A Novel Moving Boundary Reaction involving Hydroxylamine and Nitric Acid

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An initially homogeneous solution of hydroxylamine in nitric acid can react to form a two-layer system, a layer of nitrous acid in nitric acid above a layer of hydroxylamine in nitric acid, with a sharp boundary between them that moves steadily downwards.

Hydroxylamine can undergo two different reactions in solutions of nitric acid containing small amounts of nitrous acid. It can act as a nitrite scavenger,[1] as shown in equation (1), or can undergo a nitrous acid catalysed autocatalytic oxidation by nitric acid,[2] as shown in equation (2). The presence of nitrous

$$NH_3OH^+ + HNO_2 \rightarrow N_2O + H_2O + H_3O^+ \qquad (1)$$

$$NH_3OH^+ + 2HNO_3 \rightarrow 3HNO_2 + H_3O^+ \qquad (2)$$

acid is essential for reaction (2), and in its absence there is often a substantial induction period. When reaction (2) starts it can go to completion in a few seconds, and as the reaction is exothermic this leads to a sizeable rise in temperature, *ca.* 4 °C for initial $[NH_3OH^+] = 0.1$ mol dm^{-3}. Borderline conditions for the transition from hydroxylamine acting as a nitrite scavenger to a reaction in which there is a net formation of nitrous acid, (2) dominating (1), have been established.[3] An increase in $[HNO_3]$, an increase in temperature, and a decrease in $[NH_3OH^+]$ all favour reaction (2). Near the borderline the system is very sensitive to even small changes in any of these parameters; a change of as little as 10^{-4} mol dm^{-3} in $[NH_3OH^+]$ can produce a marked change in the character of the reaction.

During investigations of this borderline region we have observed a remarkable phenomenon in which reaction solutions that are initially homogeneous, and show no sign of reaction during an induction period which may last up to thirty minutes, develop two layers. The upper layer contains nitrous acid, as is shown by the characteristic absorption spectrum 350—390 nm. The absorbance shows no sign of changing with time, and in view of the known rate of reaction (1) which is relatively fast under our conditions, this implies that all of the hydroxylamine has been consumed. The lower layer shows no absorption in this wavelength range, and contains unchanged hydroxylamine. The boundary between the two layers appears quite sharp, and under our normal conditions (using a 1 cm silica spectrophotometer cell) has the shape of a flattened meniscus. The boundary moves downwards at a steady rate until it reaches the bottom of the cell. A few gas bubbles are formed on the upper side of the boundary but they do not disturb the sharpness of the interface. Rates of movement of the boundary varied from 0.004 to 0.15 mm s^{-1}.

Table 1. Typical results on moving boundary reactions between hydroxylamine and nitric acid in 1 cm cells.

$[NH_3OH^+]$ /mol dm^{-3}	$[HNO_3]$ /mol dm^{-3}	T /°C	10^4.Rate /mm s^{-1}	t_{induct} /s	Y^a
0.07	4.0	20	10	320	0.075
0.10	4.0	30	13	—	
0.10	4.0	35	14	520	0.11
0.10	4.0	40	27	270	0.11
0.15	4.0	40	19	390	0.09
0.15	4.0	40	23	—	0.096
0.15	4.0	45	48	195	0.11
0.20	4.0	45	29	930	0.076

[a] $Y = ([HNO_2]_\infty - [HNO_2]_0)/[NH_3OH^+]_0$.

We interpret this by suggesting that in the upper layer the autocatalytic reaction has gone to completion. In so doing the reacted solution will have warmed up because of the exothermic nature of the reaction and the density will be slightly reduced. This, and probably surface tension effects also will help to maintain the boundary. There is a reaction zone between the two layers into which nitrous acid diffuses downwards and hydroxylamine diffuses upwards, and reactions (1) and (2) occur. We placed a thermistor bead in the solution so that it dipped into the lower layer and we observed a rise in temperature as the boundary passed the bead.

The exact conditions under which this remarkable phenomenon is observed are rather critical, and it is not possible to reproduce the reaction on every experiment. Table 1 summarises the results of a few of over fifty experiments in which the boundary has been formed and its movement monitored. Mixing is important. The reaction solutions can be mixed in a conical flask and then poured into the spectrophotometer cell. Many of our experiments involved mixing reactants from two syringes fitted into a plastic mixing block with channels drilled to give rapid T-junction mixing. Other workers to whom we have described our results have been able to produce the moving boundary by placing the solutions in separate sections of a two compartment spectrophotometer cell, stoppering it and inverting and shaking the cell to mix.[4] The reaction solutions were undoubtedly homogeneous after mixing, but the way in which the two layers develop is not understood. The boundary always forms at the top and moves downwards. Experiments were carried out in a range of cells; silica or glass cells showed the effect, but plastic spectrophotometer cells did not give good boundaries. We noted that gas bubbles tended to stick to the walls in the latter case and this may have disrupted the boundary. Silica cells of 0.5, 1.0, and 2.0 cm length showed the effect but numerous attempts to get the reaction to go in a glass test tube were unsuccessful. However a solution in a test tube that did not react, when poured into a 1 cm cell did form a boundary! We think that surface tension effects play a role in forming and/or maintaining the boundary.

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