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Kinetics and equilibria in the nitric acid–nitrous acid–sodium thiocyanate system

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The nature of the red species formed in acidic solutions containing nitrous acid and thiocyanate ion has been confirmed to be ONSCN. The alternative literature interpretation in terms of $ONSCNH^+$ arises from neglect of activity coefficients and partial protonation of SCN^- to HNCS in moderately concentrated mineral acid. The kinetics of the nitrous acid-catalysed oxidation of thiocyanate in moderately concentrated nitric acid is controlled by rate-determining formation of N_2O_4 at even modest concentrations of thiocyanate. Literature work on this system is discussed.

The present paper describes a study to resolve a marked difference in the mechanism proposed in two separate investigations of the autocatalytic oxidation of alkali-metal thiocyanates by nitric and nitrous acids.[1–3] The autocatalytic nature of the reaction has made it of interest in the field of 'exotic' kinetics. It has been shown[3] to exhibit bistability in CSTR (continuous-flow stirred-tank reactor) studies and to show[4] travelling wave behaviour. The difference in interpretation also has implications in the field of organic and inorganic nitrosation mechanisms, and concerns the nature of the red species observed when thiocyanates are mixed with aqueous nitrous acid.

The chemistry of the nitrous acid–thiocyanate system has been studied[5] in relatively dilute perchloric and sulfuric acids, $[H^+] < 2$ mol dm^{-3}. The solutions show a characteristic red colour, $\lambda_{max} = 460$ nm, and on the basis of the variation of absorbance with $[H^+]$, $[HNO_2]$ and $[SCN^-]$ has been ascribed to the formation of nitrosyl thiocyanate, equation (1).

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

At sufficiently high values of $[H^+][SCN^-]$ a large fraction of the nitrite is converted into the coloured nitrosyl compound, and it was established that at the wavelength maximum $\varepsilon = 100$ dm^3 mol^{-1} cm^{-1}. Formation constants were measured for a range of conditions. Nitrosyl thiocyanate has been synthesised at low temperatures,[6] but decomposes at room temperature. In aqueous solution it is moderately stable at ambient temperatures, but undergoes slow decomposition to form nitrogen(II) oxide, sulfuric acid, hydrogen cyanide and isothiocyanic acid, probably due to a combination of reactions (2) and (3). The disproportionation/hydrolysis reaction (3)

$$2ONSCN \rightleftharpoons 2NO + (SCN)_2 \qquad (2)$$

$$4H_2O + 3(SCN)_2 \longrightarrow H_2SO_4 + HCN + 5HNCS \qquad (3)$$

must be a multistage process. Minor distortions to the stoichiometry can be caused[1] by an encounter-controlled nucleophilic substitution by CN^- at $(SCN)_2$ to yield $S(CN)_2$ and SCN^-. In aqueous nitric acid (which always contains traces of nitrous acid unless a nitrite scavenger has been added) an autocatalytic reaction occurs[2] in which thiocyanate is oxidised to the products shown in equation (4), while nitrate is reduced

$$(2x - 1)H_2O + HNCS + (2x + 1)HNO_3 \longrightarrow xH_2SO_4 + (2x - 1)HCN + (1 - x)S(CN)_2 + (1 + 2x)HNO_2 \qquad (4)$$

to nitrite, which functions as a catalyst. The reaction was monitored by the increase in total nitrite concentration, $[NO_2]_T = [HNO_2] + [ONSCN]$, and showed the typical sigmoidal curve of an autocatalytic reaction. In the early stages, where there was little consumption of thiocyanate, plots of $\ln[NO_2]_T$ *vs.* time were linear, yielding a pseudo-first-order rate constant k_{obs}/s^{-1}. The absorbance at 460 nm increased autocatalytically, reached a sharp maximum and then decayed rapidly to zero. The active species in the oxidation was identified as dinitrogen tetraoxide, and the mechanism is summarised in equations (5)–(10). Reaction (10) leads to an

$$HNCS \overset{K_a}{\rightleftharpoons} H^+ + NCS^- \qquad (5)$$

$$H^+ + HNO_2 + NO_3^- \xrightarrow{k_1} N_2O_4 + H_2O \qquad (6)$$

$$N_2O_4 + H_2O \longrightarrow H^+ + HNO_2 + NO_3 \qquad (7)$$

$$N_2O_4 + HNCS \longrightarrow N_2O_3 + HOSCN \qquad (8)$$

$$HOSCN + H^+ + SCN^- \rightleftharpoons (SCN)_2 + H_2O \qquad (9)$$

$$N_2O_3 + H_2O \rightleftharpoons 2HNO_2 \qquad (10)$$

increase in concentration of the catalytic species HNO_2, while the disproportionation/hydrolysis of thiocyanogen, equation (3), has been found to be a rapid reaction at low $[H^+]$ and $[SCN^-]$. Isothiocyanic acid, HNCS, is a moderately strong acid, $pK_a = -1.85$, and at the acidities used in the original investigation is largely ionised. At high values of $[H^+][NCS^-]$ the concentration of covalent HNCS is sufficiently large to trap essentially all of the N_2O_4 formed, reaction (6) becomes rate determining, and the rate might be expected to become independent of the thiocyanate concentration. However these are also the conditions that favour increased conversion of HNO_2 into ONSCN. It was found that k_{obs} increased with increase in $[H^+][SCN^-]$, levelled off and then decreased, due to the decreasing fraction of nitrite present as HNO_2. Multiplying k_{obs} by the correction factor $[NO_2]_T/[HNO_2]$ gave a corrected rate constant, k_{corr}, which was constant at high $[SCN^-][H^+]$.

The other investigation by Bazsa and Epstein[3] examined the kinetics of oxidation in 1–8 mol dm^{-3} nitric acid as part of a search for systems showing bistability. They did not measure the total nitrite concentration, but instead monitored the growth and decay of the absorbance at 460 nm. By an ingenious

Table 1 Classical formation constants for ONSCN and $ONSCNH^+$

	$[HClO_4]$/mol dm^{-3}									
	0.5	1.0	1.5	2.0	2.5	3.0	3.2	4.0	5.0	6.0
$K_1{}^a$/dm^6 mol^{-2}	11	22	32	38	60	95	109	152	—	—
$K_{1B}{}^b$/dm^6 mol^{-2}	—	20.4	30.8	38.6	54.2	73.4	—	121.7	115.9	104
$K_{2B}{}^b$/dm^9 mol^{-3}	—	20.4	20.5	19.3	21.7	24.5	—	30.4	23.2	17.4

$K_1 = [ONSCN]/[H^+][HNO_2][SCN]_T$; $K_{2B} = [ONSCN]/[H^+]^2[HNO_2][SCN]_T$. [a] Present work. [b] Data from ref. 3.

analysis of the conditions for maximum absorbance they suggested that the red intermediate was $ONSCNH^+$. They proposed the mechanism set out in equations (11)–(14) in which

$$H^+ + HNO_2 + NO_3^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2NO_2 + H_2O \quad (11)$$

$$2NO_2 + SCN^- + 3H^+ + 2NO_3^- + 2H_2O \longrightarrow H_2SO_4 + HCN + 4HNO_2 \quad (12)$$

$$HNO_2 + SCN^- + 2H^+ \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} ONSCNH^+ + H_2O \quad (13)$$

$$2NO_2 + ONSCNH^+ + H^+ + 2NO_3^- + 3H_2O \longrightarrow H_2SO_4 + HCN + 5HNO_2 \quad (14)$$

$ONSCNH^+$ is an active species. These equations have been written as in the original paper, and are stoichiometric. The authors carried out a numerical simulation using the expressions $k_2[NO_2][SCN^-]$ and $k_4[NO_2][ONSCNH^+]$ for the rates of (12) and (14) respectively, assuming further rapid stages leading to the stoichiometries specified. They predicted values for $[ONSCNH^+]_{max}$ and an induction time (from mixing to maximum absorbance at 460 nm) by assuming an initial nitrite concentration $[HNO_2]_0 = 5 \times 10^{-8}[HNO_3]_0$.

The differences in interpretation have wider implications than merely the mechanism of oxidation of thiocyanate. Nitrosyl compounds are active nitrosating agents in diazotisation and deamination reactions in both organic and inorganic chemistry, and their chemistry has been discussed in detail by Williams.[7] The formation of nitrosyl compounds, equation (15), has been studied for a number of anions, $X^- = Cl^-, Br^-$,

$$H^+ + HNO_2 + X^- \rightleftharpoons ONX + H_2O \quad (15)$$

$S_2O_3^{2-}$, NO_2^-, N_3^-, $CH_3CO_2^-$ or NCS^-. In most cases[7] formation constants have been measured spectrophotometrically, and by suitable choice of conditions the rate law and rate constant for the formation of ONX have been measured. In no case is there any evidence for the additional proton postulated in equation (10). The chemistry of ONSCN has been discussed[7] in detail and fits the same pattern as that for other nitrosyl compounds.

Results and Discussion

Nature of red species

There is strong experimental evidence that the red species is ONSCN in dilute acid, both from the variation of absorbance at 460 nm with $[H^+]$ and from the fact that the rate law for its formation[5b] is $k[H^+][HNO_2][SCN^-]$. We have confirmed this by measurements of the solvent isotope effect and find $K_D/K_H = 3.3 \pm 0.5$, in good agreement with the value of 3.5 for the formation of N_2O_3 ($X^- = NO_2^-$). If there were an additional proton then K_D/K_H should be a factor of 2–2.5 higher. This confirms that ONSCN is formed in dilute acid, but we need to consider whether an additional proton might be added in the more acidic conditions of 2–5 mol dm^{-3} nitric acid. We begin with studies of the equilibrium system in perchloric acid solution, free from the complications of the autocatalytic oxidation. The stoichiometric equilibrium constants for (1), $K_1 = [ONSCN]/[H^+][HNO_2][SCN]_T$, are shown in Table 1 together with an independently determined set of values, K_{1B}, measured by Bazsa.[8] In our experiments there was a large excess of thiocyanate over nitrite, and the stoichiometric thiocyanate concentration $[SCN]_T = [SCN^-] + [HNCS]$. There is very little difference between the two sets of data at < 2.5 mol dm^{-3} perchloric acid, though at higher values of $[HClO_4]$ the present values are somewhat higher. It is clear that there are no serious differences between the two groups in terms of experimental data. The problems arise in interpretation. The final row of Table 1 shows values for the equilibrium constant of (13), $K_{2B} = [ONSCNH^+]/[H^+]^2[HNO_2][SCN]_T$ and the approximate constancy of K_{2B} is apparent. These values are close to the figure of 19.8 dm^9 mol^{-3} deduced by Bazsa and Epstein[3] from their kinetic work in nitric acid, and is apparent evidence for postulating $ONSCNH^+$ as the red species. The difficulties with this approach are that the values are classical equilibrium constants and take no account of the effect of activity coefficients or the protonation of the thiocyanate ion in moderately concentrated perchloric acid. The UV spectra of NaNCS in perchloric acid show clear evidence for extensive protonation, as can be seen from the figure in a published[9] study. Ionisation ratios in solutions of constant formal ionic strength, 7.2 mol dm^{-3} $HClO_4$ + $NaClO_4$ (to minimise spectral shifts due to changes in medium), give $[NCS^-]/[HNCS]$ as 5.1, 2.0, 0.86, 0.36 and 0.145 at $[HClO_4]$ = 2.4, 3.2, 4.0, 4.8 and 5.6 mol dm^{-3}. Further evidence comes from solvent-extraction experiments. A great many studies have shown that a range of organic solvents will extract HNCS from acid solutions of thiocyanate salts. When the extractions are done at constant ionic strength ($NaClO_4$ + $HClO_4$) the overall partition coefficient $P = ([HNCS] + [SCN^-])_{aq}/[HNCS]_{org}$ decreases with increase in $[H^+]$, and then levels off,[9] corresponding to complete protonation. This is again direct evidence for protonation. Other evidence[10,11] comes from kinetic studies of the hydrolysis of thiocyanate, where plots of log k_{obs} *vs.* H_0 are linear in the region where protonation is complete but show deviations (lower k_{obs}) due to ionisation at low acidities. Turning to the absence of activity coefficients we note that the activity of water is 0.468 in 6 mol dm^{-3} perchloric acid which will introduce a factor of 2.14 in any calculation of K_{2B}. Values of $f_{H^+}f_{SCN^-}$ are not available for solutions in $HClO_4$, but the known large variations in activity coefficients, $f_\pm$, for $HClO_4$, HCl, HBr and other strong mineral acids makes it very likely that $f_\pm$ for H^+NCS^- will vary by a substantial factor. For $HClO_4$ $f_\pm$ (on the molality scale) varies by a factor of 4.25 from 0.5 to 6 mol kg^{-1}. We consider, therefore, that the apparent constancy of K_{2B}, which is impressive, must be due to a chance partial cancellation of corrections due to activity coefficient effects and partial ionisation. In fact there is no need to postulate equilibrium (13); it is quite adequate to accept that classical equilibrium constants will vary in moderately concentrated mineral acids, and use the value of K_1 appropriate to each acid concentration.

To complete the case it would be desirable to show that the variation of K_1 with [$HClO_4$] can be accounted for, at least semiquantitatively. This is more difficult. There is no generally agreed value for the ionisation constant of HNCS. We have proposed[9] a value of -1.85 for the pK_a based upon solvent-extraction experiments. Covington and Matheson,[12] using band-deconvolution techniques on Raman spectra, suggested a pK_a of -1.1. Crowell and Hankins,[11] using acidity functions in the interpretation of kinetic data on the acid catalysed hydrolysis of HNCS suggested values between -2 and -2.3. The calculation of the mean ion activity coefficients is a real difficulty. As an approximation we have used an acidity function approach. If H_x is an appropriate acidity function for the protonation of SCN^- then $[SCN^-]/[SCN]_T = K_a/(K_a + h_x)$. Taking the thermodynamic equilibrium constant for (1) as K_1*, and using the approximation that the activity coefficients for ONSCN and HNO_2 will vary relatively little and may be cancelled, then equation (16) can be written, with f_- as the

$$K_1{}^* = [ONSCN]a_{H_2O}/a_{H^+}[HNO_2][SCN^-]f_- \quad (16)$$

activity coefficient for SCN^-. As $h_x = a_{H^+}f_-/f_{HNCS}$, substitution in (16) yields equation (17). An approximate expression for

$$K_1{}^* = K_1a_{H_2O}[H^+](K_a + h_x)/(h_xf_{HNCS}K_a) \quad (17)$$

f_{HNCS} has been obtained[9] from the variation of partition coefficient with [$HClO_4$] at acidities where protonation appears to be complete, $\log f_{HNCS} = 0.041[HClO_4]$. The difficulty lies in the choice of K_a and of a suitable acidity function H_x. We have used our own value of $K_a = 70$ mol dm^{-3}. It is well established that even for indicator bases of a given charge type the acidity function varies with the class of compound used. We have used the H_- acidity function of Boyd,[13] based upon cyanocarbon indicators, and also the familiar H_0 function. Rochester[14] has pointed out that they do not differ greatly at low perchloric acid concentrations, but that at higher values of [$HClO_4$] H_- is somewhat more negative than H_0. As we do not have independently determined values of $[SCN^-]/[HNCS]$ for media in which H_0 and H_- have been measured we cannot check the choice of acidity functions directly.

Values of K_1* based upon H_0 and H_- are shown in Table 2. It can be seen that the fifteen-fold variation in K_1 disappears when H_0 is used, and there is only a two-fold variation when H_- is used as an approximation to H_x. It would be possible to extend this procedure by using other acidity functions and other values of K_a, but even if it resulted in improved constancy it would not really strengthen the case. Overall we conclude that the original assignment of the red species as ONSCN is correct, and there is no need to consider species such as $ONSCNH^+$, even in moderately concentrated nitric acid.

Kinetics and mechanisms of oxidation in nitric acid

We have used essentially the same technique for studying the oxidation of thiocyanate in nitric acid up to 4.5 mol dm^{-3} as we used[2] in more dilute solutions. Aliquots were analysed for total nitrite, $[NO_2]_T = [HNO_2] + [ONSCN]$, by the diazotisation/coupling method. This has the advantage of being very sensitive and enabling rate measurements to be made in the early stages of reaction where complications due to the consumption of thiocyanate can be neglected. Under our conditions conversion of nitrous acid into N_2O_4 and NO_2 is very small, and these species make a negligible contribution to $[NO_2]_T$. At these higher acidities nitrosyl thiocyanate may constitute a significant fraction of total thiocyanate, $[SCN]_T = [SCN^-] + [HNCS] + [ONSCN]$. The general behaviour was very similar to that observed[2] in more dilute nitric acid. The reaction was autocatalytic, and plots of $\ln[NO_2]_T$ *vs.* time yielded first-order rate constants k_{obs}/s^{-1}. A summary of the data is shown in Table 3. As $[SCN]_T$ increases (at constant [HNO_3]) the value of k_{obs} increases, passes through a broad maximum and then decreases. Comparison of runs at a given $[SCN]_T$ shows a large increase in k_{obs} with [HNO_3]. However the kinetics is more complicated than this. When a set of runs is carried out at constant $[SCN]_T$ but closely spaced values of [HNO_3] it is found that k_{obs} increases, passes through a maximum, followed by a shallow minimum, and then finally increases again. Results are shown in Fig. 1. In our original work[2] the decrease in k_{obs} at high $[SCN]_T$ was attributed to the decrease in [HNO_2], as an increasing fraction of nitrite was converted into ONSCN. When k_{obs} was multiplied by $[NO_2]_T/[HNO_2]$, calculated from the known value of K_1, it was found that the corrected rate constant k_{corr} levelled off at high $[SCN]_T$ as expected if the formation of N_2O_4 is rate determining. It is more difficult to apply this correction in more concentrated nitric acid because of the lack of values of the activity coefficients. As an approximation we have noted the value of H_0 for a particular [HNO_3], and then found the concentration of perchloric acid corresponding to the same H_0. We have then used the measured [ONSCN]/[HNO_2] ratios for perchloric acid to calculate an estimate for $[NO_2]_T/[HNO_2]$ for the corresponding nitric acid concentration. The corrected values are shown in columns headed *a* on the right-hand side of Table 3, and it can be seen that k_{corr} levels off at high $[SCN]_T$, as was previously observed for dilute nitric acid. An alternative approach, which avoids comparison with perchloric acid, is to use the experimental data of Bazsa and Epstein[3] to calculate a value for K_1 and hence $[NO_2]_T/[HNO_2]$. As explained below their treatment requires

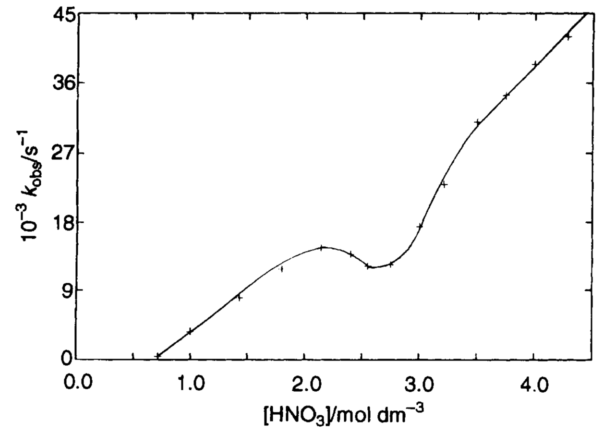

Fig. 1 Variation of k_{obs} with [HNO_3] for the oxidation of 0.01 mol dm^{-3} NaNCS at 25 °C

Table 2 Correction of K_1 for activity coefficients and partial protonation of SCN^-

	[$HClO_4$]/mol dm^{-3}						
	0.5	1.0	1.5	2.0	2.5	3.0	4.0
$K_1{}^{*a}$/dm^6 mol^{-2}	8.2	11.8	12.3	10.3	11.5	12.9	10.1
$K_1{}^{*b}$/dm^6 mol^{-2}	11.0	12.6	10.8	7.3	6.8	7.0	6.0

[a] Calculated using H_0, $K_a = 70$ mol dm^{-3}. [b] Calculated using H_-, $K_a = 70$ mol dm^{-3}.

Table 3 Values of k_{obs} and k_{corr} at 25 °C

	$10^3\ k_{obs}/s^{-1}$				$10^3\ k_{corr}/s^{-1}$							
$[HNO_3]/mol\ dm^{-3}$ =	1	2.1	3.2	4.5	1		2.1		3.2		4.5	
$10^3\ [SCN]_T/mol\ dm^{-3}$					*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
5	0.7	4.6	9.8	19.0	0.7	0.8	6.1	6.6	18.5	19.7	62	61
10	2.7	14.7	23.0	27.0	3.3	3.3	24.8	27.4	63.9	69.7	148	145
15	4.8	—	28.0	41.2	—	—	—	—	103	113	317	311
20	4.8	13.6	26.0	42.2	7.0	7.0	32.4	37.1	119	132	420	411
30	4.8	11.2	21.4	38.8	7.9	8.0	34.5	40.2	136	152	559	547
40	4.4	9.8	18.0	34.0	8.3	8.3	36.9	43.7	146	164	642	628
50	4.0	—	—	—	8.5	8.5	—	—	—	—	—	—
60	—	7.5	13.2	25.7	—	—	38.6	46.4	154	174	715	700
70	—	—	—	21.0	—	—	—	—	—	—	678	663
80	3.0	—	9.8	—	8.4	8.4	—	—	149	169	—	—

[a] Values by comparison with $HClO_4$. [b] Values using Bazsa and Epstein[3] data.

Table 4 Comparison of k_{corr} and k_1 values at 25 °C

	$[HNO_3]/mol\ dm^{-3}$			
	1	2.1	3.2	4.5
$10^3\ k_{corr}{}^{a}/s^{-1}$	8.5	40	150	700
$10^3\ k_{corr}{}^{b}/s^{-1}$	8.5	46	170	680
$10^3\ k_1[H^+][NO_3^-]^{c}/s^{-1}$	5	47	210	740
$10^3\ k_1[H^+][NO_3^-]^{d}/s^{-1}$	15	66	154	304

[a] Values by comparison with $HClO_4$. [b] Values using Bazsa and Epstein[3] data. [c] Schmid and Bähr[14] data. [d] Bazsa and Epstein model for k_1.

modification, but there is no reason to doubt the soundness of their data, and this approach has the great advantage that it refers to aqueous nitric acid as the reaction medium. We have calculated values of K_1 from Table 1 of ref. 3, and used these to correct k_{obs} to k_{corr}. The results are shown in the columns headed *b* in Table 3. It can be seen that both methods of correction give similar levelled-off values at high $[SCN]_T$. A further check is possible, as the limiting values of k_{corr} should equal the rate constant for the formation of N_2O_4. Values for this rate as a function of $[HNO_3]$ are available from the work of Schmid and Bähr[15] over the range 0–20 °C. Using their activation energy of 18.3 kcal mol^{-1} (*ca.* 76.6 kJ mol^{-1}) the rate constant at 25 °C can be calculated, and these values are shown in Table 4. Considering the approximations made the agreement between lines *a*, *b* and *c* is good, and confirms that at high concentrations of thiocyanate the rate-determining stage is the formation of N_2O_4 by reaction (6). The figures in row *d* show that the expression used by Bazsa and Epstein, in their numerical simulation, $k_1 = 0.015$ dm^6 mol^{-2} s^{-1}, gives a reasonable representation of the rate constant over a range of acidities even though it ignores activity coefficient effects, though there can be significant differences at low acidities.

Turning now to the dependence of k_{obs} upon $[HNO_3]$ there are two opposing effects, a rapid increase in the rate of formation of N_2O_4 and a decrease in the proportion of nitrite present as HNO_2. Overall it is clear that the increase in rate of formation of N_2O_4 dominates. Attempts to model the small maximum/minimum observed around 3–3.5 mol dm^{-3} nitric acid by multiplying the value of k_1 from Schmid and Bähr by a correction $[HNO_2]/[NO_2]_T$ calculated from Bazsa and Epstein's figures did not show any blip in the curve of $k_1[HNO_2]/[NO_2]_T$ *vs.* $[HNO_3]$. Whether this is due to imperfections in our corrections, or some other factor, we cannot determine. The same blip in the curve of k_{obs} *vs.* $[HNO_3]$ was observed earlier[16] in work at 0 °C.

We now turn to the Bazsa and Epstein paper. Their treatment has an elegant simplicity, but it does need more detailed consideration. The approach is based upon the assumption of a 3:1 stoichiometry for $[NO_2]:[SCN]_T$, and this is only an approximation. The authors themselves remark on the variation of the stoichiometric ratio, which changes from 2.6 to 3.2:1 as $[HNO_3]$ varies from 1 to 5 mol dm^{-3}. The figure of 2.6:1 agrees well with previous work which showed[1] the deviation below 3:1 to be due to the formation of $S(CN)_2$. It may be noted that the 2.6:1 ratio corresponds to 20% of the reacted thiocyanate forming sulfur dicyanide, a sizeable fraction of the product! In the earlier work it was also noted that the stoichiometry varied during the reaction, and only extrapolated to 3.0:1 in the early stages before HCN accumulated. It should also be noted that $[H^+] = [HNO_3]$ is not a good approximation. Davis and de Bruin[17] have, by the analysis of a large amount of physical data on aqueous nitric acid, produced values for the degree of dissociation and activity coefficients as a function of stoichiometric nitric acid concentration. For 5 mol dm^{-3} HNO_3 there is only 80.9% dissociation, corresponding to 4 mol dm^{-3} H^+. This has been confirmed[18] by Raman spectra.

Bazsa and Epstein's approach makes use of the variation of absorbance at 460 nm due to the red species. Assuming a stoichiometry of 3 HNO_2 formed for each thiocyanate oxidised they write a material balance equation (18) and argue that the

$$[SCN^-]_0 = [SCN^-] + [ONSCN] + \tfrac{1}{3}([HNO_2] + [ONSCN]) \quad (18)$$

maximum concentration of the 1:1 complex ONSCN will be formed when HNO_2 and SCN^- are in a 1:1 ratio. By setting $[HNO_2] = [SCN^-]$ and substituting in (18) they deduce equation (19). As $K_1/[H^+]$ was approximately constant at 19.8

$$K_1 = \frac{[ONSCN]_{max}}{(\tfrac{3}{4}[SCN^-]_0 - [ONSCN]_{max})^2\,[H^+]} \quad (19)$$

dm^9 mol^{-3} over a range of nitric acid they proposed that the red species was formed as in equation (13). In this treatment they neglect protonation to form HNCS. We use the same symbols as in their original paper; $[SCN^-]_0$ corresponds to what we call $[SCN]_0$, the initial stoichiometric thiocyanate concentration. The assumption of maximum [ONSCN] at a 1:1 ratio of HNO_2 and SCN^- is justified for the case where the total concentration of these species is constant, and the ratio $[SCN^-]/[HNO_2]$ varies. However in the present system if 3 HNO_2 are formed for each SCN^- consumed the maximum will occur where $\tfrac{1}{3}[HNO_2] = [SCN^-]$ as may readily be checked by direct calculation. Substitution in (19) yields equation (20). This

$$K_1 = \frac{3}{4}\,\frac{[ONSCN]_{max}}{(\tfrac{3}{4}[SCN^-]_0 - [ONSCN]_{max})^2\,[H^+]} \quad (20)$$

modifies the value of K_1 though the remainder of the equation is unchanged. If we also include a correction for the formation of HNCS and write $\alpha = [SCN^-]/[HNCS]$ then equation (21)

$$K_1 = \frac{3\,(1 + \alpha)}{4 \quad \alpha} \cdot \frac{[ONSCN]_{max}}{[H^+](\frac{3}{4}[SCN^-]_0 - [ONSCN_{max}])^2} \qquad (21)$$

is obtained. The variation of K_1 with $[HNO_3]$ that they observe will still occur, and $K_1/[HNO_3]$ will still be almost constant. However the arguments put forward earlier that this is due to a combination of the variation of activity coefficients and the protonation of SCN^- apply equally strongly.

One other comment needs to be made concerning the use of absorbance measurements at 380 nm to measure the concentration of nitrous acid. This was done using $\varepsilon = 27$ $dm^3\ mol^{-1}\ cm^{-1}$, a reasonable value. However it must be remembered that ONSCN also absorbs in the UV as well as in the visible region, and a correction must be made for this. We have measured the spectrum of a solution of $NaNCS + HNO_2 + HClO_4$ over a range of wavelengths and plotted A_{380}/A_{460} as a function of $1/[SCN^-]$. Such plots are linear, and by extrapolating to $1/[SCN^-] = 0$ the intercept gives the ratio of $\varepsilon_{380}/\varepsilon_{460}$ for ONSCN. Knowing $\varepsilon_{460} = 100\ dm^3\ mol^{-1}\ cm^{-1}$ we calculate $\varepsilon_{380} \approx 104\ dm^3\ mol^{-1}\ cm^{-1}$, while measurements at other wavelengths give $\varepsilon_{370} = 130$ and $\varepsilon_{390} = 80\ dm^3\ mol^{-1}\ cm^{-1}$. Now as the total absorbance is given by equation (22) for

$$A = \varepsilon_{ONSCN}[ONSCN] + \varepsilon_{HNO_2}[HNO_2] \qquad (22)$$

a 1 cm cell, values for $d[HNO_2]/dt$ are only obtainable from dA/dt if we know the ratio $[ONSCN]/[HNO_2]$, or if $d[ONSCN]/dt = 0$. This last condition will be true at the end of the reaction, so that Bazsa and Epstein's final yields of HNO_2 are reliable, and also at the maximum. Bazsa and Epstein[3] state that their maximum rates of HNO_2 formation occurred 'at about the time' when [ONSCN] was maximum, so their quoted maximum rates are unlikely to be distorted very much by the factor. However absorbance *vs.* time curves in the near-UV region cannot in general be used to give HNO_2 concentrations in systems containing thiocyanate without corrections for the presence of ONSCN.

We finally turn to the differences between the two mechanisms which have been postulated. The nature of the red species is not an essential feature of the Bazsa and Epstein mechanism. Equations (13) and (14) could be rewritten in terms of ONSCN with appropriate modifications to the rate constants without affecting the numerical simulation. For the conditions where the formation of N_2O_4 is rate determining it does not matter whether equation (6) or (11) is formulated in terms of N_2O_4 or $2NO_2$. The post rate-determining steps are not revealed by the kinetics. Under these conditions the question of whether the red species is 'inert' or 'active' is not important. The formation of a significant fraction of this species reduces $[HNO_2]$ and hence the rate of the forward reaction in equations (6) and (11) in both mechanisms, while its participation in a post rate-determining reaction will not affect the kinetics.

The evidence for the mechanism in equations (11)–(14) is considered to be the success of the numerical simulation in predicting $[ONSCNH^+]_{max}$ and the induction period. However the simulation uses data obtained from experimental measurements of $[ONSCNH^+]_{max}$. The calculation of the induction time depends upon an assumed value for the initial nitrite concentration using the expression $[HNO_2]_0 = 5 \times 10^{-8}[HNO_3]_0$. This also depends upon using experimental data on the variation of induction time with known concentrations of added nitrite. The simulations have been used to predict the bistability 'phase diagrams' in the CSTR experiments, but when the rate of reaction approaches the limiting rate of equation (11) the calculation will be less sensitive to the values used as rate constants for the later stages.

The one region where a distinction may be drawn is at low thiocyanate concentrations where the initial reaction is a true pre-equilibrium. The mechanism in equations (5)–(10) leads to the prediction of rate law (23). This was the law found

$$\text{rate} = k[H^+]^2[HNO_2][NO_3^-][SCN^-] \qquad (23)$$

experimentally,[2] and the appearance of the $[H^+]^2$ term was the reason for postulating HNCS rather than SCN^- as the substrate. The alternative approach of Bazsa and Epstein[3] leads to equation (24). Since there are two terms in the rate law,

$$\text{rate} = (k_1/k_{-1})^{\frac{1}{2}}[H^+]^{\frac{1}{2}}[HNO_2]^{\frac{1}{2}}[NO_3^-]^{\frac{1}{2}} \times \{k_2[SCN^-] + (k_4k_3/k_{-3})[H^+][HNO_2][SCN^-]\} \qquad (24)$$

corresponding to reactions (12) and (14), the overall order with respect to $[H^+]$ and $[HNO_2]$ will be a function of these concentrations.

We conclude that the red species formed in the autocatalytic oxidation of thiocyanate by nitric and nitrous acids is ONSCN and not $ONSCNH^+$. At higher thiocyanate concentrations the rate of reaction is controlled by the rate of formation of N_2O_4, and thiocyanate actually reduces the rate by converting some nitrite into ONSCN, thereby reducing $[HNO_2]$. At sufficiently low concentrations of thiocyanate N_2O_4 is in equilibrium with $HNO_3 + HNO_2$, and the reaction order with respect to $[SCN^-]$ is one. However the only clear-cut evidence still suggests a reaction between N_2O_4 and HNCS. There are still features that are not fully understood, in particular the variation of rate constant with $[HNO_3]$ in the region where there is a local maximum in the rate, and also the rather sharp transition from kinetics that are first order to kinetics that are zero order with respect to thiocyanate concentrations.

Experimental

Materials

All chemicals were of AnalaR grade used, without further purification.

Kinetics

Reactions were followed by colorimetric analysis for nitrite. An aliquot of the reaction mixture was quenched in 5 cm^3 of solution A (0.5 g sulfanilic acid, 13 cm^3 60% w/w perchloric acid and 10 g sodium bromide made up to 500 cm^3). Diazotisation was rapid and quantitative. The azo dye was formed by adding 10 cm^3 of solution B [0.5 g Cleve's acid (1-naphthylamine-7-sulfonic acid), 27 g sodium acetate, 1.6 cm^3 glacial acetic acid, made up to 500 cm^3]. The azo dye solution was made up to 50 cm^3 with saturated borax (sodium tetraborate), and the absorbance measured at 465 nm.

Equilibria

Spectrophotometric measurements for the formation of ONSCN followed methods described previously,[5a] using a Unicam SP8–200 instrument. Absorbance measurements were made at 30 s intervals, in a 4 cm cell. The absorbance values were plotted, and the graph extrapolated to the time of mixing to correct for any changes due to decomposition.

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