = 1 \times 10^{-5}$ M; (□) $[C]_0$ changes $[A]_0 = 0.004$ M, $[B]_0 = 0.004$ M, $[H]_0 = 1 \times 10^{-5}$ M. Note that the curve showing the dependence on $[B]$ is shifted along the Y-axis by 0.05 to see the trends better.

and hydrogen ions) in buffered medium. Figure 1 shows the reciprocal of the Landolt time (t_i) calculated from eq 20 as a function of the concentration of the reactants. As seen, the inverse of the calculated Landolt time shows a maximum as a function of sulfite concentration, a mixed first- and second-order dependence on both the hydrogen and the iodide concentrations as well as a perfect linear dependence on the iodate concentration. These calculations are in complete coincidence with all the main characteristics of the experimental findings published recently.⁸

Unbuffered Medium. In absence of buffer, eq 15 can be rewritten as

$$\frac{dx}{dt} = k_1([A]_0 - 3x)([B]_0 - x) + k'_1([H]_0 + x)([A]_0 - 3x)([B]_0 - x) + k''_1([H]_0 + x)^2([A]_0 - 3x)([B]_0 - x) + k_2([H]_0 + x)^2([C]_0 + x)^2([B]_0 - x) + k'_2([H]_0 + x) \times ([C]_0 + x)([B]_0 - x) \quad (22)$$

Rearranging eq 22 followed by integration from 0 to $[A]_0/3$ leads to the following expression:

$$t_i = \int_0^{[A]_0/3} \{([A]_0 - 3x)([B]_0 - x)Q_1(x) + ([C]_0 + x) \times ([B]_0 - x)([H]_0 + x)Q_2(x)\}^{-1} dx \quad (23)$$

whereas

$$Q_1(x) = k_1 + k'_1([H]_0 + x) + k''_1([H]_0 + x)^2; \\ Q_2(x) = k_2([H]_0 + x)([C]_0 + x) + k'_2 \quad (24)$$

Unfortunately, no closed formula can be obtained from the right-hand side of eq 23 that would indicate the exact concentration dependence of the reactants in unbuffered medium. However, substituting the corresponding initial concentrations and the rate constants into eq 23 allows us to calculate numerically the Landolt time at any given experimental circumstances. Figure 2 shows the results of the numerically calculated reciprocals of the Landolt time as a function of different reactant concentrations in unbuffered solutions. The difference between the strikingly different shape of the concentration dependence of the reciprocal of t_i in buffered and unbuffered conditions (see Figures 1 and 2)—especially the hydrogen sulfite dependence—clearly justifies the separation of these two cases.

Discussion

As mentioned in the Introduction, apparent contradiction may be noticed regarding to the concentration dependence of the Landolt time. However, knowing the exact formula gives us an opportunity to discuss the observation of the earlier researches. As we shall see, almost all the seemingly different early suggestions for the concentration dependence of the Landolt time can be harmonized by the expressions given in eqs 20 and 23 depending on the experimental circumstances applied. Let us discuss these results chronologically.

Eggert's Result. The first result on the concentration dependence of the Landolt time was published by Eggert.⁵ It was demonstrated that t_i is independent of the concentration of hydrogen sulfite and inversely proportional to the square of the concentration of both the iodate and the hydrogen ion over a fixed range of reactant concentration. We shall see that in certain experimental circumstances—i.e., at low hydrogen sulfite concentration ($<10^{-5}$ M) in huge excess of iodate and in the absence of initial iodide—similar expression to eq 5 can be derived from eq 20. Substituting $[C]_0 = 0$ into eq 18 simplifies the first term of eq 20 (including only the logarithmic part) as

$$t_i(1) = \frac{1}{[B]_0^2 K_2 + [B]_0(K_3 - 3K_1) + K_1[A]_0} \times \ln \frac{[B]_0}{3[B]_0 - [A]_0} \sqrt{\frac{K_2}{K_1} [A]_0 + 3 \frac{K_3}{K_1}} \quad (25)$$

If $[A]_0$ is small ($<10^{-5}$ M) and $[H]_0$ is in the range where

$$K_2[B]_0^2 \ll |[B]_0(K_3 - 3K_1)| \quad (26)$$

inequality is fulfilled then

$$t_i(1) = \frac{1}{2[B]_0(K_3 - 3K_1)} \ln \frac{K_3}{3K_1} \quad (27)$$

If the conditions mentioned above applied for the second term of eq 20 (including only the arctangent part) then $V^2 > 4K_2(W + K_1[A]_0)$ inequality results that the argument of arctangent is an imaginary number. Bearing in mind, however, that

$$\arctan(i \cdot x) = i \cdot \ln \sqrt{\frac{1+x}{1-x}} \quad (28)$$

the second term of eq 20 may be transformed into the following expression:

$$t_i(2) = \frac{1}{[B]_0(K_3 - 3K_1)} \ln \sqrt{\frac{1 + \frac{1}{\frac{6K_1}{V} + 1}}{1 - \frac{1}{\frac{6K_1}{V} + 1}}} \quad (29)$$

Rearranging eq 29 leads to the following simple form:

$$t_i(2) = \frac{1}{2[B]_0(K_3 - 3K_1)} \ln \frac{K_3}{3K_1} \quad (30)$$

that gives us an approximation for the Landolt time as

$$t_i = t_i(1) + t_i(2) = \frac{1}{[B]_0(K_3 - 3K_1)} \ln \frac{K_3}{3K_1} \quad (31)$$

It is, however, worthwhile to note the striking agreement between $t_i(1)$ and $t_i(2)$, i.e., the contribution of the arctangent and the logarithmic part of the Landolt time equals to each other at these conditions. As one may easily notice, eq 31 is quite similar to eq 5. The only difference is that eq 31 explicitly expresses the linear proportionality of the inverse of the Landolt time on the concentration of iodate under these experimental circumstances in contrast to Eggert's work that established quadratic iodate dependence. The reason for this essential difference is still unclear, but it might either be the consequence of the limited concentration range of the reactants whereas the rate laws established may apply or a possible experimental artifact of Eggert's work.

It seems to be also interesting to examine the simplified kinetic model leading to this expression for the Landolt time. Assuming that $[A]_0$ (initial hydrogen sulfite concentration) is small at moderate pH leads to low $[C]$ (iodide concentration) resulting that the Dushman reaction is governed by the rate term containing only the first-order iodide dependence. In this case, eq 15 can be transformed into the following form if $[B]_0 \gg [A]_0$:

$$\frac{dx}{dt} = K_1([A]_0 - 3x)[B]_0 + K_3[B]_0x \quad (32)$$

The solution of this differential equation directly leads to eq 31 for t_i meaning that Eggert's early results might already contain information about the rate term of the Dushman reaction being first order with respect to iodide ion, but remained unnoticed for decades!

Skrabal's Result. Skrabal investigated the dependence of the Landolt time at quite different experimental conditions. It was shown in his early paper⁶ that if all the concentrations were chosen large with respect to hydrogen sulfite then the Landolt time can be given by eq 6, i.e., it is linearly proportional to the concentration of hydrogen sulfite, inversely proportional to that of the iodate, and inversely proportional to the square of both the iodide and the hydrogen ion concentrations. We shall see that this expression can also be derived from our comprehensive formula (eq 20) under these circumstances and even the proportionality constant R can be explicitly determined from the rate coefficients. If $[B]_0, [H]_0, [C]_0 \gg [A]_0$, then $W \gg K_1[A]_0$, so

$$\sqrt{\frac{[A]_0^2 K_2 + 3[A]_0 V + 9(W + K_1[A]_0)}{W + K_1[A]_0}} \approx 3 + \frac{[A]_0 V}{2W}, \quad (33)$$

therefore the first term of eq 20 (the logarithmic part) may be simplified as follows:

$$t_i(1) = \frac{\ln \left(1 + \frac{[A]_0 \left(1 + \frac{[B]_0 V}{2W} \right)}{3[B]_0 - [A]_0} \right)}{[B]_0^2 K_2 + [B]_0 V + W} \quad (34)$$

Since the conditions applied result that the argument of the logarithm is approximately 1 in eq 34, one may easily obtain the following expression for the first (logarithmic) term of eq 20:

$$t_i(1) = [A]_0 \frac{1 + \frac{[B]_0 V}{2W}}{3[B]_0(K_2[B]_0^2 + [B]_0 V + W)} \quad (35)$$

If all the concentrations were chosen large with respect to hydrogen sulfite, then the second term of eq 20 can be expressed as follows since $\arctan(y) \approx y$ if y is small:

$$t_i(2) = \frac{V + 2[B]_0 K_2}{6W(K_2[B]_0^2 + [B]_0 V + W)} [A]_0 \quad (36)$$

It means that the Landolt time can be written as

$$t_i = t_i(1) + t_i(2) = [A]_0 \left(\frac{1 + \frac{[B]_0 V}{2W}}{3[B]_0(K_2[B]_0^2 + [B]_0 V + W)} + \frac{V + 2[B]_0 K_2}{6W(K_2[B]_0^2 + [B]_0 V + W)} \right) \quad (37)$$

After straightforward algebraic manipulation, the expression for the Landolt time can be simplified to

$$t_i = \frac{[A]_0}{3[B]_0 W} = \frac{1}{3k_2} \frac{[A]_0}{[B]_0 [C]_0^2 [H]_0^2} \quad (38)$$

Equation 38 suggests that the proportionality constant R equals to the inverse of three times the rate coefficient (k_2) of the Dushman reaction. In other words, it means that at large hydrogen ion, iodide and iodate concentrations all the hydrogen sulfite molecules are exclusively removed by iodine formed from the Dushman reaction as expected. Therefore, one may easily realize that the Landolt time (t_i) has nothing to do with the Landolt reaction itself in these experimental circumstances.

Church and Dreskin's Result. In unbuffered solution, Church and Dreskin⁷ established a simple relationship between the Landolt time and the concentration of the reactants. Unfortunately, as we have seen previously, no exact formula could be obtained for t_i from eq 23, but the results from the numerical integration of eq 23 might reveal the origin of eq 7. Figure 3 shows the logarithm of t_i calculated from eq 23 as a function of the logarithm of the product of the hydrogen sulfite and the iodate concentration. As seen, an almost perfect straight line may be obtained if the initial concentration of the reactants is kept close to each other; i.e., no extreme excess of either of the reactants is applied. Even the constant obtained from our

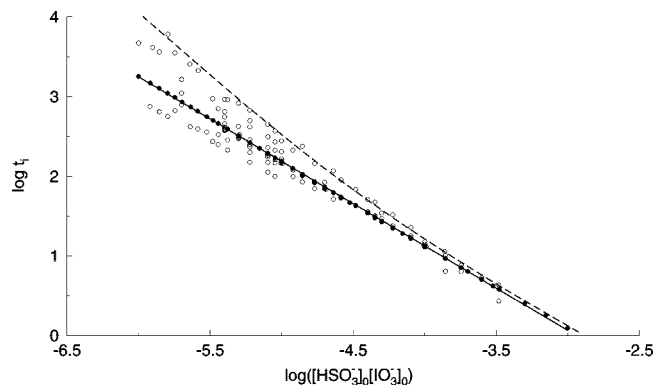


Figure 3. Logarithm of the calculated Landolt time as a function of the logarithm of the product of iodate and hydrogen sulfite concentration. Symbols represents, where the concentrations of hydrogen sulfite and iodate are equal (●) or not equal (○). Solid line shows the regression of those points where the initial concentration of the reactants is equal with each other. The slope and the intercept were found to be -1.06 ± 0.02 and -3.12 ± 0.01 , respectively. The dashed line represents the result of calculation where $[\text{HSO}_3^-]_0/[\text{IO}_3^-]_0 = 2.99$.

calculation $(7.59 \pm 0.18) \times 10^{-4} \text{ M}^2 \text{ s}$ is in acceptable agreement with the one ($0.0037 \text{ M}^2 \text{ s}$) determined by Church and Dreskin.⁷ The agreement is even better if we fit the Landolt time as a function of the product of the reactant concentrations by a hyperbolic function. In the latter case, a value of $(1.75 \pm 0.06) \times 10^{-3} \text{ M}^2 \text{ s}$ can be obtained for the constant of eq 7. The difference between these values stems from the fact that in the case of the linear plot a slightly higher value than 1 is obtained for the slope.

If, however, iodate is in large excess or the $[\text{HSO}_3^-]_0/[\text{IO}_3^-]_0$ ratio approaches 3 (dashed line of Figure 3), especially at lower concentrations, then significant deviation can be calculated from the predicted straight line. Therefore, we concluded that the empirical formula given by Church and Dreskin is not a general law for calculating the Landolt time in the whole concentration space, although it works properly in limited concentration ranges of the reactants. As seen in Figure 2, there is a considerable concentration range of both iodate and hydrogen sulfite where the Landolt time is inversely proportional to these concentrations. The slopes of these straight lines are approximately equal to each other, and therefore it provides the emergence of the dependence of t_i on the product of the iodate and hydrogen sulfite concentration. It should, however, be definitely emphasized in favor of Church and Dreskin that far from both the huge excess of iodate and $[\text{HSO}_3^-]_0/[\text{IO}_3^-]_0 = 3$ ratio, the logarithm of the theoretically calculated Landolt time may be treated as a linear function of the logarithm of the product of the reactant concentrations with having acceptable standard deviations in the case of real experiments. Therefore, their final conclusion—no surprise at all—can straightforwardly be drawn by any chemists though the theoretical calculations do not support it as a general law.

Conclusion

A complex expression for the concentration dependence of the Landolt time has been derived from the extended kinetic model of the Landolt and Dushman reactions proposed recently.⁸ To our best knowledge, this is the most comprehensive formula for the Landolt time containing the exact concentration dependence of the reactants hydrogen sulfite and iodate as well as that of the iodide and hydrogen ions. It is also shown that the previously obtained expressions for calculating the Landolt time are restricted to only relatively narrow concentration ranges but can readily be derived from our comprehensive formula. The only point that cannot be directly explained by our equation is the pure quadratic iodate dependence of the inverse of the Landolt time⁵ suggested by Eggert. It is also interesting to note that the simple expression found by Church and Dreskin⁷ is rather the result of the usage of the limited concentration range used in their experiments than a general law. In favor of them, however, it should be emphasized again that even the theoretically calculated logarithm of the Landolt time plotted against the logarithm of the product of the reactant concentrations—in certain reactant concentration range—may be misinterpreted as if eq 7 is a general law.

Acknowledgment. This work was supported by the Hungarian Research Fund (OTKA Grant No. K68172). A.K.H. is grateful for the financial support of the János Bolyai Research Scholarship of the Hungarian Academy of Sciences.

References and Notes

- (1) Landolt, H. *Chem. Ber.* **1885**, *18*, 249.
- (2) Landolt, H. *Chem. Ber.* **1886**, *19*, 1317.
- (3) Dushman, S. J. *J. Phys. Chem.* **1904**, *8*, 453.
- (4) Yiin, B. S.; Margerum, D. W. *Inorg. Chem.* **1990**, *29*, 1559.
- (5) Eggert, J. Z. *Elektrochem. Angew. Phys. Chem.* **1917**, *23*, 8.
- (6) Skrabal, A. Z. *Elektrochem. Angew. Phys. Chem.* **1922**, *28*, 224.
- (7) Church, J. A.; Dreskin, S. A. *J. Phys. Chem.* **1968**, *72*, 1387.
- (8) Csekő, Gy.; Varga, D.; Horváth, A. K.; Nagypál, I. *J. Phys. Chem. A* **2008**, *112*, 5954.
- (9) Skrabal, A.; Zahorka, A. Z. *Elektrochem. Angew. Phys. Chem.* **1927**, *33*, 42.
- (10) Edblom, E. C.; Orbán, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1986**, *108*, 2826.
- (11) Gáspár, V.; Showalter, K. J. *Am. Chem. Soc.* **1987**, *109*, 4869.
- (12) Edblom, E. C.; Györgyi, L.; Orbán, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1987**, *109*, 4876.
- (13) Rábai, Gy.; Beck, M. T. *J. Phys. Chem.* **1988**, *92*, 2804.
- (14) Rábai, Gy.; Beck, M. T. *J. Phys. Chem.* **1988**, *92*, 4831.
- (15) Horváth, A. K. *J. Phys. Chem. A* **2008**, *112*, 3935.
- (16) Keresztessy, A.; Nagy, I. P.; Bazsa, Gy.; Pojman, J. A. *J. Phys. Chem.* **1995**, *99*, 5379.
- (17) Pojman, J. A.; Komlósi, A.; Nagy, I. P. *J. Phys. Chem.* **1996**, *100*, 16209.
- (18) Li, G.; Ouyang, Q.; Swinney, H. L. *J. Chem. Phys.* **1996**, *105*, 10830.
- (19) Labrot, V.; Hochedez, A.; Cluzeau, P.; De Kepper, P. *J. Phys. Chem. A* **2006**, *110*, 14043.
- (20) Szalai, I.; De Kepper, P. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1105.

JP803790E