DALTON

Formation of an adduct between thiocyanate ion and nitrosyl thiocyanate

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Nitrosyl thiocyanate reacted with sufficiently high concentrations of thiocyanate ion to form an adduct, $[ON(SCN)_2]^-$, which absorbs strongly in the UV region. This species has different properties to that species described in the literature as $[NO(SCN)_2]^-$ formed in pulse-radiolysis experiments involving $(SCN)_2^-$ and NO. The difference probably arises from different structures, an S-nitroso as compared to an N-nitroso compound.

Acidic solutions containing both nitrous acid and thiocyanate ions have a marked red colour, due to an absorption maximum at 460 nm. From the variation of A_{460} with $[H^+]$, $[HNO_2]$ and $[SCN^-]$ it has been established[1] that the red species is nitrosyl thiocyanate, ONSCN, formed as shown in equation (1). This

$$H^+ + HNO_2 + SCN^- \rightleftharpoons ONSCN + H_2O \qquad (1)$$

species has also been isolated at low temperatures[2] by the reaction of ONCl with AgSCN. From these absorbance measurements the formation constant of ONSCN has been calculated, and ε_{max} established as 100 dm^3 mol^{-1} cm^{-1}. These measurements used relatively low concentrations of thiocyanate ion, less than 0.1 mol dm^{-3}. Later measurements,[3] using much higher values of $[SCN^-]$, several mol dm^{-3}, showed that although the colour appeared much the same to visual observation the shape of the spectrum changed. The absorbance minimum on the low-wavelength side of 460 nm disappeared and the spectrum was a smooth curve in which the absorbance rose steeply towards low wavelengths in the UV region. Changes on the high-wavelength side of 460 nm were much less marked. It was suggested that this might be due to the formation of a species $[ON(SCN)_2]^-$. Recently Czapski *et al.*[4] used pulse radiolysis to study the reaction of NO with a number of radical anions including $(SCN)_2^-$, and observed the formation of a species absorbing strongly in the UV region with $\varepsilon_{260} \approx 7570$ dm^3 mol^{-1} cm^{-1} which they suggested was $[NO(SCN)_2]^-$. This was observed to decay by a process showing first-order kinetics with a rate constant 2×10^4 s^{-1} that was independent of pH, [NO] and $[SCN^-]$ to yield a species with a much weaker UV absorption and which was suggested to be NOSCN, as shown in (2).

$$[NO(SCN)_2]^- \longrightarrow NOSCN + SCN^- \qquad (2)$$

There were a few measurements of the decay of NOSCN to form NO_2^- and SCN^-, with kinetics that had a fractional order in $[H^+]$. A comparison of the results of Czapski *et al.*[4] with our observations indicated a number of points of disagreement and we have therefore extended our own work.

Results and Discussion

Nitrosyl thiocyanate is unstable in aqueous solution; the red colour fades over a period of 10–20 min with the evolution of bubbles of NO, and in the original work,[1] which involved manual spectroscopy, this was allowed for by measuring the absorbance at a number of times and extrapolation to the time of mixing the reactants. This would not, however, detect a rapid initial reaction in the interval between mixing the solutions and measuring the first point. We have therefore used stopped-flow methods, mixing solutions of NaSCN + $NaNO_2$ with $HClO_4$, recording the initial absorbance after mixing. Fig. 1 shows a spectrum of ONSCN plotted for a series of repeat runs carried out at selected wavelengths, and the ONSCN peak at 460 nm can be clearly seen. Using the value of $\varepsilon_{460} = 100$ dm^3 mol^{-1} cm^{-1}, the equilibrium constant $K_1 = [ONSCN]/[H^+][HNO_2][SCN^-]$ is calculated as 44 dm^6 mol^{-2} for 2 mol dm^{-3} ionic strength ($NaClO_4$); this may be compared with earlier values of 21.0, 28.6 and 36.3 for ionic strengths of 0.42, 1.02 and 1.42 mol dm^{-3} obtained by manual spectrometry[1] with a Unicam SP500 spectrometer. The figure also shows a trace obtained at a much higher thiocyanate ion concentration, $[SCN^-] = 0.5$ mol dm^{-3}, where it can be seen that the absorption on the low-wavelength side of 460 nm has increased markedly, with much smaller increases on the high-wavelength side. The value of A_{460} is significantly higher than that expected for $K_1 = 44$ dm^6 mol^{-2} and $[SCN^-] = 0.5$ mol dm^{-3}, confirming the presence of another species. Unfortunately the limitations of our stopped-flow apparatus made it impossible to extend these measurements into the UV region. Measurements by the stopped-flow method made at a single wavelength, 460 nm, and with varying $[SCN^-]$ are shown in Fig. 2. On the basis of $K_1 = 44$ dm^6 mol^{-2} there ought to be 81% conversion of nitrite into ONSCN at $[SCN^-] = 1$ mol dm^{-3} and the absorbance *vs.* $[SCN^-]$ curve would be expected to be levelling off; instead the absorbance increases steadily, indicating the presence of another species.

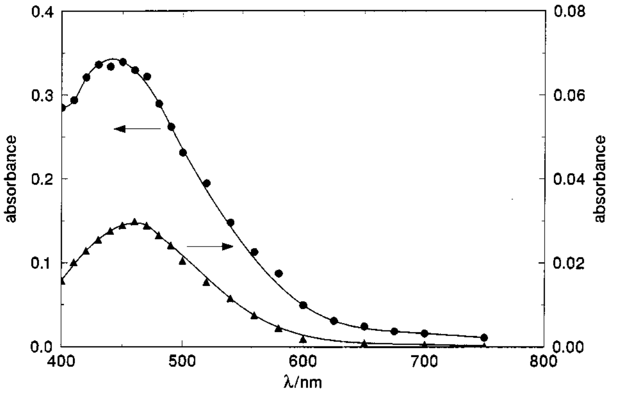

Fig. 1 Visible spectra of ONSCN obtained by stopped-flow spectrophotometry at pH 1 and 25 °C: (▲) $[SCN^-] = 0.02$, $[HNO_2] = 0.02$ mol dm^{-3}; (●) $[SCN^-] = 0.5$, $[HNO_2] = 0.02$ mol dm^{-3}

To extend our measurements to lower wavelengths we turned to conventional spectrophotometry. A spectrum of ONSCN

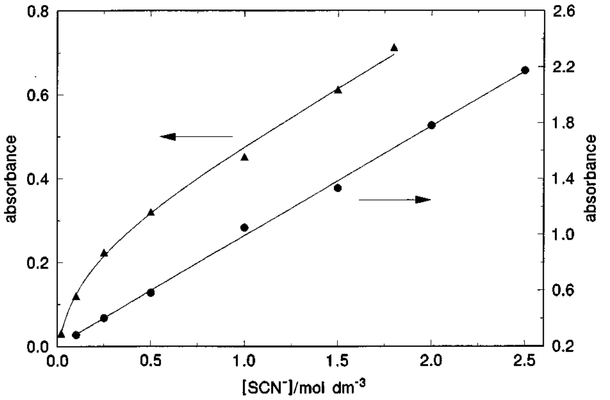

Fig. 2 Variation of absorbance with $[SCN^-]$ for solutions of $H^+ + HNO_2 + SCN^-$ at 25 °C by stopped-flow (▲) and UV spectrophotometry (●) (▲): $[H^+] = 0.1$, $[HNO_2] = 0.02$ mol dm^{-3}; $l = 2$ mm; $\lambda = 460$ nm; (●) $[H^+] = 0.1$, $[HNO_2] = 0.0001$ mol dm^{-3}; $l = 4$ cm; $\lambda = 320$ nm

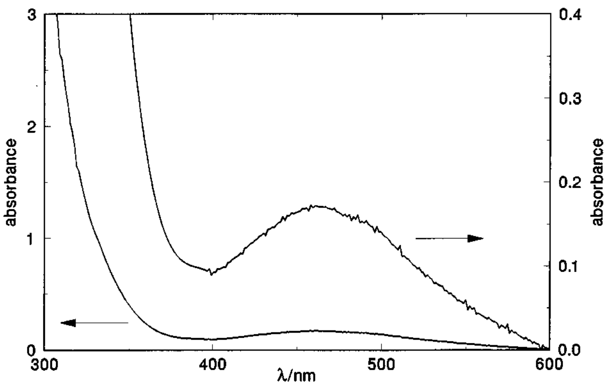

Fig. 3 The UV/VIS spectrum of ONSCN at $[H^+] = 0.1$, $[HNO_2] = 0.01$, $[SCN^-] = 0.01$, $I = 2$ mol dm^{-3} and $l = 4$ cm

obtained at low $[SCN^-]$ is shown in Fig. 3. The rate of decomposition of nitrosyl thiocyanate is a very sensitive function of concentration. To stabilise the solutions we reduced the nitrite concentration to 10^{-4} mol dm^{-3}, and used 4 cm cells to obtain reasonable absorbances. Typical spectra are shown in Fig. 4, where it can be seen that as $[SCN^-]$ increases the UV absorption increases rapidly, filling the minimum below 460 nm, so that the peak characteristic of ONSCN disappears. Plots of *A vs.* $[SCN^-]$ show a linear increase in absorbance, typical values being included in Fig. 2.

In making these measurements it was important to record the spectrum as soon as possible after mixing to avoid complications due to formation of the heterocycle *iso*-perthiocyanic acid (also known as xanthane hydride), 5-amino-1,2,4-dithiazole-3-thione ($C_2H_2N_2S_3$). The rate of formation of this yellow species is a very sensitive function of $[SCN^-]$, and Wilson and Hall[5] have shown that the rate of its formation is $v = k[H^+][SCN^-]^3$. It has a very characteristic VIS/UV spectrum with fine structure peaks, and is readily identifiable. No trace of its spectrum was seen in our work, or in the published spectra of Czapski *et al.*[4] However at our highest concentration of thiocyanate this compound precipitated on standing, and was identified by mass[5] and infrared spectroscopy.[6]

We interpret our VIS/UV spectra as showing the formation of an additional species by the reaction of SCN^- with ONSCN. The increase in absorbance with $[SCN^-]$ is almost linear, suggesting that one thiocyanate ion is involved; as there is no sign of levelling off it seems likely that under our conditions only a small fraction of the ONSCN has been converted into the new species. We suggest the reaction is shown in equation (3),

$$ONSCN + SCN^- \rightleftharpoons [ON(SCN)_2]^- \qquad (3)$$

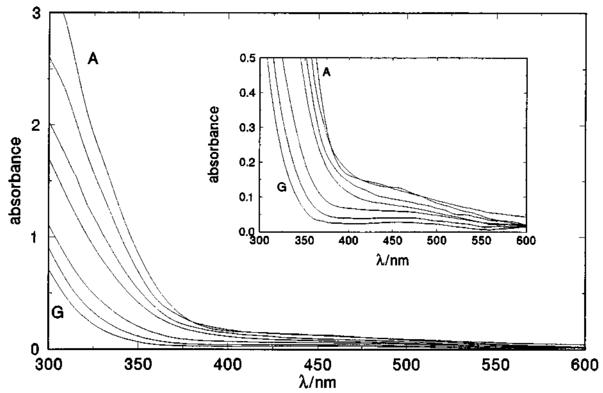

Fig. 4 The UV/VIS spectra at various $[SCN^-]$, $[H^+] = 0.1$, $[HNO_2] = 0.0001$, $I = 4$ mol dm^{-3} and $l = 4$ cm. $[SCN^-] = 2.5$ (A), 2.0 (B), 1.5 (C), 1.0 (D), 0.5 (E), 0.25 (F) and 0.1 (G) mol dm^{-3}. The spectra are shown in sequence A ⟶ G

without specifying a structure for $[ON(SCN)_2]^-$. If we assign formation constants K_1 and K_2 and absorption coefficients ε_1 and ε_2 to the species ONSCN and $[ON(SCN)_2]^-$ then the apparent absorption coefficient ε_{obs} is shown in equation (4),

$$\varepsilon_{obs} = A/[\text{nitrite}]l = \frac{\varepsilon_1 K_1[H^+][SCN^-] + \varepsilon_2 K_1 K_2[H^+][SCN^-]^2}{1 + K_1[H^+][SCN^-] + K_1K_2[H^+][SCN^-]^2} \qquad (4)$$

where $[\text{nitrite}] = [HNO_2] + [ONSCN] + [ON(SCN)_2^-]$ and l is the path length.

Fitting data of the type shown in Fig. 2 by equation (4) has limitations because the measurements do not extend to concentrations where *A* begins to level off for substantial conversion into $[ON(SCN)_2]^-$, and this introduces large error limits on the constants deduced. In addition, although there is formal constant ionic strength, at concentrations of 2 mol dm^{-3} the activity effects of $NaClO_4$ and NaNCS will be different; thus the mean ion activity coefficients at a molality of 2 are 0.744 (NaNCS) and 0.609 ($NaClO_4$). We assigned $\varepsilon_1 = 100$ dm^3 mol^{-1} cm^{-1} as this is well established. Fitting the stopped-flow data at 460 nm by equation (4) we obtain $10^{-3}\varepsilon_2 = 1.74 \pm 0.54$ dm^3 mol^{-1} cm^{-1}, $K_1 = 33.4 \pm 4.6$ dm^6 mol^{-2} and $10^2K_2 = 3.6 \pm 1.3$ dm^3 mol^{-1}. The value of K_1 is in fair agreement with earlier measurements and serves as a check on the curve fitting, but there are substantial errors associated with both K_2 and ε_2. Such calculations are very sensitive to the values assigned to parameters in the equation. If, in addition to assigning $\varepsilon = 100$ dm^3 mol^{-1} cm^{-1} we also fix K_1 as 44 dm^6 mol^{-2} then $10^{-3}\varepsilon_2 = 1.77 \pm 0.71$ dm^3 mol^{-1} cm^{-1} and $10^2K_2 = 1.32 \pm 0.59$ dm^3 mol^{-1}. As the increase in absorbance with $[SCN^-]$ is almost linear we have only a small conversion into $[ON(SCN)_2]^-$ and we are virtually measuring $K_2\varepsilon_2$ and there is not sufficient curvature to assign precise separate values to K_2 and ε_2, though it is clear that K_2 is small and ε_2 large (compared to K_1 and ε_1 respectively).

We now turn to a comparison of the present results with those of Czapski *et al.*[4] Their evidence for the formation of a species with an intense UV spectrum by an encounter-controlled reaction between NO and $(SCN)_2^-$ is very strong and $[NO(SCN)_2]^-$ seems a likely formulation. It must however be a different species to that formed by the reaction of SCN^- with ONSCN. The species $[NO(SCN)_2]^-$ decomposes with a first-order rate constant of 2.1×10^4 s^{-1} ($t_{\frac{1}{2}} = 3.3 \times 10^{-5}$ s), and would have completely decomposed long before our first measurements, even by stopped flow. Nevertheless the UV evidence for the presence of a species in our work is unmistakable and we suppose that they must be different compounds, possibly isomers. For this reason we write the formulae of the Czapski species in the same way as in their original paper, $[NO(SCN)_2]^-$

Table 1 Variation of ε_{420} with [thiourea] at 25 °C

$[(NH_2)_2CS]$/mol dm^{-3}	0.035	0.072	0.147	0.222	0.297	0.409	0.522	0.709	0.897
$\varepsilon_{420}{}^{a}$/dm^3 mol^{-1} cm^{-1}	113	113	118	119	120	126	132	132	139
$[(NMe_2)_2CS]$/mol dm^{-3}	0.02	0.06	0.10	0.14	0.18				
$\varepsilon_{420}{}^{b}$/dm^3 mol^{-1} cm^{-1}	192	196	199	204	208				

[a] $[H^+] = 0.10$, $I = 0.3$, $[(NH_2)_2CSNO^+] = 0.003\,16$ mol dm^{-3}. [b] $[H^+] = 0.49$, $I = 0.5$, $[(NMe_2)_2CSNO^+] = 0.006\,37$ mol dm^{-3}.

and NOSCN, whereas we write our species as $[ON(SCN)_2]^-$ and ONSCN emphasising that the nitroso group is bonded to sulfur. Czapski *et al.*[4] suggested that $[NO(SCN)_2]^-$ decomposed to NOSCN + SCN^-, and they show a spectrum for NOSCN that rises smoothly towards lower wavelengths in the UV region. Unfortunately their measurements do not extend above 340 nm, so it is not known whether the characteristic peak of ONSCN at 460 nm appears. The general shape of the UV spectrum is similar to our own observation on ONSCN, but the absorption coefficient at 320 nm is ≈190 dm^3 mol^{-1} cm^{-1}, much lower than our own value of 924 dm^3 mol^{-1} cm^{-1}. Again it appears that they may be observing a different species.

The hydrolysis reaction of the Czapski species NOSCN was found to obey pseudo-first-order kinetics, with a rate constant that decreased with increase of pH, 730 (pH 5.9), 458 (6.8), 126 (7.9) and 1.3 s^{-1} (1.5). This was interpreted by the mechanism in equations (5) and (6) with $k_6 \approx 800$ s^{-1} and $k_{-5}/k_6 \approx 10^7$. There

$$NOSCN + H_2O \rightleftharpoons (HO{-}NOSCN)^- + H^+ \qquad (5)$$

$$(HO{-}NOSCN)^- + H^+ \longrightarrow HNO_2 + SCN^- \qquad (6)$$

are some unusual features here. Reaction (6) is written as a bimolecular process, but k_6 is quoted as a first-order rate constant. The value of 800 s^{-1} looks to be a limiting value of the observed pseudo-first-order rate constant at high acidity. It can be compared with the value obtained by conventional methods for the hydrolysis of ONSCN. The rate constant for the forward reaction (1) is[7] 11 700 dm^6 mol^{-2} s^{-1}, and this value is supported by an independently determined value[8] at 0 °C which, when corrected for temperature variation ($E = 54$ kJ mol^{-1}), gives 10 900 dm^6 mol^{-2} s^{-1} at 25 °C. The equilibrium constant[1] for (1) is 32 dm^6 mol^{-2}, giving the rate constant for the hydrolysis reaction of 365 s^{-1}. The difference between this figure and 800 s^{-1} may be significant, but is not sufficiently large to be certain.

The reasons for the differences between our results and those of Czapski *et al.*[4] seem most likely to lie in different structures. Czapski did not, of course, on the basis of only UV evidence suggest a structure for $[NO(SCN)_2]^-$, but as we propose that we observe an isomer it is incumbent on us at least to make a suggestion. The structure of thiocyanogen $(SCN)_2$ certainly involves a sulfur–sulfur bond, and it seems likely that $(SCN)_2{}^-$ will be $[NCS{-}SCN]^-$. An encounter-controlled reaction with $NO^{\bullet}$ could lead to the formation of an N-nitroso species $[NCS{-}SCN{\cdot}NO]^-$. The sulfur–nitroso compounds (thionitrites) are characterised by red/yellow colours and absorption in the visible region, and nitrosyl thiocyanate clearly belongs in this class with an S–N=O chromophore. We do not know the structure of our adduct, but if it is derived from ONSCN then it is likely that it will have an S–NO bond and hence be different from $[NCS{-}SCN{\cdot}NO]^-$ and have a different spectrum and different stability. The decomposition of $[NCS{-}SCN{\cdot}NO]^-$ with loss of SCN^- will presumably produce nitrosyl isothiocyanate SCNNO, which will differ from our species ONSCN. Detailed calculations have been published by Westwood and Pasinszki[9] of the stability of open-chain and ring isomers of composition CN_2OS. They calculate that the gas-phase species SCNNO is some 16–17 kJ mol^{-1} less stable than ONSCN. Both are *anti* structures. These calculations indicate that the differences in stability of the N- and S-nitroso isomers is small enough that there is nothing unreasonable in postulating this as the structure of Czapski's compound, thus accounting for the differences between his results and ours.

In conclusion we cite some other evidence for the existence of other disulfide species with sulfur bonded to a nitroso group. Nitrous acid reacts with thiourea to form[10] a yellow S-nitroso product, $(NH_2)_2CSNO^+$, as shown in equation (7), with a

$$(NH_2)_2CS + H^+ + HNO_2 \rightleftharpoons (NH_2)_2CSNO^+ + H_2O \qquad (7)$$

formation constant of *ca.* 5000 dm^6 mol^{-2}. The stability of this species has been extensively examined[11] by stopped-flow methods at 420 nm, and its chemistry as a nitrosating agent has been studied in detail by Dix and Williams,[12] it shows a very similar reactivity pattern to that of ONSCN.

The absorption coefficient at 420 nm of solutions of thiourea + nitrous acid in which there is essentially 100% conversion of nitrite into $(NH_2)_2CSNO^+$ increases markedly and linearly with increase in $[(NH_2)_2CS]$. Similar behaviour is observed for solutions of $(NMe_2)_2CS$ + nitrous acid. Data are shown in Table 1. These observations parallel the effects observed in the HNO_2–SCN^- system, but in this case there is kinetic evidence that is consistent with the presence of a species $[(NH_2)_2CS]_2NO^+$, equation (8). The rate of decay of $(NH_2)_2CSNO^+$

$$(NH_2)_2CSNO^+ + (NH_2)_2CS \overset{K_3}{\rightleftharpoons} [(NH_2)_2CS]_2NO^+ \qquad (8)$$

has been measured,[11] and in the presence of a large excess of thiourea the rate law (9) is observed. This was originally

$$-d[(NH_2)_2CSNO^+]/dt = k_2[(NH_2)_2CSNO^+][(NH_2)_2CS] \qquad (9)$$

interpreted as attack by thiourea on $(NH_2)_2CSNO^+$ to form $(NH_2)_2CSSC(NH_2)_2{}^{\bullet +} + NO^{\bullet}$, the radical cation undergoing further oxidation to form the known product $(NH_2)_2CSSC(NH_2)_2{}^{2+}$. This does not account however for the increase in absorbance with $[(NH_2)_2CS]$. However if there is the formation of a small amount of a thiourea adduct which absorbs much more strongly than $(NH_2)_2CSNO^+$ and which decomposes then precisely the same rate law would be observed, the difference being that k_2 would be K_3k_3, equations (8) and (10).

$$[(NH_2)_2CS]_2NO^+ \xrightarrow{k_3} (NH_2)_2CSSC(NH_2)_2{}^{\bullet +} + NO \qquad (10)$$

The structure of the postulated adduct is not known, but as the end product of the decomposition of $(NH_2)_2CSNO^+$ is $(NH_2)_2CSSC(NH_2)_2{}^{2+}$ which is known from X-ray crystallography[13] to contain an S–S linkage it is reasonable to assume that this exists in the adduct also. We considered the possibility that the rate law (9) might be due to nitrosation of a dimer of thiourea, but investigation of the ^{13}C NMR shift of aqueous solutions of thiourea showed no sign of any variation with $[(NH_2)_2CS]$. Similarly we were unable to detect any deviation from the Beer–Lambert law for thiourea solutions, so we did not find any evidence for dimer formation.[14]

We conclude that sulfur–nitroso compounds can undergo addition reactions with other sulfur nucleophiles to form adducts in which a sulfur–sulfur bond is formed. It seems likely that the species $[NO(SCN)_2]^-$ and NOSCN observed in pulse radiolysis are N-nitroso compounds, and that the compound described by Czapski *et al.*[4] as NOSCN is different from the nitrosyl thiocyanate known as a nitrosating agent in aqueous solutions.

Experimental

Materials

All chemicals were of AnalaR grade with the exception of tetramethylthiourea and were used without further purification.

Spectrophotometric and kinetic measurements

Stopped-flow measurements were made with a Hi Tech Canterbury SF-3A instrument, fitted with a data-collection system as described previously.[11] Conventional VIS/UV spectra were measured on a Perkin-Elmer lambda nine spectrometer about 30 s after mixing. The spectrum of ONSCN, Fig. 1, was obtained from a solution of $H^+ + HNO_2 + SCN^-$ at low $[SCN^-]$ in order to avoid complications due to formation of $[ON(SCN)_2]^-$. Under these conditions there is only partial conversion into nitrosyl thiocyanate and corrections for absorption due to HNO_2 and SCN^- were subtracted. Absorption coefficients were calculated by taking the absorbance at 460 nm to be equivalent to $\varepsilon = 100$ dm^3 mol^{-1} cm^{-1}.

Acknowledgements

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