Kinetics and Mechanism of the Decomposition of $[(NH_2)_2CSNO]^+$ †

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The kinetics of decomposition of $2[(NH_2)_2CSNO]^+$ to $[(NH_2)_2CSSC(NH_2)_2]^{2+} + 2NO^{\cdot}$ have been studied spectrophotometrically in oxygen-free aqueous solutions. Reaction is inhibited by the product, nitrogen(II) monoxide, and the rate equation, based upon initial rates, takes the form shown below. The mechanism involves

$$v_0 = k_1[CS(NH_2)_2][(NH_2)_2CSNO^+] + k_2[(NH_2)_2CSNO^+]^2$$

parallel pathways, one involving the reversible formation of a radical intermediate, $[(NH_2)_2CSSC(NH_2)_2]^{+\cdot}$, while the other involves a bimolecular reaction between two molecules of $[(NH_2)_2CSNO]^+$.

In his pioneering work on the reactions of thiourea, Werner[1] showed that in acidic media, $pH < 1$, it is oxidised by nitrous acid to a disulphide, *CC'*-dithiodiformamidinium (formamidine disulphide) [equation (1)].

$$2H^+ + 2HNO_2 + 2(NH_2)_2CS \longrightarrow [(NH_2)_2CSSC(NH_2)_2]^{2+} + 2NO^{\cdot} + 2H_2O \quad (1)$$

Werner reported observing a transient red colour during reaction, and this coloured species has since been identified as a sulphur–nitroso-compound (a thionitrite), $[(NH_2)_2CSNO]^+$ [equation (2)]. The equilibrium constant for reaction (2), the rate constants for the forward and back reactions, and the visible and u.v. spectra of the coloured thionitrite have been obtained.[2] In this paper we describe a study of the conversion of $2[(NH_2)_2CSNO]^+$ to $[(NH_2)_2CSSC(NH_2)_2]^{2+} + 2NO^{\cdot}$. Thionitrites are of interest in the interaction of nitrite with food, especially meat,[3] and there has been a report[4] of the reactions of $[(NH_2)_2CSNO]^+$ as an electrophilic nitrosating agent. There has also been a recent paper on the reactions of alkyl and aryl thionitrites,[5] particularly with nucleophilic reagents.

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

EXPERIMENTAL

Materials.—Nitric oxide, nitrogen(II) monoxide, was obtained from a cylinder supplied by B.O.C., and was freed from traces of nitrogen dioxide by bubbling through traps cooled to −80 °C, followed by a series of traps containing sodium hydroxide solution. Qualitative tests by the diazo-coupling technique proved the method of purification to be very satisfactory. Other chemicals were AnalaR substances, and were used without further purification.

Kinetic Measurements.—All of the present work was done with deoxygenated solutions, in order to avoid complications due to the re-oxidation of the product nitric oxide. In the presence of dioxygen it is possible for a large excess of thiourea to be oxidised by a small amount of nitrous acid, reaction (1) being followed by (3)—(5) which regenerate nitrous acid. Reaction was followed by monitoring the decay of the absorbance due to the yellow intermediate $[(NH_2)_2CSNO]^+$ at 418 nm ($\varepsilon = 113$ dm^3 mol^{-1} cm^{-1}), where there is no significant absorption due to any other reactant or product. This wavelength corresponds to a sharp maximum in the standard holmium glass filter, and it is easy to set the monochromator of the stopped-flow apparatus reproducibly at this value. A few measurements were made at 536 nm to check that our kinetic results were not dependent on the wavelength used. Reaction against time curves measured at the two wavelengths appeared to be identical in shape when scaled to a common initial absorbance. Runs illustrating this point are shown in Figure 1. Two different kinetic methods were used.

$$2NO + O_2 \longrightarrow 2NO_2 \quad (3)$$

$$NO + NO_2 \longrightarrow N_2O_3 \quad (4)$$

$$H_2O + N_2O_3 \longrightarrow 2HNO_2 \quad (5)$$

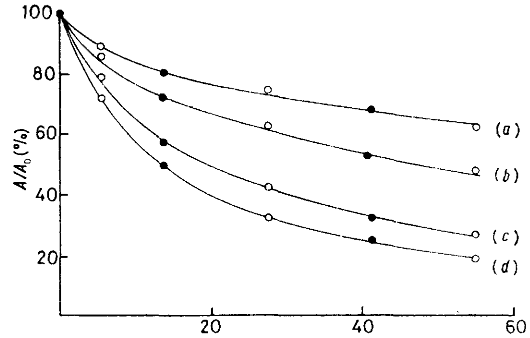

FIGURE 1 Comparison of reaction against time curves measured at two wavelengths: 418.0 (○) and 536 (●) nm, $[H^+] = 0.2$ mol dm^{-3}, $[(NH_2)_2CS]_T = 0.05$ mol dm^{-3}, 25 °C. $10^4[(NH_2)_2CSNO^+]_0 = 7.84$ (*a*), 23.5 (*b*), 78.4 (*c*), 126 (*d*) mol dm^{-3}

Method I. All solutions were deoxygenated by bubbling with a stream of white spot nitrogen, and were stored under nitrogen in vessels fitted with rubber serum caps. Solutions were transferred by means of syringes, and the reaction mixtures were made up in spectrophotometer cells that had been flushed out with nitrogen, and that were also sealed with rubber serum caps. All solutions were thermostatted to 25 °C, and the perchloric acid, sodium perchlorate, and thiourea were added first to the cell. This was placed in the thermostatted cell holder of a Unicam SP600, connected to a Servoscribe recorder. Reaction was started by injecting the sodium nitrite solution through a small hole in the lid of the cell compartment into the reaction cell. The

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† *S*-Nitrosothiouronium ion.

main limitation of this method was that we could not obtain reliable absorbance measurements for the first few seconds of reaction.

Method II. This made use of the stopped-flow technique. A Nortech Canterbury SF-3A instrument was used, and the reaction solutions were deoxygenated in the reservoirs by bubbling with white spot nitrogen for at least 30 min. The entry tube for the gas was sealed to a sintered glass disc to produce a dispersion of fine bubbles. Variation in the gas bubbling time from 20 to 60 min produced no effect that we could observe on the reaction against time plots. Solutions that were initially degassed by pumping under vacuum gave results identical to those obtained by our normal technique. The stopped-flow technique was much more successful than method I for obtaining initial rates of reaction but as the whole reaction sometimes extended over a period of minutes the stability of the light source and the photomultiplier occasionally presented problems in obtaining complete decay curves. We always checked at the end of each experiment that there had been no drift in the instrument during the run, and discarded any results where there was detectable change. In practice we found the instrument to be remarkably stable. At higher concentrations of the yellow intermediate we had some trouble with the evolution of bubbles of nitric oxide, which would show up as a spike on the absorbance against time traces when they passed through the light beam.

All of the data in the present work was obtained from tracings of voltage against time curves recorded on a Tektronix D11 storage oscilloscope, and converting these to absorbance against time curves by calculation on a programmable hand calculator, or on an ICL 1904S. Initial rate measurements were obtained by setting the scan time of the oscilloscope to a suitable short time interval over which the initial portion of reaction gave a linear absorbance against time plot. Because of the ease with which runs may be repeated under identical conditions using the stopped-flow method all of our results are the means of a substantial number (usually at least five) of repeat runs. Our greatest errors arise when measuring low absorbances, in runs with low initial concentrations of nitrite, and this is reflected in the σ values in Table 1.

TABLE 1

Typical initial rate data for the decay of the absorbance at 418 nm, $I = 0.3$ mol dm^{-3}, $[(NH_2)_2CS]_T = 0.05$ mol dm^{-3}, $[H^+] = 0.2$ mol dm^{-3}, $d = 0.194$ cm

$10^3[(NH_2)_2CSNO^+]_0$/mol dm^{-3}	0.784	1.57	2.35	3.14	4.71
$10^3[-(dA/dt)_0]$ */s^{-1}	0.480	1.31	2.14	2.48	5.80
$10^3\sigma$/s^{-1}	0.142	0.28	0.18	0.34	0.85
n	5	4	4	7	6
$10^3[(NH_2)_2CSNO^+]_0$/mol dm^{-3}	6.28	7.84	9.41	11.0	12.6
$10^3[-(dA/dt)_0]$ */s^{-1}	8.25	12.0	13.6	20.4	24.3
$10^3\sigma$/s^{-1}	0.45	1.20	0.66	1.34	1.1
n	5	5	6	5	5

* Values of $-(dA/dt)_0$ are mean of n measurements, of standard deviation σ.

RESULTS AND DISCUSSION

One potential complication in this system is that under some conditions there is only partial conversion of the nitrite to the yellow thionitrite, and it is then necessary to allow for this partial conversion in calculating rates of reaction. To avoid these problems we have worked with a large excess of thiourea over nitrous acid and have chosen conditions such that the nitrite is almost quantitatively converted to thionitrite. Under these conditions the formation of the thionitrite is a very rapid process, usually with $t_{\frac{1}{2}} < 0.05$ s, so this does not overlap with the much slower decomposition reaction. When we refer to total concentrations, we denote this by a subscript T, thus $[(NH_2)_2CS]_T = [(NH_2)_2CS] + [(NH_2)_2CSNO^+]$.

Our preliminary work used method I and gave data that fitted a pseudo-second-order equation, $A^{-1} - A_0^{-1} = kt$, quite well for individual runs (A is the absorbance at 418 nm). However such pseudo-second-order plots showed deviations in the later stages of reaction and k varied with reaction conditions. It was clearly not a true second-order reaction. To avoid complications we preferred to work with initial rates (ν_0). Experiments over a limited range of concentrations indicated a rate law of the form (6). Most of our experi-

$$\nu_0 = \{k_a + k_b[CS(NH_2)_2]\}[(NH_2)_2CSNO^+] \quad (6)$$

ments have used the stopped-flow technique II, and this method immediately revealed a kinetic feature that was not apparent from the preliminary work. In the very early stages of reaction there is often a small relatively steep decrease in absorbance, which after a few seconds changes to give a relatively smooth decay curve very similar to that observed by method I. This effect was particularly noticeable in experiments with a low initial nitrite concentration, but was not very significant at high nitrite concentrations. Second-order plots of A^{-1} against time gave good straight lines over most of the reaction, but can show a marked deviation in the very early stages, as can be seen from Figure 2. This made it clear that with method I, for which we did not get absorbance readings for the first few seconds after mixing, we were not obtaining true initial rates. All measurements made subsequent to this discovery used

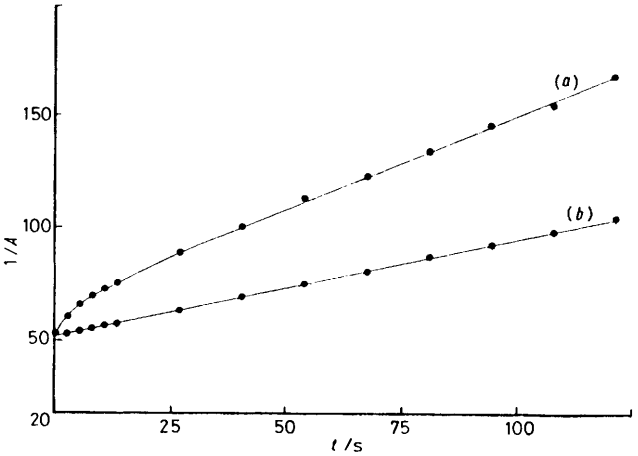

FIGURE 2 Integrated second-order plot for variation of absorbance with time at 25 °C for reaction in the presence (b) and absence (a) of nitric oxide. $[H^+] = 0.1$ mol dm^{-3}, $[(NH_2)_2CS]_T = 0.1$ mol dm^{-3}, $10^4[(NH_2)_2CSNO^+]_0 = 7.94$ mol dm^{-3}, $d = 0.194$ cm

method II and all the data recorded in the Tables and shown in the graphs used this technique. We wondered whether this effect could be due to traces of residual oxygen, but variation in time of deoxygenation made no difference. We examined a few runs with solutions containing dissolved air, or saturated with oxygen, in order to see what effect oxygen had on the reaction against time curve. These experiments showed a quite different phenomenon, an initial *horizontal* region in the absorbance against time curve. Thus we do not think that the initial small steep decrease in absorbance is due to the presence of oxygen. We assume that the horizontal part of the curve is due to the regeneration of nitrous acid by reactions (3)—(5), which then reacts with the excess of thiourea to form more $[(NH_2)_2CSNO]^+$.

Sharp decreases in the rate in the early stages of reaction are often caused by product inhibition, and as nitric oxide is a product we considered the possibility that the mechanism might involve formation of a radical cation and nitric oxide, and that this could be reversed as nitric oxide accumulated in solution. Experiments were carried out in which the solutions were first deoxygenated by passage of nitrogen, and were then saturated with nitric oxide. These gave smooth absorbance decay curves over the whole range with almost complete elimination of the steep initial part of the graph. Pseudo-second-order plots were linear to zero time. This can be seen in Figure 5 which shows a pair of otherwise identical runs, one of which was initially saturated with nitric oxide while the other had $[NO^{\bullet}]_0 = 0$. A comparison of the slopes confirms that nitric oxide acts as an inhibitor, as can also be seen from the initial rate data in Table 2. It must be emphasised that although second-order plots of individual runs appear linear, there is still a dependence of the apparent second-order rate constant upon $[(NH_2)_2CSNO^+]$, so we cannot be observing true second-order behaviour. In order to avoid these complications we have restricted ourselves to initial rate measurements for which $[NO^{\bullet}]_0 = 0$.

TABLE 2

Effect of nitric oxide on initial rate of reaction at 25 °C

$10^4[(NH_2)_2CSNO^+]$/mol dm^{-3}	15.7	31.8	63.6	127
$10^3(-dA/dt)_0$ ^{a}/s^{-1}	3.15	5.05	12.8	30.8
$10^3(-dA/dt)_0$ ^{b}/s^{-1}	0.85	2.31	10.3	20.9

[a] Initial rate in absence of NO. [b] Initial rate in solutions saturated with NO at atmospheric pressure.

We have examined the dependence of the initial rate upon concentrations of H^+, $(NH_2)_2CS$, and $[(NH_2)_2CSNO]^+$. A summary of some of our initial rate data is given in Table 1, and is shown in Figure 3. The initial reaction rate was found to be independent of acidity, and to vary linearly with thiourea concentration at constant $[(NH_2)_2CSNO^+]$ see equation (7). Typical results are shown in Figure 4. For groups of experiments at

$$v_0 = k_c + k_d[(NH_2)_2CS] \qquad (7)$$

constant acidity and thiourea concentration plots of v_0 against $[(NH_2)_2CSNO^+]_0$ were curved, and log-log graphs gave apparent orders between one and two. This order was a function of the thiourea concentration, and typical values obtained were 1.18 and 1.42 for $[(NH_2)_2CS]_T = 0.1$ and 0.025 mol dm^{-3} respectively.

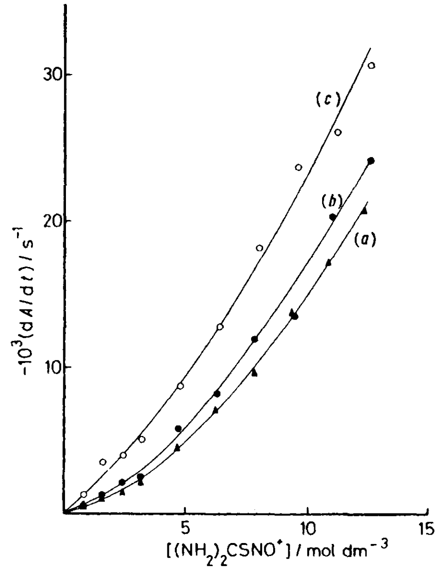

FIGURE 3 Variation of initial rate, $(-dA/dt)_0$, with $[(NH_2)_2CSNO^+]_0$ at 25 °C. $[(NH_2)_2CS]_T = 0.025$ (*a*), 0.05 (*b*), 0.10 (*c*) mol dm^{-3}; $[H^+] = 0.40$ (*a*), 0.20 (*b*), 0.10 (*c*) mol dm^{-3}; $I =$ 0.50 (*a*), 0.30 (*b*), 0.30 (*c*) mol dm^{-3}; $d = 0.194$ cm

There are many possible explanations for an apparent reaction order between one and two, but these results suggest that the k_d term in (7) is first order with respect to $[(NH_2)_2CSNO^+]$, while k_c is second order. We have checked this by plotting v_0 against $[(NH_2)_2CS]$ for various values of $[(NH_2)_2CSNO^+]_0$, and found the variation of k_c and k_d with the concentration of the yellow intermediate. Over a ten-fold change in thiourea concentration the kinetic orders with respect to $[(NH_2)_2CSNO^+]$ are 1.95 ± 0.08 and 0.91 ± 0.05 respectively giving rise to the overall equation (8). To check this equation, it can be rearranged to form (9). Plots of $(v_0/[(NH_2)_2CS][(NH_2)_2CSNO^+])$ against $([(NH_2)_2CSNO^+]/$

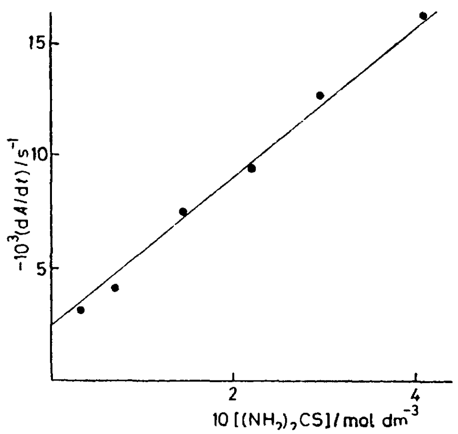

FIGURE 4 Variation of initial rate, $(-dA/dt)_0$, with $[(NH_2)_2CS]_0$ at 25 °C, $10^3[(NH_2)_2CSNO^+] = 3.2$ mol dm^{-3}

$[(NH_2)_2CS]$) gave straight lines, and from slopes and intercepts we obtained values for k_1 and k_2 of 0.65, 0.56, 0.88 and 4.72, 5.46, 5.56 $dm^3\ mol^{-1}\ s^{-1}$ respectively

$$v_0 = k_1[(NH_2)_2CS][(NH_2)_2CSNO^+] + k_2[(NH_2)_2CSNO^+]^2 \quad (8)$$

$$v_0/[(NH_2)_2CS][(NH_2)_2CSNO^+] = k_1 + k_2[(NH_2)_2CSNO^+]/[(NH_2)_2CS] \quad (9)$$

from the data shown in Figure 3. A similar plot for the nitric oxide saturated runs gave $k_1 = 0.202$ and $k_2 = 4.93$ $dm^3\ mol^{-1}\ s^{-1}$.

Turning now to the effect of nitric oxide on the rate of reaction, a comparison of absorbance against time curves for pairs of runs which only differ in the presence and absence of initially added nitric oxide shows clearly that nitric oxide acts as an inhibitor. Figure 5 shows a pair of such curves. When the initial rates are compared for such pairs of runs it is found that the inhibiting effect is larger at low initial concentrations of $[(NH_2)_2CSNO]^+$ than at high values. Data illustrating this point are in Table 2. This suggests that the inhibitory effect of nitric oxide is associated with the k_1 term rather than the k_2 term in (8). The similarity in the values of k_2 obtained from plots of (9) for nitrogen saturated and nitric oxide saturated solutions mentioned above confirms this. These measurements are restricted by the limited solubility of nitric oxide in water, which for an aqueous solution at 25 °C with a partial pressure of 1 atm is 1.93×10^{-3} mol dm^{-3}.* This is a relatively low value, compared to the amount of nitric oxide formed in some of our reaction solutions. Thus at our highest value of $[(NH_2)_2CSNO^+]_0$ the final amount of liberated nitric oxide would be equivalent to a concentration of 12.7×10^{-3} mol dm^{-3}. If this all remained in solution, our solutions would be supersaturated. We certainly observe bubbles of gas evolved in our reaction solutions.

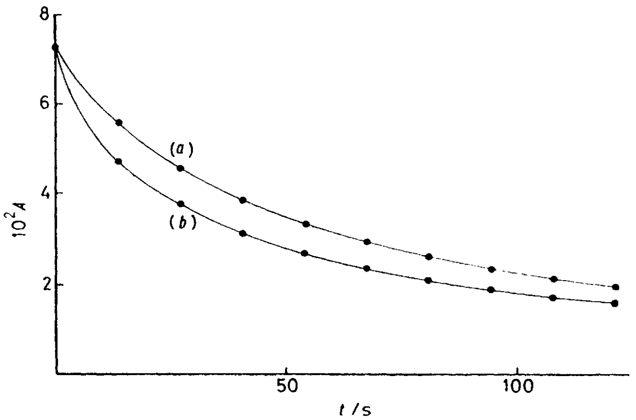

FIGURE 5 Effect of nitric oxide on initial rate of reaction $(-dA/dt)_0$ at 25 °C, $[(NH_2)_2CS]_T = 0.1$ mol dm^{-3}, $[H^+] = 0.1$ mol dm^{-3}, $10^3[(NH_2)_2CSNO^+]_0 = 3.15$ mol dm^{-3}, $I = 0.3$ mol dm^{-3}, $d = 0.194$ cm. (*a*) Solution initially saturated with nitric oxide at 1 atm; (*b*) solution initially free of nitric oxide

Turning now to the mechanistic interpretation of the results, the second term in (8) does not present any problems. It appears to describe a simple bimolecular reaction between two molecules of $[(NH_2)_2CSNO]^+$ with the formation of a disulphide link and the liberation of nitric oxide. We discuss this term again below. The first term in the rate law requires a reaction between $(NH_2)_2CS$ and $[(NH_2)_2CSNO]^+$, and as nitric oxide is an inhibitor it seems likely that the reaction is reversible, with nitric oxide as a product. In order to satisfy the

$$(NH_2)_2CS + [(NH_2)_2CSNO]^+ \underset{k_4}{\overset{k_3}{\rightleftharpoons}} [(NH_2)_2CSSC(NH_2)_2]^{+\cdot} + NO^\cdot \quad (10)$$

overall stoicheiometry the radical cation must undergo further oxidation. This could involve a bimolecular disproportionation as shown in (11), or radical cation breakdown by a unimolecular pathway (12)—(13).

$$2[(NH_2)_2CSSC(NH_2)_2]^{+\cdot} \longrightarrow [(NH_2)_2CSSC(NH_2)_2]^{2+} + 2(NH_2)_2CS \quad (11)$$

$$[(NH_2)_2CSSC(NH_2)_2]^{+\cdot} \xrightarrow[\text{slow}]{} [(NH_2)_2CS]^{+\cdot} + (NH_2)_2CS \quad (12)$$

$$[(NH_2)_2CS]^{+\cdot} + [(NH_2)_2CSNO]^+ \xrightarrow[\text{fast}]{} [(NH_2)_2CSSC(NH_2)_2]^{2+} + NO^\cdot \quad (13)$$

Another possibility is the direct oxidation of the radical cation by another mole of a nitrite species, as in (14). We are not in a position to decide between these alternatives with our present results.

$$[(NH_2)_2CSSC(NH_2)_2]^{+\cdot} + [(NH_2)_2CSNO]^+ \longrightarrow [(NH_2)_2CSSC(NH_2)_2]^{2+} + NO^\cdot + (NH_2)_2CS \quad (14)$$

Turning now to a comparison with data in the literature, we note that there are many studies of the oxidation of thiourea by metal ions or metal complexes, and these usually postulate the existence of radical cation species such as $[(NH_2)_2CS]^{+\cdot}$ {or its conjugate acid $[(NH)(NH_2)CS]^\cdot$} as intermediates.[6] An interesting kinetic analogy is with the copper(II) catalysed oxidation of thiols by hexacyanoferrate(III), where excellent second-order kinetics were obtained over the whole course of a run for a rather complex mechanism [7] involving the reversible formation of a radical cation intermediate.

Some support for our mechanism comes from studies of the decomposition of thionitrites which are known to yield disulphides and nitric oxide. One mechanism that

$$2RSNO \longrightarrow RSSR + 2NO^\cdot \quad (15)$$

$$RSNO \rightleftharpoons RS^\cdot + NO^\cdot \xrightarrow{RSNO} RSSR + 2NO^\cdot \quad (16)$$

has been suggested [6] is set in equation (16). Such a mechanism does not fit our results, because for the rate condition of $[NO^\cdot] = 0$ it would give a rate that was independent of $[(NH_2)_2CS]$. Kinetic studies of the decomposition of thionitrites indicate complex kinetics in some cases, with an apparent order greater than one,[8] calculated from the variation of half-life with concentration of thionitrite [Bu^nSNO, $t_{\frac{1}{2}} = 100$ min (9.7×10^{-3}

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* Throughout this paper: 1 atm = 101 325 Pa.

mol dm^{-3}), $t_{\frac{1}{2}} = 17$ min (6.5×10^{-3} mol dm^{-3}); Bu^{t}SNO, $t_{\frac{1}{2}} = 350$ min (2.6×10^{-3} mol dm^{-3}), $t_{\frac{1}{2}} = 180$ min (6.4×10^{-2} mol dm^{-3})]. However, recently, a study of the reactions of thionitrites[5] has shown that they react readily with a range of nucleophiles, including thiols, equation (17). Thus our suggestion of attack by nucleophilic thiourea on $[(NH_2)_2CSNO]^+$ seems a very reasonable proposal. The present rate law also parallels exactly that put forward for the oxidation of iodide ion by nitrous acid by Beck and co-workers,[9] equation (18). Nitrosyl iodide is likely to be an intermediate, and the k_e term corresponds to reaction (19) while the k_f term could corresppnd to a bimolecular reaction (21). In our system thiourea would correspond to the iodide ion in the above equations, and $[(NH_2)_2CSNO]^+$ to INO. Beck and co-workers have argued for a more complex interpretation of the k_f term than this. In their system nitrosyl iodide is only a very minor component and it is possible to envisage a number of ways in which two protons, two iodide ions, and two nitrous acid molecules can be brought together to form a transition state of a given composition. In our system virtually all of the nitrite exists as $[(NH_2)_2CSNO]^+$, and there is no need to postulate anything more complex than a simple bimolecular process for k_2 term in (8). We have confirmed directly that added bromide ion in our system does not cause any decrease in the rate of reaction.

$$R^1SNO + R^2SH \longrightarrow R^1SSR^2 + \text{`HNO'} \qquad (17)$$

$$d[I_2]/dt = k_e[H^+][HNO_2][I^-]^2 + k_f[H^+]^2[HNO_2]^2[I^-]^2 \qquad (18)$$

$$\begin{aligned} H^+ + HNO_2 + I^- &\rightleftharpoons INO + H_2O \\ I^- + INO &\longrightarrow I_2^- + NO^{\bullet} \qquad (19) \\ I_2^- + H^+ + HNO_2 &\xrightarrow[\text{fast}]{} NO^{\bullet} - I_2 + H_2O \qquad (20) \\ 2INO &\longrightarrow I_2 + 2NO^{\bullet} \qquad (21) \end{aligned}$$

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