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Kinetics and Mechanism of the Decomposition of Thionitrites derived from Thioureas

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The decomposition of $[(NMe_2)_2CSNO]^+$ to $[(NMe_2)_2CSSC(NMe_2)_2]^{2+} + 2NO^{\cdot}$ has been investigated spectrophotometrically using the method of initial rates. The thionitrite was generated by mixing deoxygenated solutions of tetramethylthiourea and nitrous acid in a stopped-flow apparatus. For reaction with a large excess of tetramethylthiourea over nitrous acid the observed rate law (below) was similar to that reported for the analogous thiourea system. In solutions initially saturated with $NO^{\cdot}$

$$v_0 = k_1[(NMe_2)_2CSNO^+][(NMe_2)_2CS] + k_2[(NMe_2)_2CSNO^+]^2$$

the first term is largely suppressed. For systems in which $[(NMe_2)_2CSNO]^+$ or $[(NH_2)_2CSNO]^+$ was generated quantitatively from $(NMe_2)_2CS$ or $(NH_2)_2CS$ by reaction with a large excess of HNO_2 the first term is again suppressed, but a new term in the rate law involving catalysis by nitrous acid occurs. The mechanisms of the decomposition reactions are discussed.

The chemistry of the thionitrites, RSNO, is a subject of current interest,[1] and they may be significant in N-nitrosation processes in biological systems. They are rather unstable substances which break down to disulphides, and nitrogen(II) monoxide, but not very much is known about the mechanism of their decomposition.[2] In a previous paper we described [3] a study of the kinetics and mechanism of the decomposition of the thionitrite species $[(NH_2)_2CSNO]^+$ derived from thiourea and nitrous acid, equation (1). Reaction was carried out in aqueous solution containing a large excess of thiourea over nitrous acid, such that the nitrous acid was rapidly and quantitatively converted to the yellow species $[(NH_2)_2CSNO]^+$, equation (2). The decay of this species was followed spectrophotometrically at 418 nm, using deoxygenated solutions to avoid complications due to the reaction of dioxygen with nitrogen(II) monoxide. The rate law (3) was observed. We now report an extension of this work to the thionitrite derived from tetramethylthiourea, together with studies of the reaction in solutions containing an excess of nitrous acid.

$$2[(NH_2)_2CSNO]^+ \longrightarrow [(NH_2)_2CSSC(NH_2)_2]^{2+} + 2NO^{\cdot} \quad (1)$$

$$H^+ + HNO_2 + (NH_2)_2CS \rightleftharpoons [(NH_2)_2CSNO]^+ + H_2O \quad (2)$$

$$v_0 = -\{d[(NH_2)_2CSNO^+]/dt\}_0 = k_1[(NH_2)_2CSNO^+][(NH_2)_2CS] + k_2[(NH_2)_2CSNO^+]^2 \quad (3)$$

Experimental

The experimental methods used were identical to those described previously,[3] except that most of the present results were obtained with a data collection and processing system. One feature was the use of high concentrations of nitrous acid, up to 0.5 mol dm^{-3} at 25 °C. Solutions of nitrous acid at these concentrations are normally very unstable; however, by mixing the deoxygenated sodium nitrite and perchloric acid solutions in the stopped-flow apparatus there was no free surface exposed to the atmosphere, and nitrogen(II) monoxide could not readily escape. By monitoring the absorbance at 395 nm we observed 6.3, 6.7, and 7.7% decomposition in 200 s for 0.1, 0.2, and 0.4 mol dm^{-3} nitrous acid respectively at 25 °C. Some gas evolution occurred, seen as spikes on the voltage–time curves on the oscilloscope as bubbles passed across the light beam. In the stopped-flow apparatus the nitrous acid solutions were sufficiently stable to yield initial rates of decomposition of thionitrite over the first few seconds. This may be of general utility as a method of studying the chemistry of concentrated solutions of nitrous acid. For the case of thiourea complications might be expected in the later stages of reaction as the product, the *CC′*-dithiodiformamidinium ion, $[(NH_2)_2CSSC(NH_2)_2]^{2+}$, is known[4] to react with nitrous acid, equation (4). Preliminary experiments indicate that the rate of this reaction is much slower than the rate of the decomposition process that we are following. This difficulty does not arise for $[(NMe_2)_2CSSC(NMe_2)_2]^{2+}$ because of the absence of NH_2 groups. Ionic strengths were maintained with added sodium perchlorate.

$$6HNO_2 + 3[(NH_2)_2CSSC(NH_2)_2]^{2+} \longrightarrow 6N_2 + 5HNCS + H_2SO_4 + HCN + 6H^+ + 8H_2O \quad (4)$$

Results

Deoxygenated solutions were used in all experiments to avoid complications due to reaction of nitrogen(II) monoxide with dioxygen. The results using tetramethylthiourea were similar to those obtained previously with thiourea, and hence they are not described in as much detail as previously.[3] The main differences are that the choice of experimental conditions was limited by the much lower solubility of tetramethylthiourea in water.

Excess of Tetramethylthiourea over Nitrous Acid.—Reaction conditions were chosen to give a rapid conversion of approximately 99% of the nitrous acid to the yellow thionitrite $[(NMe_2)_2CSNO]^+$, complete in less than 1 s. The much slower decay of this species to $[(NMe_2)_2CSSC(NMe_2)_2]^{2+} + 2NO^{\cdot}$

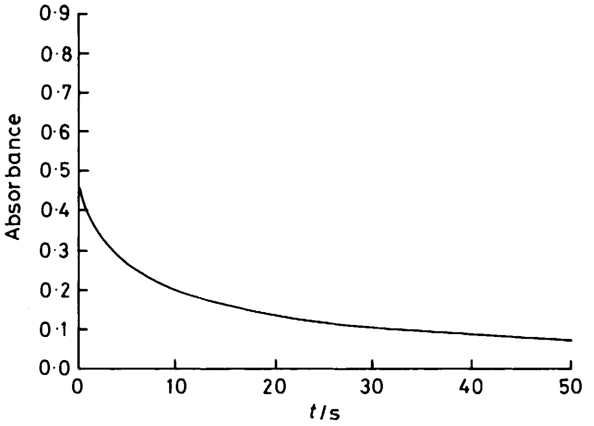


Figure. Decomposition of $[(NMe_2)_2CSNO]^+$ at 25 °C: $10^2[(NMe_2)_2CSNO^+]_0 = 1.265$, $[NO\cdot]_0 = 0$, $[(NMe_2)_2CS] = 0.05$ mol dm^{-3}; $\lambda = 418.4$ nm

was followed spectrophotometrically at 418 nm. A typical plot of absorbance *versus* time is shown in the Figure. Individual runs gave good pseudo-second-order plots of (absorbance)$^{-1}$ *versus* time (the infinity absorbance was zero) with deviations from linearity in the initial stages. The initial rate of decay is distinctly greater than would be calculated from the pseudo-second-order rate constant obtained from the later stages of reaction, and extrapolation of the second-order plot to zero time gives an erroneous value for the intercept and the initial rate of reaction. This effect was previously observed for the decay of $[(NH_2)_2CSNO]^+$.[3] The absorption coefficient of $[(NMe_2)_2CSNO]^+$ reported previously[5] ($\varepsilon = 156$ dm^3 mol^{-1} cm^{-1}) was in error due to this effect. The present work leads to a value of $\varepsilon = 194$ dm^3 mol^{-1} cm^{-1} at 418 nm. In solutions initially saturated with nitrogen(II) monoxide the rate of decay was markedly reduced, the inhibiting effect being most marked with low concentrations of $[(NMe_2)_2CSNO^+]$. A typical set of runs is shown in Table 1, and in Table 2 runs illustrating the inhibiting effect of nitrogen(II) monoxide are shown. Standard deviations (σ) and the number of repeat runs (n) are quoted to illustrate the degree of consistency and reproducibility.

For runs at constant acidity and constant excess tetramethylthiourea concentration the kinetic order with respect to $[(NMe_2)_2CSNO^+]$ was intermediate between 1 and 2. In the absence of nitrogen(II) monoxide the first-order behaviour dominated, and a plot of log v_0 against log $[(NMe_2)_2CSNO^+]$ had a slope of 1.1; in solutions initially saturated with NO· at a pressure of 1 atm (*ca.* 10^5 Pa) the rates were much lower and second-order behaviour was observed with the log–log plot having a slope of 1.83. These results are similar to those found for thiourea and are consistent with a rate law of the same form as equation (3). The orders of 1.1 and 1.83, intermediate between 1 and 2, would arise from an expression of type (5) with the nitrogen(II) monoxide inhibition being

$$v_0 = k_a[(NMe_2)_2CSNO^+] + k_b[(NMe_2)_2CSNO^+]^2 \quad (5)$$

associated with the term that is first-order with respect to $[(NMe_2)_2CSNO^+]$, as is also the case for thiourea. Equation (5) can be rearranged to give (6), and plots of $v_0/[(NMe_2)_2CSNO^+]$ against $[(NMe_2)_2CSNO^+]$ are linear with $k_a = 0.184 \pm 0.005$ s^{-1} and $k_b = 5.18 \pm 0.68$ dm^3 mol^{-1} s^{-1}.

$$v_0/[(NMe_2)_2CSNO^+] = k_a + k_b[(NMe_2)_2CSNO^+] \quad (6)$$

Table 1. Initial rate of decomposition of $[(NMe_2)_2CSNO]^+$ in excess $(NMe_2)_2CS$ at $I = 0.5$ mol dm^{-3}, 25 °C *

$[(NMe_2)_2CS] = 0.05$, $10^3[(NMe_2)_2CSNO^+]_0 = 6.2$ mol dm^{-3}

$[H^+]$/mol dm^{-3}	0.05	0.14	0.20	0.32	0.50
10^4v_0/mol dm^{-3} s^{-1}	9.2	12.9	13.4	14.3	13.0
$10^4\sigma$	0.11	0.71	0.43	0.45	0.62
n	6	7	7	7	7

$[H^+] = 0.49$, $10^3[(NMe_2)_2CSNO^+]_0 = 6.37$ mol dm^{-3}

$[(NMe_2)_2CS]$/mol dm^{-3}	0.02	0.06	0.10	0.14	0.18
10^4 v_0/mol dm^{-3} s^{-1}	6.44	13.8	24.9	35.9	44.5
$10^4\sigma$	0.30	0.80	0.82	2.78	2.67
n	7	8	10	8	8

* In Tables 1—3: n = number of measurements, of standard deviation σ.

Table 2. Effect of NO· on the initial rate of decomposition of $[(NMe_2)_2CSNO]^+$, at $I = 0.5$ mol dm^{-3}, 25 °C: $[(NMe_2)_2CS] = 0.05$, $[H^+] = 0.2$ mol dm^{-3}

	Nitrogen saturated				
$10^3[(NMe_2)_2CSNO^+]$/mol dm^{-3}	0.79	3.16	6.32	9.48	12.7
10^4v_0/mol dm^{-3} s^{-1}	1.45	6.62	13.4	22.2	31.6
$10^4\sigma$	0.09	0.34	0.43	1.26	2.14
n	7	7	7	6	6
	Nitrogen(II) monoxide saturated				
$10^3[(NMe_2)_2CSNO^+]_0$/mol dm^{-3}	0.79	3.16	6.32	9.48	12.7
10^4v_0/mol dm^{-3} s^{-1}	0.15	2.03	7.09	14.0	24.4
$10^4\sigma$	0.01	0.03	0.18	1.0	2.2
n	5	6	5	5	6

To check the parallelism with rate law (3) the acidity and concentration of tetramethylthiourea were varied. The rate was found to be independent of acidity at $[H^+] > 0.14$ mol dm^{-3}: at lower acidities the rate of formation of $[(NMe_2)_2CSNO]^+$ is too slow, and the formation reaction significantly overlaps the decomposition reaction, leading to an *apparent* decrease in the rate of decomposition. The rate constant for the formation reaction is known and computer simulation using a Runge–Kutta numerical integration technique confirmed this interpretation. When the concentration of tetramethylthiourea was varied at $[H^+] = 0.49$ and $[(NMe_2)_2CSNO^+] = 0.006\,37$ mol dm^{-3}, $I = 0.5$ mol dm^{-3}, the rate law had the form (7) with $10^2k_c = 2.48 \pm 0.09$ s^{-1} and $10^5k_d = 4.3 \pm 11$ mol dm^{-3} s^{-1}. The value of the intercept

$$v_0 = k_c[(NMe_2)_2CS] + k_d \quad (7)$$

k_d is very small and there is a large error associated with it. Again equation (7) has the form that was previously observed for thiourea in similar experiments. In all of these respects the results for tetramethylthiourea parallel those observed earlier for the decomposition of the analogous thiourea compound $[(NH_2)_2CSNO]^+$ except that the term that is first order with respect to thionitrite concentration seems to be much more dominant for tetramethylthiourea than for thiourea. If we assume that the k_a term in equation (6) refers to the same part of the full rate equation as the k_c term in (7) then the rate law can be written as equation (8). This analysis can be confirmed

$$v_0 = 3.68[(NMe_2)_2CSNO^+][(NMe_2)_2CS] + 5.18[(NMe_2)_2CSNO^+]^2 \quad (8)$$

by noting that the rate constant of the first term can also be calculated from the k_c term in (7) as $0.0248/0.006\,37 =$

3.89 dm^3 mol^{-1} s^{-1}, in good agreement with the value of 3.68. The size of intercept in (7) makes it impossible to calculate a reliable rate coefficient for the term $k_b[(NMe_2)_2CSNO^+]^2$ from k_d. We conclude that the decomposition of $[(NMe_2)_2CSNO]^+$ shows the same pattern of kinetic behaviour as does $[(NH_2)_2CSNO]^+$. Measurements of the Arrhenius activation energies over the range 0—25 °C for the terms that are first order and second order with respect to [thionitrite] give $E = 72.8 \pm 3.8$ and 62.2 ± 1.7 kJ mol^{-1} respectively for tetramethylthiourea and 60.9 ± 4.9 and 50.8 ± 0.7 kJ mol^{-1} for unsubstituted thiourea.

Excess of Nitrous Acid over Tetramethylthiourea.—In an attempt to isolate the k_b term in the rate law, experiments were carried out with a large excess of nitrous acid over tetramethylthiourea in deoxygenated solutions. Conditions were chosen so that the conversion of $(NMe_2)_2CS$ to $[(NMe_2)_2CSNO]^+$ was rapid and essentially complete. At the acidities used, around pH 1, this involved the use of concentrations of nitrous acid up to 0.5 mol dm^{-3}; the problems of working at these concentrations have been mentioned in the Experimental section. Under our conditions conversion was complete (>98%), the formation reaction having a half-life of 15 ms or less. Because of the almost complete conversion of tetramethylthiourea to thionitrite, $[(NMe_2)_2CS]$ was very low, and the k_1 term in the rate law was almost completely eliminated.

The general form of the absorbance *versus* time plots was similar to that described earlier and typical results are summarised in Table 3. Individual runs again showed pseudo-second-order behaviour, with plots of (absorbance)$^{-1}$ *versus* time being linear over a substantial part of the run, but with deviations in the initial stages. These deviations were markedly less than for experiments with an excess of tetramethylthiourea over nitrous acid, and were found to be completely suppressed when runs were carried out in solutions initially saturated with nitrogen(II) monoxide. The presence of this gas only slightly reduced the initial rate.

The results show that the rate is independent of acidity, but do not show the expected simple and clear-cut second-order dependence upon $[(NMe_2)_2CSNO^+]$. A plot of log v_0 *versus* log $[(NMe_2)_2CSNO^+]$ has a slope of 1.61; the plot from the runs in which the solutions were initially saturated with NO· had a slope of 1.67. The conversion of $(NMe_2)_2CS$ to $[(NMe_2)_2CSNO]^+$ is greater than 98%, so this cannot be due to a residual contribution to the rate of the term $k_1[(NMe_2)_2CS][(NMe_2)_2CSNO^+]$. The rates are greater than expected from the second-order term $k_2[(NMe_2)_2CSNO^+]^2$, suggesting the presence of some additional reaction pathway in the presence of excess HNO_2. The runs in which the concentration of excess nitrous acid was varied show clear evidence for catalysis by HNO_2; with $[HNO_2] = 0.5$ mol dm^{-3} the value of the initial rate is approximately five times greater than $k_2[(NMe_2)_2CSNO^+]^2$. We assume that this catalytic pathway is responsible for the decrease in order below the expected value of 2.

Excess of Nitrous Acid over Thiourea.—To complete the comparison of thiourea and tetramethylthiourea, a limited number of experiments were carried out with $[(NH_2)_2CSNO]^+$ generated by reaction of thiourea with a large excess of nitrous acid. The half-life for the conversion reaction was always less than 13 ms and the conversion was always more than 98%, so the formation reaction did not interfere with the study of the much slower decomposition process. Individual kinetic runs showed the same characteristics as described for $[(NMe_2)_2CSNO]^+$ in the previous section, and the results are summarised in Table 4.

Table 3. Initial rates of decomposition of $[(NMe_2)_2CSNO]^+$ in excess HNO_2 at 25 °C

$[HNO_2] = 0.1$, $10^3[(NMe_2)_2CSNO^+]_0 = 6.34$, $I = 0.6$ mol dm^{-3}					
$[H^+]$/mol dm^{-3}	0.05	0.10	0.20	0.35	0.49
10^4v_0/mol dm^{-3} s^{-1}	5.58	5.30	5.53	5.44	4.72
$10^4\sigma$	0.16	0.27	0.41	0.45	0.16
n	4	7	5	5	6
10^4v_{cat}/mol dm^{-3} s^{-1}	3.50	3.22	3.45	3.36	2.64
$[HNO_2] = 0.1$, $[H^+] = 0.1$, $I = 0.5$ mol dm^{-3}					
$10^3[(NMe_2)_2CSNO^+]_0$/mol dm^{-3}	0.79	3.16	6.32	9.48	12.6
10^4v_0/mol dm^{-3} s^{-1}	0.19	1.99	5.30	10.5	17.1
$10^4\sigma$	0.03	0.18	0.26	0.72	0.42
n	9	8	7	8	7
10^4v_{cat}/mol dm^{-3} s^{-1}	0.16	1.47	3.23	5.84	8.9
$10^3[(NMe_2)_2CSNO^+]_0 = 6.37$, $I = 0.5$ mol dm^{-3}					
$[HNO_2]$/mol dm^{-3}	0.05	0.10	0.22	0.50	
$[H^+]$/mol dm^{-3}	0.50	0.20	0.114	0.050	
10^4v_0/mol dm^{-3} s^{-1}	3.90	5.53	6.58	10.6	
$10^4\sigma$	0.19	0.41	0.17	—	
n	6	5	7	1	
10^4v_{cat}/mol dm^{-3} s^{-1}	1.8	3.43	4.48	8.5	

$v_{cat} = v_0 - k_2[(NMe_2)_2CSNO^+]^2$

Plots of log v_0 *versus* log $[(NH_2)_2CSNO^+]$ gave slopes in the range 1.60—1.85, so again there appears to be a component in the rate law that is first order with respect to $[(NH_2)_2CSNO^+]$ in addition to the expected term $k_2[(NH_2)_2CSNO^+]^2$. The effect of using solutions initially saturated with NO· was investigated, and there was a few percent decrease in initial rate. The rates were found to be independent of acidity, and showed clear evidence for catalysis by nitrous acid.

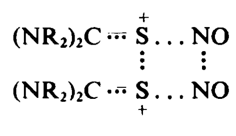
Discussion

Reaction in the Presence of Excess $(NH_2)_2CS$ *or* $(NMe_2)_2CS$.—It is convenient to set out the two rate laws and to compare the rate constants for corresponding terms. For reaction at 25 °C the initial rate laws are (9) and (10).

$$-\{d[(NH_2)_2CSNO^+]/dt\}_0 = 0.62[(NH_2)_2CSNO^+][(NH_2)_2CS] + 6.12[(NH_2)_2CSNO^+]^2 \quad (9)$$

$$-\{d[(NMe_2)_2CSNO^+]/dt\}_0 = 3.68[(NMe_2)_2CSNO^+][(NMe_2)_2CS] + 5.18[(NMe_2)_2CSNO^+]^2 \quad (10)$$

The activation parameters for the term $k_1[(NR_2)_2CSNO^+][(NR_2)_2CS]$ are $\Delta H^\ddagger = 58.3 \pm 4.9$ and 70.6 ± 4.1 kJ mol^{-1}, $\Delta S^\ddagger = -60.9 \pm 17.3$ and -4.9 ± 14.2 J K^{-1} mol^{-1} for R = H and Me respectively. For the term $k_2[(NR_2)_2CSNO^+]^2$, $\Delta H^\ddagger = 48.4 \pm 0.7$ and 60.0 ± 1.6 kJ mol^{-1}, $\Delta S^\ddagger = -67.2 \pm 2.6$ and -25.8 ± 5.7 J K^{-1} mol^{-1} for R = H and Me respectively. Consider first the process that is second order with respect to [thionitrite]. The transition state proposed in our previous paper had the form shown below, with R = H. For



$$\begin{array}{c} (NR_2)_2C \cdots \overset{+}{S} \ldots NO \\ \vdots \quad \vdots \\ (NR_2)_2C \cdots \underset{+}{S} \ldots NO \end{array}$$

Table 4. Initial rate of decomposition ($10^4 v_0$/mol dm^{-3} s^{-1}) of $[(NH_2)_2CSNO^+]$ in excess HNO_2, I = 0.5 mol dm^{-3} at 25 °C

		$10^3[(NH_2)_2CSNO^+]_0$/mol dm^{-3}					
$[HNO_2]$/mol dm^{-3}	$[H^+]$/mol dm^{-3}	0.78	3.14	6.27	9.41	12.6	Order *
0.025	0.4	0.068	0.87	2.90	5.79	10.1	1.80
0.050	0.2	0.078	0.95	3.21	6.95	10.7	1.81
0.10	0.1	0.073	1.05	3.44	7.47	12.6	1.85
0.40	0.025	0.18	1.86	5.02	10.3	15.5	1.60

$10^3[(NH_2)_2CSNO^+]_0$ = 6.3, $[HNO_2]$ = 0.1 mol dm^{-3}

$[H^+]$/mol dm^{-3}	0.129	0.219	0.310	0.395
$10^4 v_0$/mol dm^{-3} s^{-1}	4.00	4.15	4.04	3.98

* Order = slope of a plot of log v_0 *versus* log $[(NH_2)_2CSNO^+]$.

R = Me, repulsion involving the methyl groups might make such a constrained transition state unstable; the ON $\cdots$ NO interaction is likely to be very weak, and the transition state might be much more stable if there were free rotation about the sulphur–sulphur bond enabling the NMe_2 groups to avoid one another. This fits in with the higher $\Delta H^‡$ and more positive $\Delta S^‡$ values. Differences in solvation between the initial state and transition states must also be considered. In water, solvation lowers both the enthalpy and the entropy of an ion. The transition state is doubly charged, and will be more strongly solvated than the two singly charged species that constitute the initial state. The hydrophobic methyl groups will reduce stabilisation by solvation, and this effect will be more marked for the doubly charged transition state than for the two singly charged species of the initial state. The increase in volume of the transition state will produce a small effect in the opposite direction. Thus overall one would expect an increase in both $\Delta H^‡$ and $\Delta S^‡$ for the tetramethylthiourea system compared to the thiourea system.

Turning to the other term, $v_0 = k_1[(NR_2)_2CSNO^+][(NR_2)_2CS]$, where R = H or Me, we note that although the tetramethyl system is a lot more reactive than the thiourea system, it has a higher $\Delta H^‡$ value. Because it is necessary to dissect the measured rate into two terms, there is a substantial error associated with the separate rate constants. This, combined with the fact that measurements were made over a range of only 25 °C means that there are unusually large errors associated with the $\Delta H^‡$ and $\Delta S^‡$ values, and the error limit ranges are separated by only 3.2 kJ mol^{-1}. The reaction is unusual, as it involves a substitution process with two electron-paired molecules, with homolytic fission of the bond to the leaving group, NO, to form a radical and a radical cation: equation (11). The reasons for proposing a disulphide

$$[(NR_2)_2CSNO]^+ + (NR_2)_2CS \longrightarrow [(NR_2)_2CSSC(NR_2)_2]^{\cdot +} + NO^{\cdot} \quad (11)$$

radical cation as an intermediate have been given previously.[3] In the transition state the S–NO bond is presumably partly broken, thereby inducing a deficiency of electrons on the sulphur. This could be stabilised by electron release from the methyl groups. Bond formation between the sulphurs is probably also important, and electron release by the methyl groups could enhance the nucleophilic reactivity of the tetramethylthiourea towards the cationic species it is attacking {though electron release to sulphur in $[(NMe_2)_2CSNO]^+$ would act in the opposite sense}. The activation parameters suggest that entropy factors are also important in determining reactivity. In this case the charges on the transition state and the initial states are the same, but the charged species is bulkier in the transition state than in the initial state and hence the latter will be more strongly solvated. This factor will be less significant for the tetramethyl system because of the hydrophobic methyl groups. Thus $\Delta S^‡$ for thiourea is likely to be more negative than for tetramethylthiourea, the direction of the observed difference in $\Delta S^‡$ values.

We now turn to a discussion of the reaction in an excess of nitrous acid. The object of these experiments was to work under conditions where there was essentially complete conversion of the thiourea compound to thionitrite, so that the term $k[(NR_2)_2CSNO^+][(NR_2)_2CS]$ would be eliminated from the rate law thereby simplifying the kinetics. In practice this was not easy to achieve as it involved working at very high concentrations of nitrous acid (up to 0.5 mol dm^{-3}). Our earlier work showed that the presence of nitrogen(II) monoxide in solution inhibited reaction proceeding by attack of $(NH_2)_2CS$ on $[(NH_2)_2CSNO]^+$, so the observation that nitrogen(II) monoxide had no effect on the rate of decomposition of $[(NH_2)_2CSNO]^+$ and $[(NMe_2)_2CSNO]^+$ in excess nitrous acid suggests we have achieved our objective. However, additional complications seem to have been introduced because the initial rate *increases* with increase in nitrous acid concentration, and the kinetic order with respect to $[(NR_2)_2CSNO]^+$ is not the expected value of 2, but lies in the range 1.8—1.6. This suggests that we have introduced a new nitrous acid catalysed reaction pathway with a kinetic order with respect to $[(NR_2)_2CSNO^+]$ of less than 2. Extrapolation of plots of $-\{d[(NH_2)_2CSNO^+]/dt\}_0$ *versus* $[HNO_2]$ to $[HNO_2] = 0$ and dividing the intercept by $[(NH_2)_2CSNO^+]^2$ gives rate constants agreeing reasonably with the figure of 6.12 dm^3 mol^{-1} s^{-1}. Thus for $[(NH_2)_2CSNO^+]_0 = 0.0063$ and $[H^+] = 0.1$ mol dm^{-3}, such an extrapolation gives a rate constant of 6.04 dm^3 mol^{-1} s^{-1}.

While it is clear that there is a catalytic effect due to high concentrations of nitrous acid, both for $[(NH_2)_2CSNO]^+$ and for $[(NMe_2)_2CSNO]^+$, the nature of the catalysis is not clear. We have calculated a 'catalysed rate', v_{cat}, by subtracting $5.18[(NMe_2)_2CSNO^+]^2$ from the initial rates in Table 3. Rates calculated in this way show a lot of scatter; they increase with $[HNO_2]$ and $[(NMe_2)_2CSNO^+]$, but do not show any simple kinetic order. The experimental difficulties in obtaining good rate data at such high nitrous acid concentrations, the fact that the 'catalysed rate' is the difference of two numbers of comparable magnitudes, and the possibility of medium effects make us reluctant to interpret the non-integral orders. Seel[6] has shown that NO^+ and $NO^{\cdot}$ can complex to form $NO{\cdot}NO^{\cdot +}$, and one possible explanation for nitrous acid catalysis is that the loss of $NO^{\cdot}$ from $[(NH_2)_2CSNO]^+$ can be helped by reaction with HNO_2 to form $NO{\cdot}NO^{\cdot +}$ as a leaving group. This is, however, speculation. We looked for evidence for the formation of new species which might show up in changes in absorption coefficient but without success.

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