# Kinetics and Mechanism of the Autoinhibitory Iodine-Thiocyanate Reaction<sup>1</sup>

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The kinetics and mechanism of the reaction between iodine and thiocyanate have been investigated in the pH range 1-9. Two limiting stoichiometries are found: at pH > 4,  $4I_2 + SCN^- + 4H_2O \rightarrow SO_4^{2-} + ICN + 7I^- + 8H^+$ ; at pH < 4,  $3I_2$ + SCN<sup>-</sup> + 4H<sub>2</sub>O  $\rightarrow$  SO<sub>4</sub><sup>2-</sup> + HCN + 6I<sup>-</sup> + 7H<sup>+</sup>. At 25.0 ± 0.1 °C and ionic strength 0.2 M (NaClO<sub>4</sub>) the expression for the rate of disappearance of total iodine,  $[I_2]_T$ , under initial conditions (time  $\rightarrow 0$ ) is  $(-1/a) d[I_2]_{T,0}/dt = k[SCN^-][I_2]_{T,0}/(1 + c_1)/(1 + c_2)/(1 + c_2)/$ +  $K_{10}[I^-])([I^-])$ , where a = 3 for pH < 4 and 4 for pH > 4, and  $K_{10} = [I_3^-]/([I_2][I^-])$ . Thus, the reaction occurs via pH-independent (A) and pH-dependent (B) pathways and  $k = A + B/[H^+]$  with  $A = (5.19 \pm 0.5) \times 10^{-4} \text{ s}^{-1}$  and B = (2.93) $\pm$  0.3)  $\times$  10<sup>-6</sup> M s<sup>-1</sup>. A mechanism is postulated consistent with this rate law involving the intermediate HOSCN. The pH-independent pathway proceeds through formation and hydrolysis of HOSCN. The pH-dependent pathway is initiated by nucleophilic attack of thiocyanate on HOI to give the same intermediate with rate constant  $k_{\rm B} = (3.67 \pm 0.9) \times 10^7$  $M^{-1}$  s<sup>-1</sup>. The initial rapid reaction is followed quickly by deceleration because product iodide inhibits the reaction by suppressing formation of HOI and forming relatively unreactive I<sub>3</sub><sup>-</sup>.

#### Introduction

A fruitful approach to the design of chemical oscillators is based on the oxidation of sulfite ion as in the "mixed Landolt" or EOE oscillator.<sup>3</sup> Other sulfur-based oscillators utilize methylene blue-sulfide-oxygen,<sup>4</sup> thiosulfate-chlorite,<sup>5</sup> sulfide-hydrogen peroxide,<sup>6</sup> thiosulfate-hydrogen peroxide-Cu(II),<sup>7</sup> and thiourea-bromate.<sup>8</sup> In addition, the reactions of thiocyanate ion in a continuous stirred tank reactor (CSTR) with chlorite,9 bromate,10 and hydrogen peroxide-Cu(II)<sup>11</sup> show oscillatory behavior. Although not oscillatory, the oxidation of thiocyanate by iodate is complex and proceeds through the intermediate iodine, which can also oxidize thiocyanate.<sup>12</sup> As a beginning step in the understanding of the rich chemistry involved in interactions between thiocyanate and iodine species, we report in this paper a study of the kinetics of the oxidation of thiocyanate by iodine in the pH range 1-9.

Iodine is a mild two-electron oxidant. The main sulfur-containing oxidation product with thiocyanate is sulfate.<sup>13</sup> Previous studies of the kinetics of the iodine oxidation of thiocyanate have resulted in conflicting results and mechanisms. For example, the mechanism postulated to explain the kinetics in basic solution rejects IOH as a redox participant and invokes reactive complexes such as  $I_2SCN^{-13}$  Studies in acidic media, where the reaction is much less rapid, indicate that the I<sub>2</sub>SCN<sup>-</sup> complex is inert,<sup>14</sup> and that IOH is redox active.<sup>15</sup> Since many sulfur-based oscillators such as hydrogen peroxide-thiosulfate are "pHregulated",<sup>7</sup> it is important to establish a mechanism over a pH range wide enough to embrace acidic as well as basic media. Therefore, experiments are described which cover such a pH range

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and for which a mechanism is proposed consistent with the entire data set.

### **Experimental Section**

Materials. The following analytical grade chemicals were used without further purification: resublimed iodine (Aldrich), silver nitrate (British Drug Houses), potassium thiocyanate, sodium perchlorate, sodium thiosulfate, potassium iodide (free-flowing granular), and perchloric acid 70% (Fisher). The perchloric acid was standardized with standard N/10 sodium hydroxide (Fisher). The iodine was standardized both spectrophotometrically and by titration against standard sodium thiosulfate with freshly prepared starch as indicator.

Methods. The reaction was followed by monitoring the absorbance of  $I_2$  and  $I_3^-$  at their experimentally determined isosbestic point of 474 nm ( $\epsilon = 830 \text{ M}^{-1} \text{ cm}^{-1}$ ), the redox potential at a platinum electrode with calomel reference electrode, the potential of an iodide-specific electrode, and the pH. Cyanide interferes with the quantitative measurement of iodide on a specific-ion electrode. The response from the iodide-specific electrode was thus assumed to arise from a combination of iodide and cyanide ions, except in the initial stages of the reaction where only iodide ion contributed.

The reactions were carried out in 25-mL quartz reactors with Teflon caps to prevent the escape of volatile iodine. Aqueous iodine solutions were prepared by vigorously shaking resublimed iodine with distilled water and allowing the solution to settle overnight before a spectrophotometric standardization was performed. Stock solutions were kept at  $8 \times 10^{-4}$  M. The standardized iodine solutions were stored in vessels wrapped in aluminum foil to exclude light irradiation. In this way, stock solutions could keep for 3 days without any appreciable decrease in iodine titer. All reactions were performed at  $25 \pm 0.1$  °C and 0.2 M ionic strength  $(NaClO_4)$ 

Initial Rate Measurements. Reaction progress was monitored spectrophotometrically. For total elapsed reaction times shorter than about 5 min, data were collected on a Hi-Tech SF-3L stopped flow spectrophotometer. After suitable amplification, the photomultiplier output is digitized via a 12-bit Metrabyte A/D converter and interfaced to a Tandy HD-1200 microcomputer for analysis. For longer times Beckman 25 or Perkin-Elmer 552A recording spectrophotometers were used. At least seven replicate runs were averaged for each initial rate data point.

Stoichiometric Determinations. Reaction mixtures of the iodine-thiocyanate reaction were kept for at least 48 h in sealed volumetric flasks wrapped in aluminum foil before any quantitative analyses were performed. In separate experiments, the initial iodine concentration was held constant at  $2 \times 10^{-4}$  M while the

<sup>(1)</sup> No. 49 in the series Systematic Design of Chemical Oscillators. No. 48: Orbán, M.; Epstein, I. R. J. Am. Chem. Soc., in press.

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Figure 1. Absorbance at 460 nm against time at different initial iodide concentrations showing the inhibitory effect of iodide.  $[I_2]_{T,0} = 2.00 \times 10^{-4} \text{ M}$ ,  $[\text{SCN}^-]_0 = 2.00 \times 10^{-4} \text{ M}$ .

initial thiocyanate concentration was gradually increased from  $5 \times 10^{-6}$  to  $5 \times 10^{-3}$  M. Each batch experiment was repeated at least seven times and quantitatively analyzed for iodine by thiosulfate titration and spectrophotometric measurement at 460 nm, for sulfate by barium sulfate precipitation, and for cyanide plus iodide by precipitation of silver cyanide and iodide.<sup>16</sup>

## Results

Stoichiometry. The stoichiometry of the reaction varies with pH. At pH > 4 we found the stoichiometry

$$4I_2 + SCN^- + 4H_2O \rightarrow SO_4^{2-} + 7I^- + ICN + 8H^+$$
 (R1)

and at pH < 2 the stoichiometry

$$3I_2 + SCN^- + 4H_2O \rightarrow SO_4^{2-} + 6I^- + CN^- + 8H^+$$
 (R2a)

In fact, at most of the experimental conditions, the stoichiometry was intermediate between (R1) and (R2a). That is, let the coefficient of iodine in the balanced equation be a; then, 3 < a < 4. At all pH conditions when iodine was in excess the 1:1 ratio of moles of thiocyanate consumed to moles of sulfate produced was maintained: we found 98% of the sulfate expected from (R1) or (R2a). At high pH the observed ratio of moles of thiocyanate consumed to moles of hydrogen ions produced was 1:8 (R1). At low pH this ratio was much more difficult to establish since the initial acid concentration was much greater than the acid produced by the reaction. The silver iodide plus silver cyanide assay in high acid was never found exactly as predicted by stoichiometry (R2a) and the precipitate was mainly AgI.

At high acid, the important equilibria

$$H^+ + CN^- \rightleftharpoons HCN$$
 (R3)

$$ICN + H^+ + I^- \rightleftharpoons HCN + I_2$$
 (R4)

are shifted to the right. Reactions performed in high acid produced a gas which we assumed to be HCN, explaining the low assay of AgI and, especially, AgCN. Thus a more appropriate stoichiometry in high acid is (R2b) where a = 3.

$$3I_2 + SCN^- + 4H_2O \rightarrow SO_4^{2-} + 6I^- + HCN + 7H^+$$
 (R2b)

Let the total iodine concentration be  $[I_2]_T$ ; then, reactions carried out with  $[SCN^-]_0 > [I_2]_{T,0}$  (where the subscript 0 denotes zero time) gave lower than expected assay values for sulfate (about 85% of the expected amount). This difference could be explained by depletion of iodine after incomplete oxidation of thiocyanate,



Figure 2. Dependence of initial rate on thiocyanate ion concentration. Linear least-squares analysis yields a small positive intercept experimentally indistinguishable from zero.  $[I_2]_{T,0} = 4.00 \times 10^{-4} \text{ M}, [H^+] = 1.00 \times 10^{-2} \text{ M}, [I^-]_0 = 5.00 \times 10^{-4} \text{ M}.$ 



Figure 3. Dependence of initial rate on total iodine concentration. Linear least-squares analysis yields a small positive intercept experimentally indistinguishable from zero.  $[H^+] = 1.00 \times 10^{-2} \text{ M}$ ,  $[SCN^-] = 5.00 \times 10^{-4} \text{ M}$ ,  $[I^-]_0 = 1.00 \times 10^{-4} \text{ M}$ .

e.g., formation of sulfur in oxidation states +2 and +4. In the absence of a driving force toward oxidation, intermediate oxidation states of sulfur can easily form polymeric species, without ever forming sulfate.

Reaction Dynamics. Initially, the reaction is fast and one notices a rapid decrease in the absorbance of iodine. There follows, however, a rapid deceleration after, typically, about a minute into the reaction. The onset of the deceleration is governed by the ratio of initial reactant concentrations,  $[SCN^{-}]_0/[I_2]_{T,0} = r$ . When r is high (e.g., r > 15), no inhibition of the reaction is observed and pseudo-first-order kinetics in the consumption of iodine obtain. When r is low (e.g., r < 0.2), inhibition is also not noticeable. When  $[SCN^{-}]_0 \sim [I_2]_{T,0}$ , especially for 0.5 < r < 2, the reaction autoinhibits.

Figure 1 shows typical traces of absorbance vs time at different initial iodide ion concentrations illustrating the inhibitory effect of iodide. Plots of initial rates against  $[SCN^-]_0$  (Figure 2) and  $[I_2]_{T,0}$  (Figure 3) are linear with intercepts experimentally indistinguishable from zero. Therefore, the reaction is first order with respect to each of  $[SCN^-]$  and  $[I_2]_T$ .

The extent of the first, rapid stage of the reaction is determined by r and the initial iodide concentration  $[I^-]_0$ . When r is low, 1 mol of thiocyanate consumes 1 mol of iodine in the first stage of the reaction. High iodide concentrations inhibit the first stage; when the initial iodide concentration is greater than or equal to the initial iodine concentration, the first stage disappears. In most experiments we used iodine concentrations higher than the initial thiocyanate concentrations, ensuring total oxidation of thiocyanate to sulfate. The inhibition is strongest when  $[I^-]_0 > [I_2]_{T,0}$ . When  $[I^-]_0$  is low, the initial rate is proportional to  $1/[I^-]_0$ ; when  $[I^-]_0$ 

<sup>(16)</sup> Vogel, A. I. Textbook of Quantitative Inorganic Analysis, 3rd ed.; Wiley: New York, 1961; p 1216.



Figure 4. Inverse acid dependence of initial rate. A positive intercept indicates existence of a pH-independent path.  $[I_2]_{T,0} = 2.00 \times 10^{-4} \text{ M},$  $[SCN^-]_0 = 1.00 \times 10^{-4} \text{ M}, [I^-]_0 = 1.00 \times 10^{-4} \text{ M}.$ 

is high, the initial rate varies as  $1/[I^-]_0^2$ . There is no distinct cutoff point; generally, both dependences exist, except in the extremes of either very high or very low iodide concentrations.

Acid inhibits the reaction and a plot of initial rate against  $1/[H^+]$  is linear with a positive intercept (Figure 4).

#### Mechanism

The experimental results suggest two plausible mechanisms represented by schemes A and B. In addition to the rapid scheme A

$$I_2 + SCN^- \rightleftharpoons I_2SCN^-$$
 (rapid) (R5)

$$I_2SCN^- \rightleftharpoons ISCN + I^-$$
 (rapid) (R6)

ISCN + H<sub>2</sub>O 
$$\xrightarrow{k_A}$$
 HOSCN + I<sup>-</sup> + H<sup>+</sup> (rate determining)  
(R7)

scheme B

$$I_2 + H_2O \Rightarrow HOI + I^- + H^+$$
 (rapid) (R8)

HOI + SCN<sup>- 
$$\xrightarrow{^{8}}$$</sup> HOSCN + I<sup>-</sup> (rate determining) (R9)

equilibria R5, R6, and R8 the following two rapidly established reactions are significant at high iodide ion (R10) and high hydroxide ion (R11) concentrations.

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$$I_2 + I^- \rightleftharpoons I_3^-$$
 (rapid) (R10)

$$IOH + OH^- \Rightarrow IO^- + H_2O$$
 (rapid) (R11)

The rate equation derived from schemes A and B is

$$\frac{1}{a} \frac{-\mathbf{d}[\mathbf{I}_2]_{\mathsf{T}}}{\mathbf{d}t} = \frac{k}{(1 + K_{10}[\mathsf{I}^-])[\mathsf{I}^-]} [\mathrm{SCN}^-][\mathbf{I}_2]_{\mathsf{T}}$$
(1)

where

$$k = A + \frac{B}{[\mathrm{H}^+]} = k_{\mathrm{A}} K_5 K_6 + \frac{k_{\mathrm{B}} K_8}{[\mathrm{H}^+]}$$
(2)

Absorbance is converted to concentration in eq 1 by use of  $(\epsilon_i l)$ , where  $\epsilon_i$  is the molar absorptivity coefficient (830 M<sup>-1</sup> cm<sup>-1</sup>) at the iodine-triiodide isosbestic point and l is the path length (0.2 cm for the stopped flow and 1.00 cm for either of the two spectrophotometers used).

In this treatment it is assumed that  $I_3^-$  does not undergo reactions analogous to (R5) and (R8). Since iodide is a product of the reaction, as the reaction proceeds, more iodide is produced, shifting the equilibrium in (R10) toward the right, and hence depleting the system of the reactive species,  $I_2$ . The depletion of iodine through formation of triiodide is the process that explains the observed autoinhibition.

Evaluation of the data when  $[I^-]$  is constant but  $1 > (K_{10}[I^-])$ yields the following values for the kinetics parameters A and B:  $A = (5.19 \pm 0.5) \times 10^{-4} \text{ s}^{-1}$  and  $B = (2.93 \pm 0.3) \times 10^{-6} \text{ M s}^{-1}$ . From the  $[H^+]$  dependence and the value of  $K_8$  under our conditions<sup>17</sup> we obtain  $k_{\rm B} = (3.6 \pm 0.9) \times 10^7 \,{\rm M}^{-1} \,{\rm s}^{-1}$ .

#### Discussion

Schemes A and B implicate two distinctly different chemical species in the initial elementary step of the oxidation of thiocyanate by iodine: molecular iodine and hypoiodous acid. We consider scheme A and iodine first, and then scheme B and hypoiodous acid.

Three processes can occur in an elementary step reaction between  $I_2$  and SCN<sup>-</sup>. They are electron transfer, atom transfer, and complex formation. It is possible to rule out electron transfer as a likely process for this reaction on thermodynamic grounds. Electron transfer from thiocyanate ion to molecular iodine would produce  $I_2^-$  and SCN<sup>•</sup>. Aqueous solution values of  $E^{\circ}(SCN^{\bullet}/$ SCN<sup>-</sup>) = 1.62 V and  $E^{\circ}(I_2/I_2^{-}) = 0.21 V^{18}$  can be combined to give  $\Delta E^{\circ} = -1.41$  V for the reaction  $I_2 + SCN^- \rightarrow I_2^- + SCN^{\circ}$ , which indicates a very unfavorable equilibrium. Despite the ease with which molecular iodine can be reduced to  $I_2^{-,19}$  its formation is prevented by the difficulty of forming the SCN<sup>•</sup> radical.

Electron-transfer reactions of a more complex nature have been considered such as (R12) and the half-reaction (R13).20-22

$$I_2 + 2SCN^- \rightleftharpoons (SCN)_2 + 2I^-$$
 (R12)

$$I_2 + 4SCN^- \rightleftharpoons 2I(SCN)_2^- + 2e^-$$
 (R13)

However, in our experiments we can ignore (R12) because thiocyanogen can oxidize iodide to iodine,<sup>23</sup> which means that equilibrium R12 lies to the left, and (R13) is possible only in the presence of strong oxidizing agents such as iodate and peroxide.12

The importance of complex formation is strongly implicated by scheme A. Indeed, it is possible that complex formation could lead to scission of the I-I bond without accompanying oxidation of thiocyanate as in (R14). The initial stage of the iodine-

$$I_2 + 2SCN^- \rightleftharpoons I(SCN)_2^- + I^- \qquad (R14)$$

thiocyanate reaction showed a rapid consumption of iodine which corresponded to roughly a 1:1 complex of iodine to thiocyanate. however.<sup>24</sup> This observation makes (R5) a more probable reaction than (R14).

For scheme A, (R6) is most important. There has been no prior evidence of its occurrence. Our experiments with an iodide-specific electrode have shown a rapid increase in iodide concentration during the initial stage of the reaction. The rapid increase in iodide cannot be attributed to hydrolysis reaction (R8) because the equilibrium is already established before the start of the reaction's initial stage. The increase in iodide cannot be attributed to (R9) either since this reaction is rate-determining. It remains that (R6) must be responsible for the initial increase in iodide concentration. It is possible that (R6) and (R5) combine to produce a composite reaction, (R15), as suggested by Briot and Smith,<sup>13</sup> since it is assumed that the establishment of their equilibria is rapid. This reaction

$$I_2 + SCN^- \rightleftharpoons ISCN + I^-$$
 (R15)

can also be thought of as a single-step atom transfer to generate ISCN, from which HOSCN arises by hydrolysis.

The interhalogen ISCN should have properties that lie between those of iodine and bromine. For example, thiocyanogen can oxidize iodide.23 Thus, although the hydrolysis equilibrium of iodine lies overwhelmingly to the left in neutral to acidic conditions,

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<sup>(22)</sup> Lewis, C.; Skoog, D. A. J. Am. Chem. Soc. 1962, 84, 1101. (23) Stedman, G.; Whincup, P. A. E. J. Chem. Soc. A 1969, 1145.

<sup>(24)</sup> The same observation was made in the oxidation of thiourea by

molecular bromine: Simoyi, R. H.; Epstein, I. R. J. Phys. Chem. 1987, 91, 5124.

we expect ISCN to have a higher hydrolysis equilibrium constant than iodine. Scheme A should therefore predominate in acidic media

Scheme B begins to contribute to the rate of the reaction as the concentration of IOH rises. The value we have obtained for  $k_{\rm B}$  is high, but it is approximately 2 orders of magnitude below the diffusion-controlled limit for two neutral species.<sup>25</sup> We expect this process to be rapid, since it can occur by nucleophilic attack of SCN<sup>-</sup> on IOH with an equilibrium that should lie far to the right.

As the iodide concentration increases, more of the unreactive  $I_3$  is formed. In addition, scheme A is retarded at (R6) and scheme B is retarded at (R8) by iodide. We have found no evidence for a pH-independent path at high iodide concentrations, and the data could be fit to scheme B only. Scheme B holds when the initial iodide concentration is high and at the later stages of the reaction, when  $[I_2]$  has decreased and  $[I^-]$  has gone up.

Nearly all oxidations of thiocyanate have been postulated to pass through HOSCN. Formation of HOSCN is accompanied by a decrease in pH, which we have observed in our experiments. Further reactions of HOSCN with itself and with iodine should lead rapidly to the formation of sulfate.<sup>26</sup> Such a sequence could, for example, be

> $2HOSCN \Rightarrow HO_2SCN + H^+ + SCN^-$ (R16)

$$HOSCN + I_2 + H_2O \rightarrow HO_2SCN + 2I^- + 2H^+$$
(R17)

 $HO_2SCN + I_2 + 2H_2O \rightarrow SO_4^{2-} + 2I^- + CN^- + 5H^+$  (R18)

Reactions R16-R18 should be fast, because a test for sulfates on the reaction mixture at the beginning of the reaction gives a positive result.

The oxidation of thiocyanate by hydrogen peroxide was also found to involve both a pH-independent and pH-dependent rate law.<sup>27,28</sup> The mechanism we have proposed covers a wide range of pH. The depletion of iodine (replaced by IOH) as the pH increased forced us to stop our kinetic analysis at pH 9, since we monitored the reaction at the isosbestic point of  $I_2$  and  $I_3^-$  and we could no longer obtain a reasonably strong spectrophotometric signal.

Autoinhibition is a striking feature of the iodine-thiocyanate reaction.<sup>29</sup> To develop an appreciation of its effects we have attempted to integrate eq 1. Straightforward integration is difficult, however, due to the complex stoichiometry that requires inclusion of  $I_3^-$  and IOH in the iodine mass balance relation. We have therefore used a simplified approach that still illustrates the main consequences of autoinhibition.

Consider a reaction between iodine and thiocyanate with no initially added iodide ion in aqueous solution buffered at pH 4. Under these conditions stoichiometry R1 prevails, [IOH] is small compared with  $[I_3^-]$ , and the total initially added iodine concentration, i, is related to the iodide produced by reaction R1 according to  $i \approx [I_2]_T - (4/7)[I^-]$  to a reasonably good approximation for at least 60-70% reaction. As outlined in the Appendix, an integrated equation in which time is related to the reaction progress variable  $x = [I^-]$  can be obtained. The awkwardness of the resulting expression prevents inversion of this equation to yield a dependence of, for example, concentration of iodide ion on time. However, since  $[I_2]_T = f(x)$  and t = g(x), it is possible to match calculated values of  $[I_2]_T$  and t, hence, absorbance and time, and to plot the result, which is shown in Figure 5.

The rapid decrease in absorbance over the first 60% of the reaction in the first  $3^{1}/_{2}$  min is followed by a relatively slower decrease as the autoinhibitory effect is manifested. In fact, under these conditions, the reaction requires an additional 10 min to go



Figure 5. Simulation of decrease in absorbance at 460 nm with increase in time for the autoinhibitory reaction between iodine and thiocyanate ion. Absorbance at zero time = 0.249. Method of integration outlined in Appendix.  $[I_2]_{T,0} = 3.00 \times 10^{-4} \text{ M}$ ,  $[\text{SCN}^-]_0 = 2.50 \times 10^{-4} \text{ M}$ ,  $k = 9.00 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ ,  $K_{10} = 770 \text{ M}^{-1}$ ,  $\epsilon_i = 830 \text{ M}^{-1} \text{ cm}^{-1}$ .

to 80% completion. A second-order reaction of similar stoichiometry but without autoinhibition requiring a comparable time for 80% completion would not exhibit as rapid an initial decrease in absorbance. To the experimentalist, one consequence of the autoinhibitory retardation of reaction progress in the later stages is a lack of reproducibility, as reactant concentrations are sensitive to effects of atmospheric oxidation and light-induced reactions. The disparity between the initial and final phases of the kinetics, which confers a multistep appearance to the reaction that it actually does not have, may well have contributed to the earlier conflicting studies of the kinetics and mechanism of this reaction.

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## Appendix

The approximate integration of eq 1 was carried out as follows. Conditions: pH constant between 2 and 4 so that reaction follows stoichiometry R1. Initial thiocyanate ion concentration in stoichiometric excess. No iodide ion initially present. Assumptions: amount of iodine hydrolysis at t = 0 is negligible. Triiodide ion formed in late stages of the reaction is not included in the iodine mass balance. Let the concentration of iodide ion produced in reaction R1 be x, and let  $i_{2,0}$  and  $s_0$  be total initial iodine and thiocyanate ion concentrations, respectively. Substitution of the relations  $[I_2]_T = i_{2,0} - (4/7)x$  and  $[SCN^-] = s_0 - (1/7)x$  into eq 1 followed by rearrangement and integration yields the following expression

$$7kt = \int \frac{(1+K_{10}x)x \, dx}{(i_{2,0} - (4/7x)(s_0 - (1/7)x)} + C_1 \quad (A1)$$

The method of partial fractions is used to simplify the integral in eq A1 by converting it into two integrals of form  $\int x \, dx/(m)$ -nx), which is available in a standard table of integrals such as that in the Handbook of Chemistry and Physics. The resulting integrated equation is solved for t.

 $t = [k(4s_0 - i_{2,0})]^{-1} \{ (7s_0K_{10} + 1)[x + 7s_0 \log (s_0 - (1/7)x)] -$  $[(7/4)i_{2,0}K_{10} + 1][x + (7/4)i_{2,0}\log(i_{2,0} - (4/7)x)] + C$ (A2)

Values of x were used to generate corresponding values of t and the absorbance,  $\epsilon_i l(i_{2,0} - (4/7)x)$ , at 460 nm. These values were then used to generate the plot shown in Figure 5.

**Registry No.** I<sub>2</sub>, 7553-56-2; SCN<sup>-</sup>, 302-04-5.

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