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Travelling reaction fronts in the nitric acid oxidation of thiocyanate

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The autocatalytic reactions involving nitric acid as an oxidant are a potential family of systems in which travelling reaction fronts can be generated, although observation of the front may be difficult. The oxidation of thiocyanate yields a well defined red coloured reaction front whose properties have been investigated. A computer model gives a good description of the travelling waves, and the results are consistent with a simple analytical treatment.

1. Introduction

The study of travelling reaction wave fronts has received less attention than has been given to oscillating reactions, possibly because it is a less spectacular phenomenon and does not show such a diversity of behaviour. However, studies of gravitational and density effects (Nagypál *et al.* 1986; Bazsa & Epstein 1985), electric field effects (Ševčíková & Marek 1984) and magnetic field effects (Boga *et al.* 1990), have shown that very interesting phenomena exist. Travelling reaction fronts are found in systems where there is an autocatalytic reaction. Reaction can be initiated at a particular spot or region in an initially homogeneous reaction medium. As reaction proceeds and the catalyst concentration builds up it diffuses into the adjacent solution and initiates reaction there. As this proceeds the catalyst diffuses into the next region of solution and so on. Provided that the rate of the autocatalytic reaction is sufficiently greater than the rate of diffusion this has the effect of producing a wave of chemical reaction that propagates through the solution. The two common approaches to investigate these systems have been the study of the wave travelling along a tube (usually mounted vertically) or, alternatively, as a circular reaction front travelling outwards from a central starting point in a thin film in a petrie dish. Some work has been done using standard spectrophotometer cells, 1 cm × 1 cm and this approach has been used in most of the present work. The autocatalytic reactions involved are normally exothermic, and so if the concentrations are sufficiently high there can be complications due to temperature gradients within and close to the reaction zone. These have been observed experimentally (Bazsa & Epstein 1985). In general, the dissipation of heat is a relatively rapid process and does not cause serious complications, though convection effects can be observed. The effect of density differences has been discussed (Nagypál *et al.* 1986).

Although a number of different travelling wave front systems have been studied since the original observation (Luther 1906), two algorithms for the systematic design of such systems exist. Nagypál *et al.* have developed an algorithm for the design of travelling wave fronts in inorganic redox reactions. They note that many redox reactions involving oxyanions are acid catalysed processes, and they consider

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the number of protons released/consumed in various redox half-equations and calculate the change in the number of protons *per electron*. This serves to identify combinations of oxidizing and reducing agents that are potentially autocatalytic because they generate protons. Reaction can be initiated by the addition of a drop of acid to one end of the reaction solution contained in a tube and the travelling front identified by the colour change due to the addition of a suitable acid–base indicator. This approach has served to identify some twenty new systems of potential interest (Szirovicza *et al.* 1989).

Another systematic approach is to look at the oxidation reactions of nitric acid. Most of these reactions are catalysed by trace amounts of nitrous acid, due to the formation of the active species dinitrogen tetroxide or nitrogen dioxide:

$$H^+ + HNO_2 + NO_3^- \rightleftharpoons N_2O_4 + H_2O, \quad [1]$$

$$N_2O_4 \rightleftharpoons 2NO_2^{\bullet}. \quad [2]$$

In many reactions nitric acid is reduced to nitrous acid, thereby producing an increase in catalyst concentration; the active species may be either of the nitrogen (IV) oxides. Thus there is a family of such autocatalytic oxidation reactions which may give rise to travelling reaction fronts. Systems studied in detail include the oxidation of thiocyanate (Hughes *et al.* 1969), hydroxylamine (Pembridge & Stedman 1979), formic acid (Longstaff & Singer 1954), formaldehyde (Horváth *et al.* 1988), and ferroin (Lengyel *et al.* 1988). So far no oscillating reactions involving the autocatalytic nitric acid oxidations have been observed (Epstein & Bazsa 1986), though it may be possible to find such systems (Bazsa & Lengyel 1990).

The first example of such a travelling reaction front discovered was due to a serendipitous observation (Gowland & Stedman 1983) during a study of the kinetics of reaction between hydroxylamine and nitric acid. Hydroxylamine shows two contrasting types of behaviour in nitric acid + nitrous acid. At high $[HNO_3]$ and low $[NH_3OH^+]$ hydroxylamine is oxidized autocatalytically to form nitrous acid [3], whereas at low $[HNO_3]$ and high $[NH_3OH^+]$ it acts as a nitrite scavenger [4] (Pembridge & Stedman 1979)

$$NH_3OH^+ + 2HNO_3 \rightarrow 3HNO_2 + H_2O + H^+, \quad [3]$$

$$NH_3OH^+ + HNO_2 \rightarrow N_2O + 2H_2O + H^+. \quad [4]$$

Gowland worked in the borderline region where nitrite formation and nitrite destruction were approximately in balance, and noted a linear plot of transmission (%) against time at wavelengths characteristic of nitrous acid. Inspection of the reaction vessel, a 1 cm × 1 cm cell, showed a sharp well-defined boundary about half-way down the cell; this boundary moved downwards at a slow but measurable rate. By moving the position of the cell the spectrophotometer beam was made to pass through the upper and lower layers. The upper layer gave the four-fingered spectrum, 340–390 nm, characteristic of nitrous acid, showing that decomposition of hydroxylamine was complete, while the lower layer showed no absorption, indicating unreacted starting material. A large number of repeat experiments showed that the reaction occurred spontaneously for initially homogeneous solutions and that there was a variable and non-reproducible induction period. Addition of nitrite removed the induction period, while the addition of a nitrite scavenger such as sulphamic acid prevented reaction starting. Once the reaction zone had formed it moved downwards at a constant rate. Preliminary accounts of this work have appeared (Gowland & Stedman 1983; Garley *et al.* 1990).

In the above experiments, the solutions were colourless and the reaction front was only observable because of differences of refractive index. It was easy to see if the cell was standing freely, and the experimenter could move so as to see the boundary from the most favourable direction of observation. When the cell was mounted in a constant temperature housing and viewed through a cathetometer the contrast was much reduced, and it was difficult to observe. In the original publication it was claimed that the reaction front did not form in tubes. This was wrong, and was probably due to failure to observe the boundary. The suggestion that surface tension effects might help maintain the boundary was also mistaken (Gowland & Stedman 1983). Bazsa has looked for travelling waves in the formaldehyde/nitric acid reaction, another colourless system, and failed to see them though we have recently obtained evidence that such waves exist (K. M. Williams and G. Stedman, unpublished results). A much easier system to study is the oxidation of thiocyanate, as in this case coloured species make the reaction front readily observable. Solutions of alkali metal thiocyanates in aqueous nitric acid are initially colourless and then rapidly turn pink, deep red and finally colourless or a pale blue colour. The main reaction is the autocatalytic oxidation reaction [5], with nitrous acid as the catalytic species. The pink or red colour is due to the formation of nitrosyl thiocyanate

$$H_2O + 3HNO_3 + HNCS \rightarrow H_2SO_4 + HCN + 3HNO_2 \qquad [5]$$

($\lambda_{\max}$ 460 nm, $\epsilon_{\max}$ 100 mol^{-1} dm^3 cm^{-1})

$$H^+ + HNO_2 + SCN^- \rightleftharpoons ONSCN + H_2O. \qquad [6]$$

When the initial concentration of thiocyanate is sufficiently high then the nitrous acid produced is in equilibrium with an observable amount of blue dinitrogen trioxide, $\lambda_{\max}$ 625 nm (Bunton & Stedman 1958)

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O. \qquad [7]$$

The ferroin/nitric acid reaction also produces a coloured reaction front that can readily be observed.

2. Experimental

The rates of reaction front movement were measured in standard 1 cm × 1 cm cells, mounted in a constant temperature cellholder. The position of the front was measured using a cathetometer and focusing the image on the cross-wires. For experiments with nitric acid/hydroxylamine mixtures the direction of illumination was important in order to be able to see the reaction front through the telescope. Work in a dark corner of a room with illumination from the side worked best. For reactions in the thiocyanate/hydroxylamine/nitric acid system there were no difficulties. For experiments in tubes the rates of movement were obtained by comparison with a standard ruler. Solutions were made up by mixing the nitric acid and hydroxylamine first so that traces of nitrite in the nitric acid were scavenged: the thiocyanate was then added. Reaction was initiated by the cautious addition of a few drops of a 10% (by volume) solution of butyl nitrite in dodecane. The concentration of nitrous acid in the final solution was usually too great for concentrations to be determined by direct spectrophotometry, as the absorbance values were too high. Instead a 1 cm^3 portion was taken, diluted a known amount, and the absorbance measured at 370 nm ($\epsilon = 57$ mol^{-1} dm^3 cm^{-1}). The concentrations of nitrous acid were very high in some experiments, up to 0.5 mol dm^{-3}, the inevitable consequence of using substantial initial concentrations of thiocyanate. However, it made observation of the boundary much easier. There must have been losses in the sampling and dilution procedure, and our values of $[HNO_2]_\infty$ are less reliable than we like. When the solution was undisturbed in a cell with a hydrocarbon layer floating on the surface, absorbance measurements at 370 nm indicated that decomposition losses were small during the course of an experiment.

Computations were carried out using a simple Euler method of numerical integration on an Archimedes 310 microcomputer, dedicated to the problem. This was found to be more satisfactory than use of the Mainframe. Attempts to use a Runge–Kutta method were more time consuming. Checks in which the time interval was reduced from 0.02 to 0.001 s gave identical results (though the latter took 69 h to run). The standard parameters used were $k_1[H^+][NO_3^-] = 1.259\ s^{-1}$ (Schmid & Bähr 1964); $k_2 = 10^3\ s^{-1}$ (Gratzel *et al.* 1969); $k_3 = 10^6\ mol^{-1}\ dm^3\ s^{-1}$; $k_4 = 6600\ mol^{-1}\ dm^3\ s^{-1}$; $k_5 = 10.75\ mol^{-1}\ dm^3\ s^{-1}$ (Dosanjh 1991). The value of k_4 includes the dissociation constant of NH_3OH^+ and predicts the limiting $[HNO_2]_\infty/[NH_3OH^+]_0$ ratio for the NH_3OH^+/HNO_3 reaction. The rate for the nitrite scavenging process [21] and [22] was calculated as $914[NH_3OH^+][HNO_2][SCN]\ mol\ dm^{-3}\ s^{-1}$ (M. S. Garley and G. Stedman, unpublished results). The ratio $[SCN^-]/[HNCS]$ was taken as 1.23 for 5 mol dm^{-3} nitric acid and a value of 5×10^{-6} was used for the diffusion coefficient of all species.

3. Results

Attempts to follow the travelling reaction front in nitric acid and sodium thiocyanate by initiating the reaction at the meniscus produced a striking red coloured layer that moved downwards. Initially the red layer had a curved profile similar to that of the meniscus, but after it had travelled a short distance it became a horizontal flat layer (visual observation). However, it was impossible to prepare a solution of nitric acid completely free from nitrous acid, and so the autocatalytic reaction also started in the bulk of the solution. As a consequence, the reaction front advanced in a reacting solution, and was generally able to move only a few millimetres before the bulk of the solution reacted. To obtain satisfactory results, it was necessary to add a nitrite scavenger to prevent this prior reaction. Possible scavengers were hydrazine, sulphamic acid, hydrazoic acid and hydroxylamine. Epstein & Bazsa (1985) used low concentrations of hydrazine in a study of the homogeneous reaction of thiocyanate with nitric acid. We used hydroxylamine because of our previous experience with the hydroxylamine/nitric acid system (Pembridge & Stedman 1979; Gowland & Stedman 1981).

Reaction was initiated by floating a few drops of a 10% (by volume) solution of butyl nitrite in dodecane on the surface of the aqueous mixture. Diffusion across the interface followed by rapid acid-catalysed hydrolysis of the alkylnitrite produced nitrous acid and initiated reaction immediately below the meniscus reproducibly and cleanly. The fact that there was a hydrocarbon layer floating on the surface had the added advantage of stabilizing the nitrous acid by cutting down losses due to escape of nitric oxide. Reaction could also be initiated by other sources of nitrite such as a solution of dinitrogen tetraoxide in a hydrocarbon solvent, or by the direct addition of a few drops of aqueous sodium nitrite. These approaches had the advantage of eliminating the problems arising from a variable and sometimes lengthy induction period.

Table 1. *Results for moving reaction front in* 4 mol dm^{-3} *nitric acid/thiocyanate/hydroxylamine solutions at* 25 °C

$[NH_3OH^+]_0$/(mol dm^{-3})	0.02	0.05	0.10	0.15	0.20
$[SCN^-]_T$/(mol dm^{-3})			$10^2 \times$ rates of front movement/(cm min^{-1})		
0.05	9.23	6.05	3.25	2.25	1.67
0.10	11.2	6.39	5.91	4.24	2.31
0.15	14.2	10.9	8.78	4.40	6.62
0.20	17.8	15.0	10.3	7.94	6.14
			$10 \times [HNO_2]_\infty$/(mol dm^{-3})		
0.05	1.65	2.10	1.66	1.67	2.79
0.10	3.19	2.80	2.05	1.69	1.22
0.15	4.07	5.15	3.72	4.01	—

The results of a typical set of runs in 4 mol dm^{-3} nitric acid are shown in table 1. As thiocyanate exists as a mixture of SCN^-, HNCS and ONSCN the total stoichiometric concentration is represented as $[SCN^-]_T$. Qualitatively the results fit general expectations. An increase in the concentration of the nitrite generator thiocyanate increases both the rate of boundary movement and the yields of nitrous acid, while an increase in the concentration of the nitrite scavenger hydroxylamine decreases rate and yield. Other measurements show that the rate of boundary movement increases with nitric acid concentration, and also with increases in temperature.

Epstein has drawn attention to some of the complications that may arise in the study of travelling reaction fronts, and to the importance of the dimensions of the tube in which the front travels. The passage of the reaction wave may be driven by convection effects as well as by diffusion. This may be checked by varying the dimensions of the tube, such effects being minimized by use of narrow tubes. In our system a variety of rectangular cell of lengths 4, 1, 0.5 and 0.1 cm gave no difference in rate. We also examined the reaction in cylindrical tubes of diameters 2–5.6 mm, and again found no effect of tube dimensions. One potential complication in our system was the formation of gas bubbles, nitrous oxide due to [4] and nitric oxide due to the self-decomposition of nitrous acid [8]. Some gas bubbles were evolved,

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O, \qquad [8]$$

mainly in experiments at higher initial thiocyanate concentrations, but they did not cause any difficulty. The bubbles appeared to be released at the top of the reaction zone, and did not break up the regular structure. Reactions at higher thiocyanate concentrations were, of course, more exothermic and we noticed occasional red coloured streamers of solution rising from the reaction zone. It was assumed that this was a convection effect due to warm reaction solution and it is possible that formation of a bubble might initiate such convective motion. The rates measured in such experiments did not seem to be abnormal.

Bazsa & Epstein (1985) in their study of the iron(II)/nitric acid reaction obtained interesting variations in rate when the tube was tilted at different angles, and also in earlier studies when different rates were observed for the reaction front moving downwards and upwards. We have briefly examined the effect of tube orientation, and find that our system $r\cos\theta$ is constant, where r is the rate of front movement measured along the length of the tube and θ is the angle between the tube and the vertical. This simply implies that in our system the rate of vertical movement of the

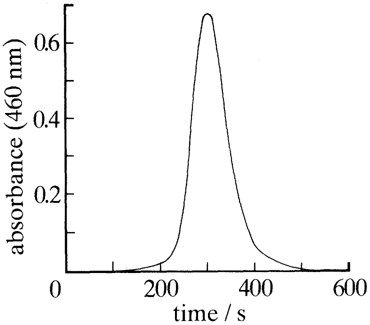

Figure 1. Measured wave front profile. Decomposition of 0.05 mol dm^{-3} SCN$^-$ and 0.15 mol dm^{-3} NH_3OH^+ in 5 mol dm^{-3} HNO_3.

front is a constant. In an attempt to make the reaction front move upwards reaction was initiated with a solution of butyl nitrite in carbon tetrachloride. Because of its density this forms a layer at the bottom of the spectrophotometer cell. We were unable to generate a stable reaction front, but observed instead a rather spectacular phenomenon. A thin red layer appeared at the interface between the two layers, and then a thin red thread-like jet of liquid rose through the aqueous medium to the air/nitric acid meniscus, where it then spread out in a horizontal layer that moved downwards. The threadlike stream started from the highest point of the convex carbon tetrachloride surface, and followed a path that wandered around. It seems likely that this is due to an increase in temperature and decrease in density of the reacting solution producing a 'thin stream' of reacting liquid. Attempts to get the boundary to move upwards in narrow capillary tubes were frustrated by problems with bubble formation.

In addition to the macroscopic measurement of rate of movement of the reaction front it was also desirable to obtain concentration profiles of reactants, intermediates or products through the reaction zone. To do this spectrophotometrically required a light beam significantly narrower than the width of the boundary. Observations with a cathetometer suggested a reaction zone width of *ca.* 0.3–0.4 mm, based on visual detection of the red colour of nitrosyl thiocyanate in a 1 cm cell. To achieve this narrow beam a 1 cm × 1 cm cell was masked with two parallel strips of black tape on one of its optical faces so as to leave a horizontal 0.15 mm slit between the adjacent edges. The cell was filled with reaction mixture and reaction was initiated in the usual way. An absorbance/time trace at 460 nm gave a zero absorbance baseline until the reaction zone began to pass the slit, after which the instrument traced out the absorbance profile due to nitrosyl thiocyanate. A minor problem with this approach was that over a period of weeks the tape may creep, and the slit width change. As the 0% and 100% transmission lines were set with each run this did not cause difficulties in practice.

A typical trace is shown in figure 1. The width of the reaction zone was estimated by extrapolating the tangents at the two points of inflexion on either side of the peak to cut the baseline, and from the known rate of front movement the width was calculated. The width was around 1.4 mm, considerably greater than the value estimated visually. However, the eye does not detect the wings of the peak with much sensitivity where there is a low absorbance. These traces occasionally showed a sharp spike when a bubble impinged on the light path, but this did not cause any significant problems. With this arrangement the spectrophotometer was, of course, operating at much lower light intensities than the optimum values, and the traces showed more noise than normal. We checked the Beer–Lambert law under these conditions using stable solutions of $[Fe(H_2O)_5NCS]^{2+}$ at 460 nm, and found it to be obeyed, so it was justifiable to use the absorbance readings to calculate concentrations.

4. Discussion

The oxidation of thiocyanate by nitric acid produces nitrous acid, but the stoichiometry is more complex than shown in [5]. At low nitric acid concentrations, 1 mol dm^{-3}, the ratio $[HNO_2]_\infty/[SCN^-]_T$ is close to 2.6 due to the formation of some sulphur dicyanide by [9] and [10] as well as the main products, sulphuric acid and hydrogen cyanide (Hughes *et al.* 1969; Bazsa & Epstein 1985)

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

$$(SCN)_2 + CN^- \rightarrow S(CN)_2 + SCN^-. \qquad [10]$$

As the nitric acid concentration rises to 8 mol dm^{-3} this ratio rises to 4. It has been suggested that this may be due to the oxidation of hydrogen cyanide (Bazsa & Epstein 1985). For 4 mol dm^{-3} nitric acid the ratio is 3.1. This provides information about the role of hydroxylamine. If it functions 100% as a nitrite scavenger then

$$[HNO_2]_\infty = 3.1[SCN^-]_T - [NH_3OH^+]_0.$$

If, however, some hydroxylamine is oxidized to nitrous acid then $[HNO_2]_\infty$ will be higher. As, however, some of the nitrous acid concentrations were as high as 0.5 mol dm^{-3} it is almost certain that there were some losses in the sampling and analysis procedure. From the results in table 1 it seems that when $3.1[SCN^-]_T > [NH_3OH^+]_0$ hydroxylamine functions mainly as a nitrite scavenger. The fact that nitrous acid is observed as a product in experiments, where $3.1[SCN^-]_T < [NH_3OH^+]_0$ shows that here some hydroxylamine must have been oxidized to nitrous acid.

The mechanism of the oxidation of thiocyanate is summarized below in [11]–[15]. Under the present conditions of acidity and thiocyanate concentration the rate determining stage is the formation of dinitrogen tetroxide. The conversion of hypothiocyanous acid to sulphuric acid and hydrogen cyanide is a rapid process, and [15] merely represents the stoichiometry:

$$H^+ + HNO_2 + NO_3^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2O_4 + H_2O, \qquad [11]$$

$$H^+ + NCS^- \underset{\text{fast}}{\rightleftharpoons} HNCS, \qquad [12]$$

$$N_2O_4 + HNCS \xrightarrow{k_3} HOSCN + N_2O_3, \qquad [13]$$

$$N_2O_3 + H_2O \underset{\text{fast}}{\rightleftharpoons} 2HNO_2, \qquad [14]$$

$$H_2O + HOSCN + 2HNO_3 \xrightarrow[\text{fast}]{} H_2SO_4 + HCN + 2HNO_2. \qquad [15]$$

Nitrosyl thiocyanate does not appear in the mechanism, and is thought to be an inactive intermediate. An alternative view is due to Bazsa & Epstein who prefer nitrogen dioxide as the active N^{IV} species. They also propose that the red-coloured species is $NOSCNH^+$, and that this is a reactive species, being oxidized by nitrogen dioxide to provide an alternative pathway for the formation of sulphuric acid and hydrogen cyanide (Epstein & Bazsa 1985). The question of whether dinitrogen tetroxide or nitrogen dioxide is the active nitrogen species is probably not very important, as under many conditions it is the rate of formation of N_2O_4 (or $2NO_2^{\bullet}$) that determines the rate. The question of whether the red species is an active or an inactive intermediate is more significant. The main reason for postulating $NOSCNH^+$ as a reactive species is the observation of bistability in a continuous flow stirred tank reactor, which requires a step in the mechanism with a total order in reactants greater than two. However, there may be alternative explanations of bistability than an $NO_2/ONSCNH^+$ reaction. Evidence against this comes from the original work (Hughes *et al.* 1969), where the oxidation was followed from the increase in total nitrite concentration determined by a diazotization/coupling procedure. Here the rate of reaction decreased with increased thiocyanate concentration at high $[SCN^-]_T$, ascribed to the conversion of a sizeable proportion of nitrite to inactive nitrosyl thiocyanate. Recent work (Munkley 1990) shows the same behaviour at nitric acid concentrations used in this work.

Turning now to the role of hydroxylamine, the mechanism is set out below:

$$H^+ + HNO_2 + NO_3^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2O_4 + H_2O, \qquad [16]$$

$$N_2O_4 + NH_2OH \xrightarrow{k_4} HNO + N_2O_3, \qquad [17]$$

$$N_2O_4 + HNO \xrightarrow[\text{fast}]{} HNO_2 + N_2O_3, \qquad [18]$$

$$N_2O_3 + H_2O \underset{\text{fast}}{\rightleftharpoons} 2HNO_2, \qquad [19]$$

$$HNO_2 + NH_3OH^+ \xrightarrow{k_5} N_2O + 2H_2O + H^+, \qquad [20]$$

$$H^+ + HNO_2 + SCN^- \underset{\text{fast}}{\rightleftharpoons} ONSCN + H_2O, \qquad [21]$$

$$ONSCN + NH_2OH \xrightarrow[\text{slow}]{} N_2O + H_2O + H^+ + SCN^-. \qquad [22]$$

The main function of hydroxylamine is to act as a nitrite scavenger [20], but it may be noted that thiocyanate powerfully catalyses the nitrite destruction reaction by [21] and [22]. The concentration of the free base form of hydroxylamine in 4 mol dm^{-3} nitric acid is very low (pK_a of the hydroxylammonium ion is 6) and most of the dinitrogen tetraoxide reacts with the much more abundant HNCS [13], which constitutes about 50% of the thiocyanate. Because both thiocyanate and hydroxylamine are involved in nitrite generation and in nitrite scavenging, a detailed discussion requires a computer model which is described in the next section.

5. A computer model

With a system as complex as this one the only semi-quantitative approach is to design a computer model, and to solve the differential equations by numerical integration. We consider reaction occurring in one hundred consecutive plane parallel cells, each of thickness 0.0025 cm. We assume that all of the cells are initially

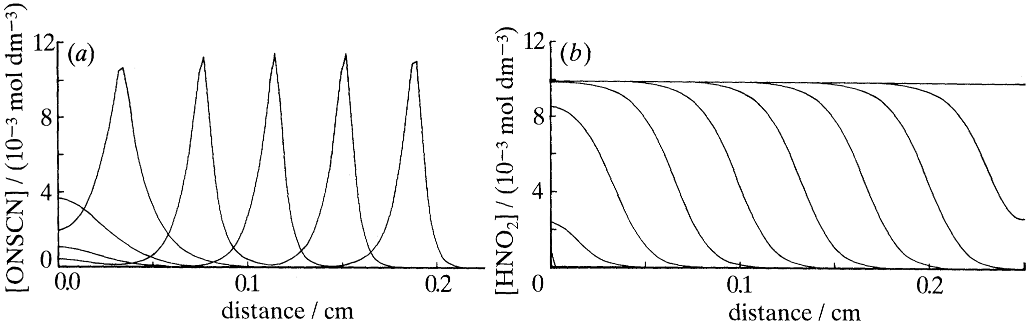

Figure 2. Computed wave front profiles. (*a*) Decomposition of 0.02 mol dm^{-3} SCN^- and 0.02 mol dm^{-3} NH_3OH^+ in 5 mol dm^{-3} HNO_3 at 25°; profiles calculated for 24 s intervals, wave travelling left to right. (*b*) Decomposition of 0.015 mol dm^{-3} NH_3OH^+ in 5 mol dm^{-3} HNO_3 at 25°; profiles calculated from 20 s intervals, wave travelling left to right.

Table 2. *Computed values of reaction front velocity in* 5 mol dm^{-3} *nitric acid at* 25 °C

$[NH_3OH^+]_0$/(mol dm^{-3})	0.002	0.01	0.02	0.03	0.04	0.05	0.06
$[SCN^-]_T$/(mol dm^{-3})	0.02	0.02	0.02	0.02	0.02	0.02	0.02
v_0/(cm min^{-1}) (calc)	0.094	0.093	0.094	0.092	0.090	0.089	—[a]
v_0/(cm min^{-1}) (expt)	—	—	0.071	—	—	0.072	—
$[NO_3OH^+]_0$/(mol dm^{-3})	0.02	0.02	0.05	0.10	0.10	—	
$[SCN^-]_T$/(mol dm^{-3})	0.10	0.050	0.05	0.05	0.10	—	
v_0/(cm min^{-1}) (calc)	0.078[b]	0.083	0.091[b]	0.073[b]	0.070[b]	—	—
v_0/(cm min^{-1}) (expt)	0.127	0.094	0.082	0.060	0.079	—	—
$[NH_3OH^+]_0$/(mol dm^{-3})	0.002	0.01	0.02	0.04	0.06	0.08	
$[SCN^-]_T$/(mol dm^{-3})	0	0	0	0	0	0	
v_0/(cm min^{-1}) (calc)	0.040	0.086	0.110	0.124	0.119	0.106	
$[NH_3OH^+]_0$/(mol dm^{-3})	0.100	0.200	0.250	0.300	—	—	
v_0/(cm min^{-1}) (calc)	0.097	0.068[b]	0.059[b]	0.053[b]	—	—	
v_0/(cm min^{-1}) (expt)	—	0.104	—	0.067	—	—	

[a] No reaction front developed. [b] No reaction front developed unless computation allowed for diffusion of nitrite into first cell (see text).

filled with reaction mixture of a given composition of nitric acid, hydroxylamine and thiocyanate and we assume a finite concentration of the initiator, nitrous acid, in the first cell. The concentration of nitrite in all of the other cells is taken initially as zero. From the known initial concentrations and the assigned values of the rate constants we compute the change in concentration of reactants, intermediates and products in the first cell during a short time interval, 0.02 s, including the effect of diffusion of nitrous acid from cell 1 to cell 2. The calculation is then repeated for a further 0.02 s for cells 1 and 2, this time allowing for diffusion from 1 to 2, from 2 to 1, and for nitrite diffusion from 2 to 3. By extending this calculation for a very large number of cycles one obtains a profile of the concentrations of all relevant species in all of the one hundred cells for a very large number of values of time. By plotting out such concentration–distance profiles for a number of selected times one can obtain a plot of the type shown in figure 2*a*, from which values of the rate of movement of the front and its width can be calculated. The discontinuous shape of the peaks is due to joining up a finite number of points. A series of results for 5 mol dm^{-3} nitric acid are shown in table 2. By setting the initial thiocyanate concentration equal to zero the model can also be used to predict the behaviour in the hydroxylamine/nitric acid

Table 3. *Effect of changes in parameters used in computation*
($[HNO_3] = 5$ mol dm^{-3}; $[SCN^-]_T = 0.02$ mol dm^{-3}; $[NH_3OH^+] = 0.02$ mol dm^{-3})

0.094[a]	0.085[b]	0.062[c]	0.141[d]	0.131[e]	0.079[f]	0.053[g]	0.075[h]

[a] Standard value; [b] double k_5; [c] double $[SCN^-]/[HNCS]$; [d] double k_1; [e] double D; [f] halve k_3; [g] divide k_3 by 10; [h] double k_2.

system. A plot of the predicted behaviour is shown in figure 2*b*, with some of the numerical data in table 2.

It is important to check the effect of varying the values assigned to the various rate constants on the calculated front velocity. Some results are shown in table 3, where it can be seen that doubling the value of k_1, the rate constant for the formation of dinitrogen tetroxide, and doubling the value assigned to the diffusion coefficient D increased the calculated rate by factors of 1.51 and 1.4 respectively. An analytical treatment of travelling waves in the acidic nitrate/ferroin system predicted the velocity to vary with the square root of k_1 and D (Pota *et al.* 1989), so our factors are close to the predicted $\surd 2$. The same treatment suggested a wave front width proportional to $\surd D$ and to $1/\surd k_1$. Our computations give factors of 1.41 and $(1.44)^{-1}$ respectively. The detailed mechanisms of the two systems are, of course, different but the results suggest that Pota's approach may be generally useful for travelling waves involving autocatalytic nitric acid oxidations.

It turns out to be possible to make only a limited comparison between the experimentally measured rates of front movement and those calculated by the computer program because the concentration ranges in which they 'work' only overlap to a limited extent. It is instructive to consider why this is so. The calculations assume an idealized system, with nitric acid completely free of any traces of nitrous acid, and the calculations predict a well-defined reaction zone to be generated even with 0.002 mol dm^{-3} hydroxylamine. In practice we found that below about 0.02 mol dm^{-3} hydroxylamine reaction in the bulk of the solution occurred too readily for us to be able to follow the formation and movement of the reaction front for any useful distance, the concentration of the nitrite scavenger being too low.

The other limitation is shown up by the fact that the computer model predicts that at sufficiently high concentrations of hydroxylamine the reaction front will not develop. This is in agreement with expectations, but the actual 'critical' values of $[NH_3OH^+]_0$ are substantially lower than the values observed experimentally. This might, of course, be due to poor choice of numerical values for one or more of our parameters. Another possibility is that our model is not sufficiently realistic. In the experimental system there was a 10% (by volume) solution of butyl nitrite in dodecane, approximately 0.85 mol dm^{-3}, floating on the surface. As butyl nitrite diffused across the hydrocarbon/aqueous solution interface and was rapidly hydrolysed to nitrous acid, then the nitrite so generated consumed some of the hydroxylamine scavenger. Further nitrite then diffused across as there was still a large concentration gradient and more nitrite was generated and hence more hydroxylamine was consumed. Thus, in the vicinity of the interface the hydroxylamine concentration dropped below the critical value needed to control the autocatalytic reaction. Once this started, nitrite was generated which then diffused further into the solution and started reaction further down. In an attempt to model such a process, we have modified the program to include a step in which nitrite diffuses into the first cell (from the butyl nitrite layer). When this is done the model predicts a short induction period followed by the development of a reaction front. These calculations are shown in table 2, marked with a superscript b.

Comparing the calculated values (calc) with the experimental ones (expt) it is seen that there is good agreement, better than we had expected. This suggests the main features of our model are correct. The calculated rates are most sensitive to the values assigned to k_1 and to D. The model is less successful in predicting the width of the reaction zone; the calculated value is 0.26 mm, whereas our measured values are several times greater than this. Table 2 also includes the calculation of rates of front movement in the hydroxylamine/nitric acid system. The striking feature is that the addition of thiocyanate makes relatively little to the rate of movement (as is also observed experimentally). In both systems the maximum rate of nitrite generation is controlled by the same initial step, the formation of dinitrogentetroxide. The addition of thiocyanate provides an extra pathway for nitrite generation, but also catalyses nitrite scavenging by [21] and [22]. There may be advantages in pursuing further work on the nitric acid oxidation of thiocyanate replacing hydroxylamine by a compound that has only a nitrite scavenging role.

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