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Formation of Trithiocyanate in the Oxidation of Aqueous Thiocyanate

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Oxidation of SCN^- in acidic media by a deficiency of aqueous chlorine generates a transient UV absorption feature in less than 3 ms. This intermediate has the same spectral and kinetic features as were found in prior studies of the oxidation of SCN^- by H_2O_2 or ClO_2. The UV absorbance increases strongly with increasing concentration of SCN^- but not with increasing [H^+]. These observations are evidence that $(SCN)_2$ and $(SCN)_3^-$ both contribute to the absorbance and are in equilibrium with each other. Values of the corresponding molar absorptivities and the equilibrium constant are derived. Hydrolysis of $(SCN)_2$ to HOSCN is shown to have a small equilibrium constant.

The discovery of thiocyanate, SCN^-, as a key component of an antibacterial system in human saliva has caused a large amount of interest and study on the oxidation of this species. Most of these studies focus on the oxidation using H_2O_2 as the oxidizing agent, which is a reaction of particular significance in the salivary medium.[1−4] It is widely proposed that the oxidation of SCN^- leads to the production of the pseudohalogen molecule thiocyanogen, $(SCN)_2$,[5−7] but this unstable species has been detected only rarely and with conflicting results.[5,7−13]

In recent work in this laboratory using either ClO_2 or H_2O_2 as oxidant in acidic solutions an intermediate was observed by rapid-scan stopped-flow spectrophotometry. This intermediate displayed a very distinct UV spectrum and decayed with second-order kinetics.[7,11] It was proposed to be $(SCN)_2$, and its decomposition was proposed to occur with rate-limiting disproportionation of HOSCN, the latter species being formed through an equilibrium involving $(SCN)_2$, as in eq 1:

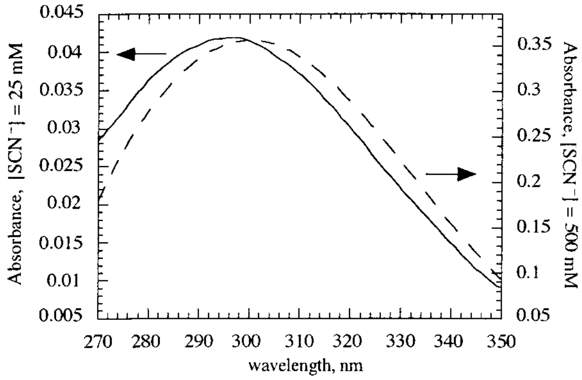

Figure 1. Shift of λ_{max} for the observed intermediate with increasing [SCN^-]. Spectra presented with [H^+] = 0.5 M, $[Cl_2]_{tot}$ = 0.2 mM, μ = 1 M ($LiClO_4$), 1.8 cm path length, and T = 298 K. The absorbance due to SCN^- has been subtracted from these spectra.

$$(SCN)_2 + H_2O \rightleftharpoons HOSCN + SCN^- + H^+ \qquad K_{hyd} \quad (1)$$

In these prior studies a detailed analysis of the decomposition of the observed intermediate was not performed due to spectroscopic[11] or kinetic complications.[7]

We now report stopped-flow results indicating that aqueous Cl_2/HOCl oxidizes SCN^- very rapidly (<3 ms), producing an intermediate spectroscopically and kinetically identical to the one proposed to be $(SCN)_2$ in earlier work in this lab (see the solid line in Figure 1). Note that the spectra in Figure 1 are obtained directly, whereas those we reported previously were obtained by kinetic modeling of rapid-scan data.[7,11] We propose that this intermediate is produced by the following reactions:

$$Cl_2 + 2SCN^- \rightarrow 2Cl^- + (SCN)_2 \qquad (2)$$

$$H^+ + HOCl + 2SCN^- \rightarrow Cl^- + (SCN)_2 + H_2O \qquad (3)$$

Addition of Cl^- up to 100 mM yields no apparent change in the yield of the intermediate. This rapid production of $(SCN)_2$ allows for a detailed study of its chemistry in acidic aqueous solutions.

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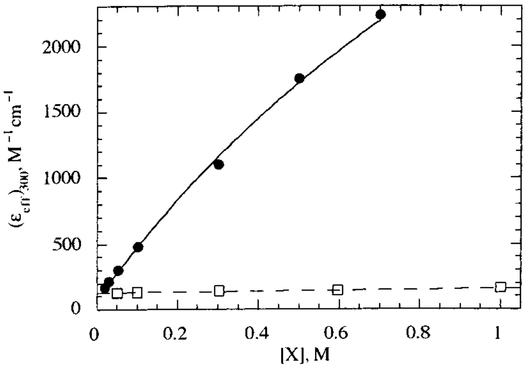

Figure 2. Dependence of ϵ_{eff} on [SCN$^-$] and [H$^+$]. For the open squares, X = H$^+$. In this series of data, [SCN$^-$] = 25 mM, $[Cl_2]_{tot}$ = 1.03 mM, μ = 1 M ($LiClO_4$), and T = 298 K. The dashed line represents a linear fit of the ϵ_{eff} vs [H$^+$] data. For the filled circles, X = SCN$^-$. In this series of data, [H$^+$] was varied from 0.3 to 1 M in order to maintain the stability of the intermediates produced, $[Cl_2]_{tot}$ = 0.37 mM, μ = 1 M ($LiClO_4$), and T = 298 K. The solid line represents the fit of the data to eq 7.

The initial absorbance at $\lambda = 300$ nm, $(A_0)_{300}$, is highly dependent on [SCN$^-$]. However, $(A_0)_{300}$ does not exhibit a similar dependence on [H$^+$], as shown in Figure 2. The data are presented as ϵ_{eff} vs [X], where X = SCN$^-$ or H$^+$ and ϵ_{eff} is defined as follows:

$$\epsilon_{eff} = (A_0 - A_\infty)_{300}/([Cl_2]_{tot}l) \qquad (4)$$

Here, A_0 is the absorbance immediately after mixing, A_∞ is the absorbance after decomposition of the intermediate, l is the optical path length, and $[Cl_2]_{tot}$ is the total initial concentration of reducible chlorine:

$$[Cl_2]_{tot} = [Cl_2]_0 + [HOCl]_0 \qquad (5)$$

For all experiments the first half-lives for decay of the intermediate exceeded 2 s, thus ensuring that the A_0 values are unaffected by decay during the instrument dead time.

Note that, from the stoichiometry presented in eqs 2 and 3, $[Cl_2]_{tot}$ is exactly equal to the starting value for $[(SCN)_2]$. In fact, a plot of $(A_0)_{300}$ vs $[Cl_2]_{tot}$ is linear with an intercept of zero and a slope equal to the value of ϵ_{eff} at the [SCN$^-$] and [H$^+$] values of the solutions used. The qualitatively different dependencies of the ϵ_{eff} values with respect to [SCN$^-$] and [H$^+$] indicate that a shift in the hydrolysis equilibrium shown in eq 1 is not responsible for the observed behavior. Furthermore, the wavelength of maximum absorbance, λ_{max}, exhibits a small but significant shift toward longer wavelengths with increasing [SCN$^-$], as shown in Figure 1. These pieces of evidence indicate the presence of at least two absorbing species. Furthermore, the additional absorbing species is the product of some interaction between the first absorbing species, presumably $(SCN)_2$, and SCN$^-$. Therefore, we propose that the second absorbing species is trithiocyanate, $(SCN)_3^-$, formed in the following equilibrium:

$$(SCN)_2 + SCN^- \rightleftharpoons (SCN)_3^- \qquad K_{(SCN)_3^-} \qquad (6)$$

The trihalide ions (e.g., I_3^-) are a well-known and thoroughly studied set of molecules. Reports of tri-pseudohalide ions are far less common, but such reports do exist, notably for $(CN)_3^-$.[14,15] $(SCN)_3^-$ itself has been reported in the electrolytic oxidation of SCN$^-$ in molten NaSCN/KSCN eutectic,[16] in the electrolytic oxidation of SCN$^-$ in acetonitrile,[17] and in spectroelectrochemical studies using a gold minigrid electrode in aqueous solution.[9,10] This last report is questionable on the basis of other reports that gold dissolves anodically in aqueous solutions of SCN$^-$.[18,19] One group has used electrochemical oxidation of SCN$^-$ to determine $K_{(SCN)_3^-}$ = 50 (±25) M^{-1} cm^{-1} and $(\epsilon_{(SCN)_3^-})_{320nm}$ = 750 (±100) M^{-1} cm^{-1} in acetonitrile.[17]

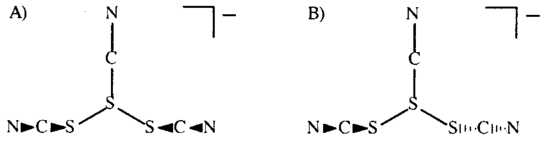

Figure 3. PM3 structures modeled for $(SCN)_3^-$: (A) C_s symmetry; (B) C_2 symmetry. Note that the "bonds" drawn in this structure are meant only to imply connectivity and geometry and not bond order.

As part of the present study, $(SCN)_3^-$ was modeled using the PM3 method in the MacSpartan Plus software suite.[20] Two structures containing all S−S bonds, one with C_s symmetry and the other with C_2 symmetry, were modeled and found to have similar stabilities. These structures can be seen in Figure 3.

Assuming that $(SCN)_2$ and $(SCN)_3^-$ are the only absorbing species in the solution and that [HOSCN] remains very small, the following relationship can be derived:

$$\epsilon_{eff} = \frac{\epsilon_{(SCN)_2} + \epsilon_{(SCN)_3^-} K_{(SCN)_3^-}[SCN^-]}{1 + K_{(SCN)_3^-}[SCN^-]} \qquad (7)$$

The ϵ_{eff} vs [SCN$^-$] data can be fit by this equation using a nonlinear least-squares program. Using such a program, the following values were calculated: $\epsilon_{(SCN)_2}$ = 75 (±7) M^{-1} cm^{-1}, $\epsilon_{(SCN)_3^-}$ = 7500 (±2300) cm^{-1} M^{-1}, and $K_{(SCN)_3^-}$ = 0.6 (±0.2) M^{-1}. This result implies that $(SCN)_3^-$ is always a minor species, never exceeding 50% of $[(SCN)_2]$. The excellent quality of this data fit can be seen from the plot shown in Figure 2. The values of $K_{(SCN)_3^-}$ and $\epsilon_{(SCN)_3^-}$ are strongly correlated because the resolution of these individual values is derived from the slight curvature observed in the ϵ_{eff} vs [SCN$^-$] plot. However, the product of these two numbers is very well resolved, as is the value of $\epsilon_{(SCN)_2}$. Another noteworthy complication in this treatment of the data is the possibility of specific medium effects due to the changing composition of the solution. There is, for instance, a slight rise in ϵ_{eff} with increasing [H$^+$], which should not

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occur if the model which we have proposed is correct. This rise is most likely due to the changing of the cationic species in solution from Li^+ to H^+ with increasing $[H^+]$ (the $[H^+]$ value is varied using $HClO_4$ and the ionic strength is maintained at 1 M using $LiClO_4$). Similarly, the change of the anionic species from ClO_4^- to SCN^- in the $[SCN^-]$-varied studies could significantly affect the separation of variables in eq 7. Despite these caveats, it is clear that the formation constant for $(SCN)_3^-$ is quite small while $\epsilon_{(SCN)_3^-}$ is quite large. The substantial reduction in $K_{(SCN)_3^-}$ relative to the value reported in acetonitrile is as expected, given the similar solvent effects for the analogous formation of I_3^- and Br_3^-.[21] The small value obtained for $K_{(SCN)_3^-}$ is similar to that reported for $(CN)_3^-$, which is believed to have a structure analogous to that shown in Figure 3 for $(SCN)_3^-$.[14,15] The significant disagreement between our value for $\epsilon_{(SCN)_3^-}$ and that reported in acetonitrile[17] calls the latter result into question.

Analysis of the data in Figure 2 including the potential contribution of $(SCN)_2$ hydrolysis leads to an upper limit of 0.001 M^2 for K_{hyd}. Simulations indicate that the models developed previously for the reactions of SCN^- with H_2O_2 or ClO_2 can accommodate this revised value for K_{hyd} through adjustment of other parameters.[7,11]

The results presented herein show that the intermediate we previously identified as $(SCN)_2$ in the reactions of ClO_2 and H_2O_2 with SCN^- is actually an equilibrium mixture of $(SCN)_2$ and $(SCN)_3^-$.[7,11] This enhancement to our understanding, however, has no effect on the kinetic treatments in those papers, largely because the species $(SCN)_3^-$ was always a minor component of the solutions. On the other hand, our new results provide the most likely explanation of disagreement between prior literature reports on the UV spectrum of $(SCN)_2$.[5,11,13]

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