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Kinetics of Iodine Hydrolysis

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Introduction

The hydrolysis of iodine plays an important role in many inorganic and organic redox and substitution reactions. It is also a component reaction of many chemical oscillators. Surprisingly, there are only two direct measurements of the kinetics of this reaction: Eigen and Kustin[1] (1962) and Palmer and van Eldik[2] (1986). Both groups studied the kinetics of the reaction by temperature-jump; yet, even though both groups obtained similar relaxation times, they reported substantially different rate constants. We have analyzed both studies and find that Palmer and van Eldik's contains several inconsistencies in interpretation. We address these problems in detail and present a consistent set of rate and equilibrium constants for this apparently simple but actually complex system.

Analysis

The overall stoichiometry of iodine hydrolysis between pH 2 and 7 is

$$I_2 + H_2O \rightleftharpoons HOI + I^- + H^+ \qquad (1)$$

A significant portion of the iodide produced reacts with iodine to form triiodide, depending on initial iodine concentration. Because of its high molar absorptivity, triiodide is a convenient indicator of changes in equilibria or kinetics in eq 1, and was used by both groups for detecting the relaxation process. In the pH range 3–7, the mechanism proposed by Eigen and Kustin is given by reactions 2–5 (Table I). This reaction sequence was also accepted by Palmer and van Eldik. Other equilibrium processes needed for a more complete description of the system at different pH values are also listed in Table I.

We used reactions 2 and 4–7 as independent equilibria for performing equilibrium concentration calculations[3] (Figure 1). Below pH 2, protonation of HOI is significant, and the iodine hydrolysis becomes independent of pH at pH <0. The stoichiometry of iodine hydrolysis is then given by reaction 8. At pH >7, iodine starts to decrease significantly and I_2OH^- builds up.

Table I. Equilibrium Processes in Iodine Hydrolysis

no.	reaction	equilibrium constant
1	$I_2 + H_2O \rightleftharpoons HOI + I^- + H^+$	$K_1 = 5.4 \times 10^{-13}\ M^2$ [a]
2	$I_2 + H_2O \rightleftharpoons I_2OH^- + H^+$	$K_2 = K_1/K_4 = 1.6 \times 10^{-10}\ M$
3	$I_2 + OH^- \rightleftharpoons I_2OH^-$	$K_3 = K_1/(K_4K_w) = 1.6 \times 10^4\ M^{-1}$
4	$I_2OH^- \rightleftharpoons HOI + I^-$	$K_4 = K_w/(K_7K_9) = 3.34 \times 10^{-3}\ M$
5	$I_2 + I^- \rightleftharpoons I_3^-$	$K_5 = 698\ M^{-1}$ [b]
6	$H_2OI^+ \rightleftharpoons HOI + H^+$	$K_6 = K_1/K_8 = 0.045,$[a] $0.03\ M$[c]
7	$HOI \rightleftharpoons IO^- + H^+$	$K_7 = 2.3 \times 10^{-11}\ M$[d]
8	$I_2 + H_2O \rightleftharpoons H_2OI^+ + I^-$	$K_8 = 1.2 \times 10^{-11}\ M$[c]
9	$IO^- + I^- + H_2O \rightleftharpoons$ $I_2OH^- + OH^-$	$K_9 = 0.13$[d]

[a] Allen, T. L.; Keefer, R. M. *J. Am. Chem. Soc.* **1955**, *77*, 2957. [b] Palmer, D. A.; Ramette, R. W.; Mesmer, R. E. *J. Soln. Chem.* **1984**, *13*, 673. [c] Bell, R. P.; Gelles, E. *J. Chem. Soc.* **1951**, 2734. [d] Chia, Y.-T. Ph.D. Thesis, University of California, Berkeley, 1958.

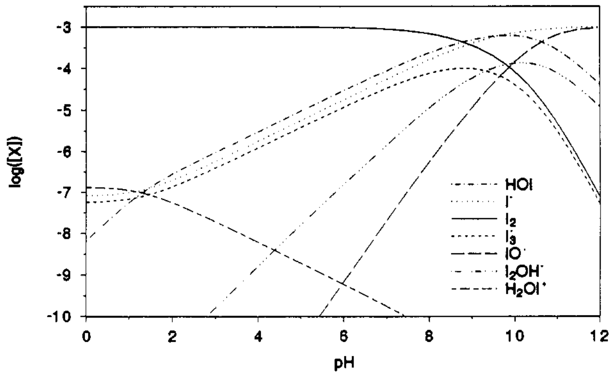

Figure 1. Concentration distribution in iodine hydrolysis using the first equilibrium constants given in Table I for reactions 2 and 4–7; $[I_2]_0 = 1.0 \times 10^{-3}$ M.

Above pH 9.5, hypoiodous acid starts to deprotonate to form IO^- ions. Above pH 7, the disproportionation of HOI to produce IO_3^- and I^- perturbs the pure equilibrium system, even at very short times. In the pH range 2–7, the equilibrium process is clear and is given by eq 1.

Eigen and Kustin used the following expression to obtain the overall rate constants for reaction 1:

$$k_{obs}^{EK} = k_1 + k_{-1}([HOI][I^-] + [H^+][I^-] + [HOI][H^+]) \qquad (10)$$

where k_{obs} is the reciprocal relaxation time. The derivation of this formula is detailed by Eigen and Kustin. Rate constant k_{-1} was determined from the slope of the k_{obs}^{EK} *vs* ($[HOI][I^-] + [H^+][I^-] + [HOI][H^+]$) curve, and k_1 was calculated from the equilibrium constant and k_{-1} because of the large error in the intercept.

Palmer and van Eldik used the following expression to obtain rate constants:

$$k_{obs}^{PE} = k_4 + k_{-4}([HOI] + [I^-]) \qquad (11)$$

They argued that, because reactions 2, 3, and 5 are fast, the relaxation time is related solely to process 4 and is pH *independent*. Chemical kinetics reasoning says, however, that if a reactive species of the rate-limiting step (I_2OH^-) participates in a rapid protonation equilibrium, then the observed rate constant will depend on pH. Palmer and van Eldik's expression states something quite different, but no derivation of eq 11 is given. (Prototypes of this mechanism are treated in relaxation kinetics texts, e.g., Bernasconi's monograph.[4] We derive the correct expression for the relaxation time below.) We calculated the pH dependence of the relaxation time by numerically integrating[5] the differential equation system derived from reactions 2–5 using the Palmer and van Eldik rate constants listed in the third column of Table II. The calculated relaxation time depends strongly on pH (Figure 2a) and is 20 times longer than the experimental relaxation time even at pH 7, where the reaction is fastest, and is almost 4 orders of magnitude longer at pH 3 than found experimentally.

Palmer and van Eldik assumed that reaction 4 is the slowest equilibrium process in the system and that its rate is well separated from the others; consequently, this process determines the relaxation time. We show here, however, that in the above mechanism it is impossible to construct a pH-independent relaxation time expression. Following Palmer and van Eldik, we let reactions 2, 3, and 5 be fast preequilibria. We choose reaction 3 to express the concentration of I_2OH^-, because the relaxation

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(1) Eigen, M.; Kustin, K. *J. Am. Chem. Soc.* **1962**, *84*, 1355.
(2) Palmer, D. A.; van Eldik, R. *Inorg. Chem.* **1986**, *23*, 928.
(3) Zékány, L.; Nagypál, I. In *Computational Methods for the Determination of Formation Constants*; Leggett, D. J., Ed.; Plenum Press: New York, 1985.
(4) Bernasconi, C. F. *Relaxation Kinetics*; Academic Press: New York, 1976.
(5) Ermentrout, B. *PhasePlane Version 3.0*; Wadsworth: Belmont, CA, 1990.

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Table II. Rate Constants for the Steps of Iodine Hydrolysis

rate const	E&K[a]	P&E[b]	this work
k_1 (s^{-1})	2.1		
k_{-1} (M^{-2} s^{-1})	3.1×10^{12}		
k_2 (s^{-1})	2.1	~ 2	3.2
k_{-2} (M^{-1} s^{-1})	1.6×10^{10}	$\sim 10^{10}$	2×10^{10}
k_3 (M^{-1} s^{-1})	$\sim 10^{10}$	$\sim 10^{10}$	8×10^{8}
k_{-3} (s^{-1})	$\sim 6 \times 10^{5}$	$\sim 3 \times 10^{5}$	5×10^{4}
k_4 (s^{-1})	3×10^{7}	994	1.34×10^{6}
k_{-4} (M^{-1} s^{-1})	5×10^{9}	3.2×10^{5}	4×10^{8}
k_5 (M^{-1} s^{-1})		6.2×10^{9} [c]	6.2×10^{9}
k_{-5} (s^{-1})		8.5×10^{6}	8.9×10^{6}
k_6 (s^{-1})			9×10^{8}
k_{-6} (M^{-1} s^{-1})			2×10^{10}
k_8 (s^{-1})			0.12
k_{-8} (M^{-1} s^{-1})			1×10^{10}

[a] Eigen and Kustin. [b] Palmer and van Eldik. [c] Turner, D. H.; Flynn, G. W.; Sutin, N.; Beitz, J. V. *J. Am. Chem. Soc.* **1972**, *94*, 1554.

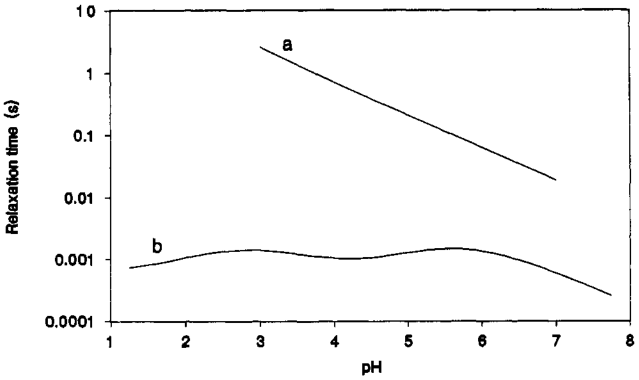

Figure 2. Calculated relaxation times in iodine hydrolysis using (a) Palmer and van Eldik's rate constants (third column, Table II) and (b) recommended rate constants from this work (fourth column, Table II).

time of reaction 3 is always shorter than 10 μs if k_3 is a diffusion-controlled rate constant. Consequently, for evaluating the relaxation time, we consider only reactions 3–5. The procedure to obtain the correct form for the van Eldik and Palmer relaxation time is as follows.[6]

1. With five variables (because the solutions are buffered, $[OH^-]$ and $[H^+]$ are not variables), two constraints ((a) $[I_2]_0 = [I_2] + [I_2OH^-] + [HOI]$; (b) $[HOI] = [I^-] + [I_3^-]$), and two rapid equilibria, the number of relaxation times is 1.

2. The relaxation equation for the iodide concentration is

$$\frac{d\delta_{I^-}}{dt} = k_4\delta_{I_2OH^-} - k_{-4}[HOI]\delta_{I^-} - k_{-4}[I^-]\delta_{HOI} \qquad (12)$$

where δ is the difference in concentrations between the initial state and the final equilibrium state.

3. It follows from the fast equilibrium processes and conservation equations that

$$\delta_{I_2OH^-} \cong -K_3[OH^-](1 + K_5[I_2])\delta_{I^-} \qquad (13)$$

$$\delta_{HOI} \cong (1 + K_5[I_2])\delta_{I^-} \qquad (14)$$

because $K_3[OH^-]$, $K_5[I^-] \ll 1$.

4. After back-substitution of eqs 13 and 14 into eq 12, we obtain for the relaxation time

$$k_{obs} = \frac{1}{\tau} = k_4\frac{K_3K_w}{[H^+]}(1 + K_5[I_2]) + k_{-4}\{[HOI] + [I^-](1 + K_5[I_2])\} \qquad (15)$$

Equation 15 implies that the relaxation time will depend strongly on pH. The triiodide equilibrium must also be used to obtain correct concentration dependences. With independently determined equilibrium constants, we can see that it is impossible to use the above equation to fit any type of pH-independent measurements in the pH range 3–7.

The cause of the large difference between experimental and calculated relaxation times that results from using Palmer and van Eldik's rate constants is their small value for the rate constant of the reaction between HOI and I^- (k_{-4}). At significantly larger values of k_{-4}, the condition that all the other processes are faster cannot hold. Therefore, contrary to Palmer and van Eldik's basic assumption, the mechanism cannot be separated into faster and slower processes, and the relaxation time expression for reactions 2–5 is not related to a single process.

Recommended Data Treatment

Because of the high iodine concentration, the only possible candidate for rapid equilibrium is iodine–triiodide. This postulate is confirmed by numerical integration; the relaxation time related to this process is about 0.1 μs. Therefore, the relaxation equations yield two relaxation times, because there are five species, two conservation equations, and only one rapid equilibrium in the system of reactions 2–5. The two relaxation times can be obtained by solving the characteristic equation of the following matrix:

$$\begin{pmatrix} a_{11} - 1/\tau & a_{12} \\ a_{12} & a_{22} - 1/\tau \end{pmatrix} \qquad (16)$$

where

$$a_{11} = k_2 + k_{-2}[H^+] + k_3[OH^-] + k_{-3}$$

$$a_{12} = (k_{-2}[H^+] + k_{-3})(1 + K_5[I_2])$$

$$a_{21} = k_4 + k_{-4}[I^-]^2$$

$$a_{22} = (k_4 + k_{-4}[I^-])(1 + K_5[I_2]) + k_{-4}[HOI]$$

Discussion

From the above, it is clear that the analysis of Palmer and van Eldik is not a reliable source of rate constants for component processes of iodine hydrolysis. Eigen and Kustin handled the problem in a simple way; they used an overall reaction with overall rate constants that satisfy the equilibrium conditions. Their equation is valid, where the contributions of reaction 8 and reaction 3 to the overall processes are less than 10%, and the reaction between HOI and I^- is diffusion limited. Numerical integration confirms that their *overall* rate constants give the desired relaxation times in the range of their experiments.

In the absence of the original relaxation curves, we cannot fit the parameters of the differential equation system. However, simple numerical integration to obtain relaxation times at different pHs with variation of the rate constants is feasible. To determine a more appropriate set of rate constants for the long relaxation time, we used diffusion-limited rate constants for protonation reactions and varied k_3 and k_{-4} without changing the equilibrium constants of reactions 3 and 4. The rate constants in the fourth column of Table II yield long relaxation times (Figure 2b) which have two flat maxima over the pH range 1.5–6.5. Choosing a higher value for k_3 will significantly decrease the relaxation times at higher pHs; increasing k_{-4} decreases the relaxation time at lower pHs. The accuracy of *T*-jump experiments is usually not sufficiently high to detect such small variations in the long relaxation time due to change in pH.

From the concentration distributions, at pH <2 a significant amount of H_2OI^+ builds up, and its reaction with iodide will give a sizable and increasing contribution to the reverse of reaction 1 as the proton concentration increases. At high pH (>7), the

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(6) Hammes, G. G.; Steinfeld, J. I. *J. Am. Chem. Soc.* **1962**, *84*, 4639.

major route of iodine hydrolysis proceeds through $I_2 + OH^-$, which becomes faster as pH increases.

Most iodine-containing oscillatory reactions occur in highly acidic media. If one were to use reaction 1 in a highly acidic medium, the concentration of iodide calculated from reaction 1 would be lower than in the real situation. Furthermore, with decreasing pH, the value of $k_{-1}[H^+]$ needed to fit the data will be larger than allowed for a second-order diffusion-controlled process. The solution is to change the mechanism to reaction 8 and to assume $H_2OI^+ + I^-$ is diffusion controlled. This assumption is justified, because HOI and H_2OI^+ are expected to behave similarly. The standard redox potentials for two-electron oxidation are close (0.985 and 1.030 V),[7] for example. Electrostatic considerations suggest that H_2OI^+ should react at least as fast with I^- as HOI does. Since the latter reaction is also nearly diffusion controlled, $H_2OI^+ + I^-$ should be diffusion controlled.

Above pH 6 the forward rate of iodine hydrolysis using reaction 1 should be independent of pH. From modeling calculations, however, we know that the reaction occurs mainly through the $I_2 + OH^-$ reaction, which is pH dependent and becomes faster with increasing pH. In this case, it would be better to use the equation

$$I_2 + OH^- \rightleftharpoons HOI + I^- \qquad K = \frac{[HOI][I^-]}{[I_2][OH^-]} = \frac{K_1}{K_w} \quad (17)$$

for describing the equilibrium, because it also contains information about the kinetics features; namely, the $I_2 + OH^-$ reaction is responsible for iodine consumption. This reaction is pH dependent, and the reverse reaction, in which HOI reacts with iodide, is a pH-independent process.

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(7) Bard, A. J., Parsons, R., Jordan, J., Eds. *Standard Potentials in Aqueous Solutions*; Marcel Dekker: New York, 1985.