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Thiocyanogen as an Intermediate in the Oxidation of Thiocyanate by Hydrogen Peroxide in Acidic Aqueous Solution

James N. Figlar and David M. Stanbury*

Department of Chemistry, Auburn University, Auburn, Alabama 36849

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The kinetics of the reaction of H_2O_2 with excess SCN^- in acidic media was studied by use of Ti(IV) as an indicator for the concentration of H_2O_2. Pseudo-first-order behavior was realized by this method, and these data confirm the acid-catalyzed rate law and rate constant reported some 40 years ago for this reaction under conditions of excess H_2O_2. Under the same conditions except without Ti(IV), repetitive-scan spectra reveal the formation and decay of an intermediate that absorbs in the UV. In the proposed mechanism, HOSCN is produced in the first step and it is converted rapidly to $(SCN)_2$ through its equilibrium reaction with SCN^-. The observed intermediate is believed to be $(SCN)_2$, which decays on a longer time scale. Excellent global fits of this mechanism to the repetitive-scan data are obtained with rate constants constrained by the Ti(IV) data and published previously in our study of the ClO_2/SCN^- reaction. These fits yield a spectrum for $(SCN)_2$ that is characterized by $\lambda_{max} = 297$ nm and $\epsilon_{297} = 147$ M^{-1} cm^{-1}, in fine agreement with our prior report.

Introduction

The oxidative chemistry of thiocyanate has enjoyed continued interest in a variety of fields including, but not limited to, the following: oligooscillating reactions,[1−3] outer-sphere electron transfer,[4−6] and catalytic peroxidation by lactoperoxidase[7,8] and other peroxidases.[9−13] The mechanistic pathways associated with the evolution of the oxidized products of thiocyanate have been an area of strong debate and a source of often contradictory information.[14] In a recent report on the reaction of ClO_2 and SCN^-, it was noted that thiocyanogen $(SCN)_2$ is a likely intermediate in that reaction in 1 M $HClO_4$ and an aqueous spectrum of this species was extracted.[14] The complex mechanism proposed for that reaction was intimately tied to the decomposition of $(SCN)_2$ and offered reasonable rate constants for a number of steps, most importantly for the hydrolytic decomposition of $(SCN)_2$. The extracted spectrum for this species was found to overlap significantly with the broad absorbance band of the reactant ClO_2, which may have adversely affected the parameters of the fit. An independent confirmation of the spectrum of $(SCN)_2$ and its decay rate law would serve as an important test of the mechanism proposed for the ClO_2/SCN^- reaction and could make a valuable contribution to the general field of thiocyanate oxidative chemistry.

The present work discloses information on aqueous $(SCN)_2$ based on the reaction of H_2O_2 with SCN^-. This reaction was investigated in considerable detail about 40 years ago by Wilson and Harris, although without the benefit of modern spectrophotometric methods.[15,16] It was found that the reaction has a rate law that is first order in each of the reactants between pH 12 and 4,[15] but at higher acidities it is acid-catalyzed.[16] A recent capillary electrophoresis study of the acid-independent reaction has called the rate law into question, but no data were obtained bearing on the acid-catalyzed reaction.[17] Detailed studies by Wilson and Harris of the acid-catalyzed kinetics were performed under conditions of excess H_2O_2, and under these conditions the reaction shows mild inhibition by HCN, which is also a product. When the HCN inhibition can be neglected, the rate law simplifies to

$$-d[H_2O_2]/dt = k[H_2O_2][SCN^-][H^+] \qquad (1)$$

The overall reaction in acidic media is

$$3H_2O_2 + SCN^- \rightarrow HSO_4^- + HCN + 2H_2O \qquad (2)$$

Deviations from this ideal stoichiometry can occur through the formation of $S(CN)_2$ and its hydrolysis products. $S(CN)_2$ was proposed to arise through the reaction of HCN with an intermediate, HOSCN. The overall proposed mechanism had as initial steps

$$H_2O_2 + SCN^- + H^+ \rightarrow HOSCN + H_2O \qquad \text{(slow)} \quad (3)$$

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$$H_2O_2 + HOSCN \rightarrow HO_2SCN + H_2O \qquad \text{(fast)} \qquad (4)$$

Further reactions of HO_2SCN would lead to final products. Thus, the reaction of HCN with HOSCN could diminish the rate of consumption of H_2O_2 by as much as a factor of 2. More recent evidence for HOSCN as the product in the first step is the adherence of the third-order rate constant to a LFER (linear free energy relationship) correlating rates of reactions of nucleophiles with H_2O_2, all of which are believed to have analogous rate-limiting steps.[18] A potential complication in the reaction of H_2O_2 with SCN^- is copper catalysis, which can lead to oscillations and bistability.[19−21] Apparently this catalysis occurs only at high pH such that catalysis by adventitious copper ions can be neglected under the acidic conditions relevant to the present study.

In the course of our study of the reaction of ClO_2 with SCN^- in highly acidic media, we developed a mechanism in which the equilibrium between HOSCN and $(SCN)_2$ was central:

$$(SCN)_2 + H_2O \rightleftharpoons HOSCN + SCN^- + H^+ \qquad (5)$$

This equilibrium is as expected given that SCN^- is generally regarded as a pseudohalide. In view of equilibrium 5, it is reasonable to anticipate that the reaction of H_2O_2 with SCN^- would yield $(SCN)_2$ as an intermediate under conditions of high concentrations of H^+ and SCN^-. Moreover, through the study of the reaction with low concentrations of H_2O_2, the yield of HCN would be low enough that the complicating reaction of HOSCN with HCN could be avoided.

Accordingly, the present paper describes spectrophotometric studies of the reaction of H_2O_2 with excess SCN^- in acidic media. These studies afford an opportunity to test the ideas described above, to obtain a spectrum of aqueous $(SCN)_2$ without the spectral interferences encountered in our study of the ClO_2/SCN^- reaction, and to verify the kinetics of decomposition of $(SCN)_2$.

Experimental Section

Reagents. Aqueous solutions of hydrogen peroxide were prepared from sodium stannate stabilized and nonstabilized 30% stocks purchased from Fischer. The stock solutions were standardized iodometrically with freshly prepared thiosulfate (Fischer). Distilled deionized water was used for all dilutions and experiments. NaSCN (Baker and Fischer) was recrystallized from water, and thiocyanate concentrations were determined idometrically. Fischer 75% perchloric acid was used in these experiments without further purification. Titanium(IV) chloride (99.9%) was purchased from Aldrich and used without further purification.

Synthesis of Peroxotitanium(IV). TiO_2^{2+} was prepared by the methods described by Thompson[22] with few alterations. Fresh $TiCl_4$ (5 mL) was dispensed in a N_2 purged glovebox and immediately transferred to an exhaust hood and added dropwise to a 20−50 mL portion of water (note this reaction is extremely exothermic and must be performed with caution). The resultant solution was passed through a Dowex 50W-X8 H^+ cation exchange column which was pretreated with three passes of strong HCl followed by three passes of pH 2.0 $HClO_4$. The TiO^{2+} was eluted with 2 M $HClO_4$ and collected in 10 equivalent volume fractions. Concentrations of each fraction were determined spectroscopically as described previously[22] by adding an excess of peroxide to the TiO^{2+} solutions and measuring the absorbance of the resultant TiO_2^{2+} complex at 410 nm ($\epsilon_{410} = 717\ M^{-1}\ cm^{-1}$).

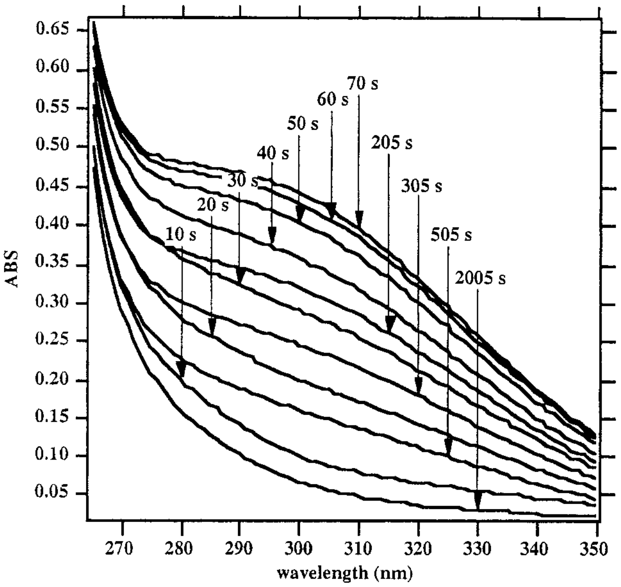

Figure 1. Multiwavelength rise and fall profile of the H_2O_2/SCN^- reaction. The raw kinetic data were taken on the HP 8453 spectrophotometer at 25 °C in 1 M $HClO_4$, path length 1 cm, $[H_2O_2]_o = 15$ mM, $[SCN^-]_o = 180$ mM. The data displayed are sparsed to highlight the rise−fall behavior in the UV.

Kinetic Methods. Kinetic measurements were conducted on a HP 8453 diode array spectrophotometer with a 1 cm cell. The temperature was maintained at 25 °C with a Brinkmann RM6 circulating water bath. In most experiments, the ionic strength (μ) was maintained at 1.25 M through the addition of appropriate amounts of $HClO_4$ and $LiClO_4$. Equal volumes of reactants were delivered to the cell which was then capped and vigorously stirred prior to measurements. Initial experiments indicated a photochemical reaction which deposited a white precipitate (presumably sulfur arising from SCN^- photolysis[23]) onto the cell walls at the beam point of entry and exit. This interference was negated by placing a UV optical cutoff filter (HP 08451-60302, 50% transmittance at 265 nm) in the light path prior to the sample. Spectral changes were monitored in the UV−vis region (265−400 nm) and analyzed additionally by using the Specfit software package.[24] Mechanistic simulations were also performed by utilizing the Specfit package.

Results

Detection of an Intermediate. Monitoring the direct reduction of H_2O_2 in excess thiocyanate (280 mM) in 1 M $HClO_4$ produces spectroscopic traces indicative of simple rise−fall behavior in the UV as shown by the overlay spectra in Figure 1. An alternative view is given by the single-wavelength trace at 410 nm shown in Figure 2. Qualitatively similar behavior was observed for a series of reactions with $[SCN^-]_0$ decreasing to 10 mM, although flooding conditions do not apply for the latter. Despite this seemingly uncomplicated biphasic kinetics, fitting the data at high $[SCN^-]$ was not achieved to any degree of success by employing a routine double-exponential function corresponding to a $A \rightarrow B \rightarrow C$ mechanism. Nevertheless, it is clear that an intermediate is produced, which absorbs in the UV. Its maximum absorbance at 295 nm is comparable to the absorbance reported to arise from $(SCN)_2$ produced in the reaction of ClO_2 with SCN^- under similar conditions.[14] The intermediate is produced on a time scale comparable to that for the consumption of H_2O_2 as predicted by Wilson and Harris' rate law for the reaction of H_2O_2 with SCN^-.[16] Qualitatively,

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Table 1. Mechanism for the Reaction of Hydrogen Peroxide and Thiocyanate

no.	reaction		rate constant
SR1	$H^+ + SCN^- + H_2O_2 \rightarrow HOSCN + H_2O$	k_1	$3.3 \times 10^{-2}\ M^{-2}\ s^{-1}$
SR2	$2HOSCN \rightarrow HO_2SCN + SCN^- + H^+$	k_{disp}	$8.0 \times 10^2\ M^{-1}\ s^{-1}$
SR3	$2HO_2SCN \rightarrow O_3SCN^- + HOSCN + H^+$		$2 \times 10^8\ M^{-1}\ s^{-1}$
SR4	$O_3SCN^- + H_2O \rightarrow HSO_4^- + HCN$		$5 \times 10^8\ s^{-1}$
SR5	$(SCN)_2 + H_2O \rightleftharpoons HOSCN + H^+ + SCN^-$	K_{hyd}	$4.4 \times 10^3\ s^{-1}$
			$3.05 \times 10^5\ M^{-2}\ s^{-1}$

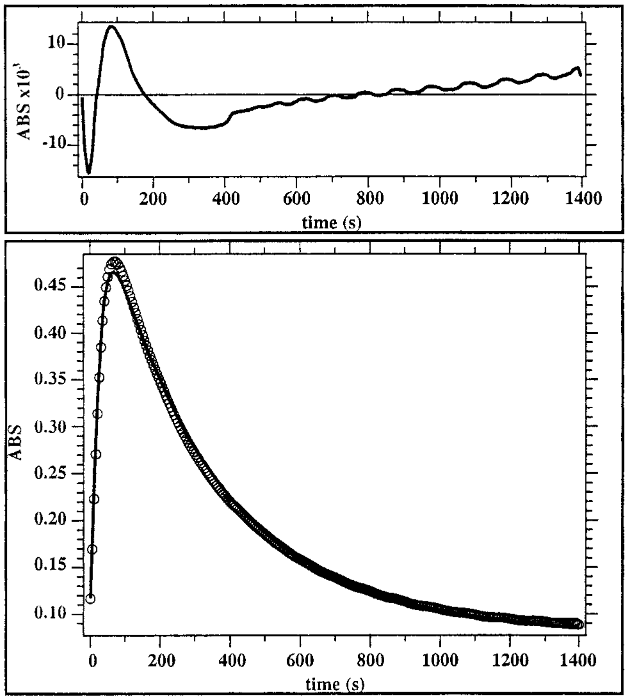

Figure 2. Single-wavelength (295 nm) decay profile of the H_2O_2/SCN^- reaction and results of the numerical integration of the multiwavelength data to the mechanism presented in Table 1. Best fit results associated with the rate constants are displayed therein. Open circles represent the experimental data points, and the solid line represents the fit. Top box displays the residuals of the fit. Data taken at 25 °C in 1 M $HClO_4$, path length 1 cm, $[H_2O_2]_o = 15$ mM, $[SCN^-]_o = 180$ mM.

the intermediate decays on the same time scale as we found for the decay of $(SCN)_2$ in the reaction of ClO_2 with SCN^-.[14]

On the basis of these observations, a reasonable hypothesis for the mechanism (Table 1) can be developed by combining portions of the mechanisms previously proposed for the reactions of SCN^- with H_2O_2 and ClO_2: SCN^- in acid reacts with H_2O_2 to give HOSCN, which then forms $(SCN)_2$ through an acid-driven equilibrium comproportionation with SCN^-. Decay of $(SCN)_2$ obeys second-order kinetics because of the second-order decomposition of HOSCN. There appears to be no analytical solution to the system of differential equations arising from this mechanism. Thus, as is described below, we use a numerical ODE (ordinary differential equation) solver in order to fit the parameters of the mechanism to the data. The task is greatly simplified as the number of adjustable parameters is reduced, and the parameter most directly accessible is the rate constant for the consumption of H_2O_2. Although the rate law for the acidic reaction of SCN^- with H_2O_2 appears to be well established, the data upon which it is based were obtained under conditions of a large excess of H_2O_2.[15,16] As the intermediate reported in the present study is generated with excess SCN^-, it is necessary to verify the rate law for H_2O_2 consumption under these conditions. Further motivation for this reinvestigation is the recent report that the rate law for the acid-independent reaction given by Wilson and Harris is incorrect.[17]

Table 2. Kinetic Data for the Reaction of TiO_2^{2+} and SCN^- in High Acid Concentrations[a]

$10^4 \times k_{obs}$, s^{-1}[b]	replicates	$[H_2O_2]_{tot,o}$, mM	$[Ti]_{tot}$, mM	$[H^+]$, M
1.12(5)	3	0.3	4.78	1.0
1.74(19)	4	0.3	3.00	1.0
4.70(24)	3	0.3	1.20	1.0
9.03(41)	3	0.3	0.598	1.0
13.8(7)	4	0.3	0.239	1.0
22.5(2)	3	0.3	0.120	1.0
2.76(72)	3	0.3	0.239	0.1
9.49(39)	3	0.3	0.239	0.5
13.8(7)	4	0.3	0.239	1.0
6.86(161)	4	0.01	0.624	1.0
5.31(61)	3	0.025	0.624	1.0
5.21(70)	3	0.05	0.624	1.0
5.35(36)	3	0.1	0.624	1.0

[a] $[SCN^-] = 250$ mM, 25 °C, $\mu = 1.25$ M $LiClO_4$ where applicable. [b] Measured the consumption of TiO_2^{2+} at 410 nm. Parenthetical values represent the error as 3 standard deviations.

Peroxotitanium as an Indicator in the Oxidation of SCN^- by H_2O_2. Preliminary studies of the reaction of H_2O_2 with excess SCN^- revealed that there is no simple direct spectrophotometric method to monitor the loss of H_2O_2 because of the high background absorbance from SCN^- in the UV, the photochemical complications arising from monitoring in the far-UV, and the absorbance of the intermediate in the nearer regions of the UV. These difficulties can be avoided by employing an appropriate UV cutoff filter and by using peroxotitanium(IV) (TiO_2^{2+}) as a nonparticipant chemical indicator that absorbs in the visible region. This use of peroxotitanium(IV) is suggested by the work of Lydon and Thompson, which shows that the complex is formed rapidly and reversibly and that it is generally much less reactive than H_2O_2 itself.[25] This complex forms as given by

$$TiO^{2+} + H_2O_2 \rightleftharpoons TiO_2^{2+} + H_2O \qquad K_{Ti} \tag{6}$$

The stability constant for this equilibrium was reported by Thompson in 1 M perchloric acid and was found to be $8.7 \times 10^3\ M^{-1}$.[22] Under conditions similar to those suggested by Lydon and Thompson,[25] pseudo-first-order behavior can be observed for the reaction of H_2O_2 and SCN^- by monitoring the decay in absorbance of TiO_2^{2+} at 410 nm over time. This method achieves pseudo-first-order kinetics for a variety of conditions, and a typical reaction trace is shown in Figure S1 of the Supporting Information. The pseudo-first-order rate constants can be evaluated by a single-exponential fit, and the results are shown in Table 2. Note that under these conditions most of the peroxide is bound as TiO_2^{2+}.

Interpretation of these pseudo-first-order rate constants is achieved by considering the following derivation. Under conditions applicable to these experiments, the rate of decay of

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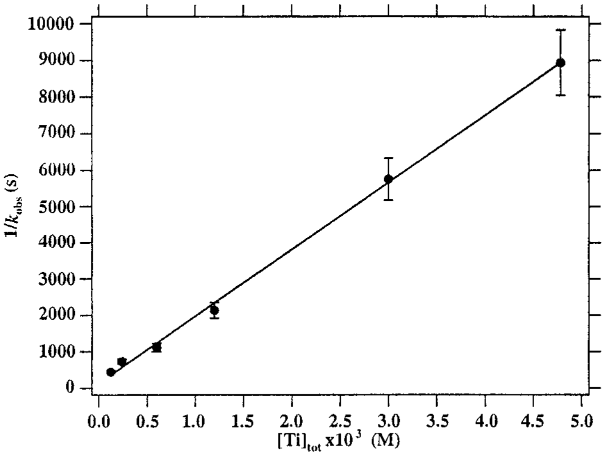

Figure 3. Plot of $1/k_{obs}$ vs $[Ti]_{tot}$ at $[H_2O_2]_{tot,0} = 0.3$ mM, $[SCN^-] = 250$ mM, $[H^+] = 1$ M, $\mu = 1.25$ M ($HClO_4$). The linear plot has a slope of (1.84 ± 0.04) × 10^6 s/M and an intercept of 130 ± 90 s with $R = 0.9991$.

hydrogen peroxide in the absence of Ti(IV) according to Wilson and Harris reduces to eq 1.[16] Because of the rapid equilibria that are established in the presence of Ti(IV), we define the following two quantities:

$$[H_2O_2]_{tot} = [TiO_2^{\ 2+}] + [H_2O_2] \qquad (7)$$

$$[Ti]_{tot} = [TiO_2^{\ 2+}] + [TiO^{2+}] \qquad (8)$$

In the presence of excess Ti(IV), the concentration of free H_2O_2 is essentially buffered through reaction 6. Moreover, it is assumed as suggested by Lydon and Thompson that SCN^- reacts with H_2O_2 but not TiO_2^{2+}.[25] As described in the Supporting Information, when $[Ti]_{tot} \gg [TiO_2^{2+}]$ these considerations lead to rate law 9:

$$-\frac{d[TiO_2^{\ 2+}]}{dt} = \frac{k_1[SCN^-][H^+][TiO_2^{\ 2+}]}{K_{Ti}[Ti]_{tot} + 1} \qquad (9)$$

Equation 9 leads to pseudo-first-order kinetics for loss of TiO_2^{2+} with k_{obs} defined by

$$k_{obs} = \frac{k_1[SCN^-][H^+]}{K_{Ti}[Ti]_{tot} + 1} \qquad (10)$$

Equation 10 predicts a first-order dependence of k_{obs} on $[H^+]$ and a zero-order dependence on $[H_2O_2]_{tot,0}$, both of which are demonstrated by the data in Table 2. The inverse of eq 10 is

$$\frac{1}{k_{obs}} = \frac{K_{Ti}[Ti]_{tot}}{k_1[SCN^-][H^+]} + \frac{1}{k_1[SCN^-][H^+]} \qquad (11)$$

which implies a linear dependence of $1/k_{obs}$ on $[Ti]_{tot}$. Figure 3 displays such a plot for data obtained in 1 M $HClO_4$ with 250 mM SCN^-. This linear graph has a slope of (1.84 ± 0.04) × 10^6 s/M and an intercept of 133 ± 90 s. Note that the intercept is not well defined by the data, and its value is highly sensitive to the results obtained at low $[Ti]_{tot}$. The data at low $[Ti]_{tot}$, however, were obtained under conditions that do not comply strictly with the approximation that $[Ti]_{tot} \gg [TiO_2^{2+}]$. These same reactions also displayed small deviations from pseudo-first-order behavior in the initial portions of the traces. Accordingly, the intercept in Figure 3 does not lead directly to a reliable value for k_1. On the other hand, the slope has a well-defined value of (2.2 ± 0.05) × 10^{-6} M^{-1} s^{-1} for k_1/K_{Ti}. From the literature value for K_{Ti} given above, this ratio leads to a value of 1.9 × 10^{-2} M^{-2} s^{-1} for k_1. This result is in fine agreement with that reported by Wilson and Harris,[16] and it shows that rate law 1 applies under conditions of both excess SCN^- and excess H_2O_2. Moreover, our value for k_1 implies an intercept of 210 s for Figure 3, which is in agreement with the observed result. The agreement between our raw data and eq 10, along with the agreement between our value for k_1 and that reported by Wilson and Harris, gives strong support to the assumption that Ti(IV) acts only as an indicator and, if anything, deactivates H_2O_2 as suggested by Lydon and Thompson.[25]

Discussion

Table 1 presents a five-step mechanism that accounts for our observations and is consistent with the chemistry reported in the literature. This mechanism consists of two sets of reactions which account for the rise−fall behavior noted in the UV for the SCN^-/H_2O_2 reaction. The first set, consisting of reactions SR1 and SR5, describes the direct two-electron oxidative conversion of SCN^- to hypothiocyanous acid, which produces a discernible intermediate, $(SCN)_2$, in 1 M H^+ by equilibrium comproportionation. The second set of reactions, SR2−SR4 and SR5 again, is widely accepted and accounts for the second-order decay of $(SCN)_2$ to the likely and well-documented products of hydrolysis.[26,27]

Our proposed mechanism differs from that proposed by Wilson and Harris[16] both by the number of steps and by the proposed end products of the reaction. Most notably, the mechanism of Wilson and Harris omits the formation of $(SCN)_2$ through equilibrium SR5. Another difference is that Wilson and Harris propose the reaction of HOSCN with H_2O_2 as the major fate of HOSCN. While this reaction with H_2O_2 may be appropriate under the conditions of excess H_2O_2 used by Wilson and Harris, we find it necessary to use a pathway second-order in HOSCN under our conditions of excess SCN^-. Our mechanism omits the reaction of HOSCN with HCN, as we believe that it plays an insignificant role with the low concentrations of HCN generated in the present study. Finally, Wilson and Harris propose hydrolysis of HO_2SCN where we propose its disproportionation; in fact, our data do not allow us to distinguish between these two possibilities.

Success of the Model. The mechanism in Table 1 provides for the net stoichiometry given by reaction 2 as well as adhering to the rate law given in eq 1. The numerical integration of the system of differential equations arising from this mechanism provides compelling evidence of its applicability for this reaction system. These simulations were performed with the Bulirsch−Stoer stiff integration routine available in the Specfit software package, making use of the reactions in Table 1 with the associated rate constants. The spectra of H_2O_2, $(SCN)_2$, and products were treated as variables in these fits. The results at 295 nm, shown in Figure 2, provide quantitative agreement between the observed kinetics and simulations as demonstrated by the fine overlap of the traces in 1 M H^+ with 180 mM SCN^-. The spectra of H_2O_2, $(SCN)_2$, and products generated by these fits are shown in Figure 4. The spectra obtained are entirely consistent with expectations for H_2O_2 and products, while the spectral trace for thiocyanogen is fairly consistent with expectations in terms of λ_{max} and molar absorptivity from that previously

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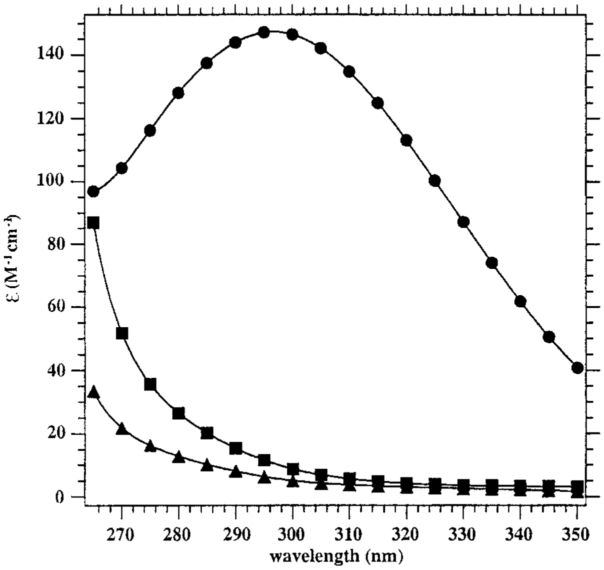

Figure 4. Spectra generated by a three-component fit of the mechanism in Table 1 with the rate constants as given. Data taken at 25 °C in 1 M $HClO_4$, path length 1 cm, $[H_2O_2]_o = 15$ mM, $[SCN^-]_o = 180$ mM. Circles represent the data associated with $(SCN)_2$, squares represent the proxy spectra of products, and triangles represent the spectrum for H_2O_2. All data are sparsed at an interval of 5 nm for clarity. The aqueous spectrum for $(SCN)_2$ extracted from these kinetic fits is characterized by $\lambda_{max} = 297$ nm and $\epsilon_{297} = 147$ M^{-1} cm^{-1}.

reported.[14] We note that step SR5 causes the ratio [HOSCN]/[$(SCN)_2$] to be a constant during any one experiment, and thus, the spectra of HOSCN and $(SCN)_2$ cannot be deconvoluted in these fits. Hence, the $(SCN)_2$ spectrum returned by the fits is actually the sum of the contributions of these two species. On the other hand, step SR5 causes the ratio [HOSCN]/[$(SCN)_2$] to be dependent on the concentration of SCN^-. Simulations performed with the same parameters gave excellent fits for reactions with [SCN^-] as low as 10 mM. In these latter reactions, the concentration of SCN^- is not in large excess and hence decreases significantly during the reaction; this decrease does not pose a problem in the integrations as it is accounted for explicitly in the model. These simulations yielded spectra of $(SCN)_2$ that were essentially identical, which implies that HOSCN does not absorb significantly in this spectral region.

Details of the Mechanism. 1. Direct Reaction of H_2O_2 and SCN^-, SR1. The initial step of the acidic reaction of H_2O_2 and SCN^- is accounted for by the simple two-electron reduction of H_2O_2 to H_2O and HOSCN. This type of reduction (nuclephilic displacement at peroxide) is commonly invoked for peroxide reactions where there is a lack of species present to stabilize "Fenton-like" radicals produced by one-electron reductions.[16,18,28] Similarly, the two-electron oxidation product of SCN^- is a commonly reported intermediate for these types of processes and accounts, through widely accepted decomposition pathways, for the products reported for this reaction. A value of 5.3 has been reported for the pK_a of HOSCN,[29] while the pK_a of HSCN is −0.9.[30] Under the acidity conditions of the present study, the concentration of $OSCN^-$ is, therefore, completely negligible and the concentration of HSCN is never very significant. Inclusion of these equilibria in the mechanism produced no changes in the fits, and therefore, they were removed. Additionally, the pseudo-first-order decay pattern established in the TiO_2^{2+} reactions suggested no significant role for $OSCN^-$, as it had in the autocatalytic reaction of ClO_2.[14]

The rate constant used in SR1, $(3.3 \pm 0.3) \times 10^{-2}$ M^{-2} s^{-1}, was established by Wilson and Harris[16] and confirmed through our work as described above. Further evidence for its validity is demonstrated by the numerical fitting of this mechanism. All data sets can be fit by this mechanism, and when this rate constant is allowed to vary while the rate constants related to the decay of thiocyanogen remain constant, the stiff integrator converges on an answer which produces this value within reasonable limits (±10%). This was an important result because it allowed for the further refinement of the second phase of the mechanism for which a good deal of conflicting evidence has been reported in the literature.

2. Hydrolysis of $(SCN)_2$, SR2−SR5. As was the case in the reduction of ClO_2 by thiocyanate under strongly acidic conditions,[14] the hydrolytic equilibrium of $(SCN)_2$ represented by K_{hyd} is a critical step in these simulations. Similarly, the rate constant k_{disp} for the disproportionation of HOSCN is also crucial, while SR3 and SR4 are projected to be rapid steps that merely account for the formation of products, not for affecting the quality of the fit. As we have discussed for the ClO_2/SCN^- reaction, the decomposition kinetics of $(SCN)_2$ in strong acid obeys a rate law that permits determination of the value for $k_{disp}K_{hyd}^2$ but not the independent values for k_{disp} and K_{hyd}. Despite the less complex mechanism invoked and the smaller degree of spectral interferences associated with the H_2O_2/SCN^- system, the values of k_{disp} and K_{hyd} are still inseparable. As a consequence, fits were performed with the rate constants held constant, the component spectra being treated as variables. By trial and error with manual adjustment of the rate constants, it was found that when K_{hyd} was increased by a factor of 1.5 or k_{disp} was decreased by roughly the same magnitude from the previously reported values, excellent fits to the raw data were obtained. In Table 1, we arbitrarily show the altered value of K_{hyd} while retaining the prior value for k_{hyd}, recognizing that equally good fits can be obtained for other combinations of rate constants within reasonable limits, so long as the value of $k_{disp}K_{hyd}^2$ is unperturbed.

In our prior study of the ClO_2/SCN^- reaction, a 14-step mechanism was required to explain the complex behavior.[14] The hydrolytic decomposition of $(SCN)_2$ played an important role in that study, although the spectral data upon which it was based were somewhat obscured by the strong UV absorbance of ClO_2. An important result from the current study is thus the strong support it gives for the mechanism proposed for the ClO_2/SCN^- reaction. Despite this corroboration of our previous work, we believe independent studies of $(SCN)_2$ hydrolysis are required to gain a more complete understanding of this process. Direct determination of the magnitude of K_{hyd} remains a goal, and the question of whether HO_2SCN decays through hydrolysis or disproportionation needs to be answered. A conflict that remains to be resolved is the rapid decomposition of HOSCN that our model requires and the relative stability of HOSCN reported by others in less acidic media.[7,17,29,31] Efforts to probe these issues in the current study were hampered by slowness of SR1, which leads to formation of $(SCN)_2$ occurring on a time scale comparable to that of its decay.

$(SCN)_2$ UV Spectrum. The spectrum of $(SCN)_2$ derived by kinetic fitting is shown in Figure 4 and is similar to our

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previously reported spectrum of this species in aqueous solution.[14] The importance of this second finding involves the clarity of this broad band absorbance from which a more definitive λ_{max} (297 nm) is extracted. The changes in UV absorbance throughout these experiments are almost entirely due to $(SCN)_2$ and do not suffer from alternative species overlap, making this evaluation more reliable. The spectrum is characterized by $\lambda_{max} = 297$ nm and $\epsilon_{297} = 147$ M^{-1} cm^{-1} and is in good agreement with our previous work[14] as well as that shown by Bacon and Irwin in CCl_4.[32] Dolbear and Taube cite a report on the spectrum of $(SCN)_2$ in aqueous solution in the Ph.D. thesis of Long;[33] the λ_{max} (302 nm) is consistent with our findings, but the molar absorptivity (840 M^{-1} cm^{-1}) is roughly 6 times larger. We attribute this disagreement to the preliminary nature of the cited work.

Conclusions

The UV-monitored kinetics of the H_2O_2/SCN^- reaction under strongly acidic conditions provide definitive evidence for the appearance and decay of an oxidative thiocyanate intermediate. Through the use of peroxotitanium(IV) as an indicator for this reaction, pseudo-first-order behavior for the loss of H_2O_2 was achieved, confirming the rate constant previously reported, while at the same time limiting the variables for nonlinear fitting routines. By the fitting of the multiwavelength data to a logical mechanism for the rise and fall of thiocyanogen, an excellent spectrum for this species in aqueous solution was extracted. This work continues the elucidation of often contradictory information regarding the decay of thiocyanogen in aqueous solution. Furthermore, this research supports the importance of thiocyanogen in the oxidative reactions of thiocyanate in acidic media.

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Supporting Information Available: A single-wavelength (410 nm) decay profile of the reaction of TiO_2^{2+} and SCN^- in 1 M $HClO_4$ at 25 °C (Figure S1) and the derivation of eq 9. This material is available free of charge via the Internet at http://pubs.acs.org.

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