Autocatalytic waves in the nitric acid–hydroxylamine system: analytical description of the wave velocity

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It is shown that the velocity (c) of the autocatalytic travelling waves in the nitric acid–hydroxylamine system can be described by the formula $c^2 = 4D\{(3k_1/2) - k_2[NH_3OH^+]_0\}$ deduced from a previously proposed mechanism. Comparisons with other systems are included.

Keywords: Autocatalysis; hydroxylamine; nitric acid; travelling wave; velocity

1. Introduction

Recently we have described [1–3] some features of the travelling wave in the nitric acid–hydroxylamine system, the first known wave in the class of oxidation reactions by nitric acid. Here we present additional experimental material and, on the basis of a previously proposed mechanism, an analytical formula for the wave velocity.

2. Experimental

Chemicals of AnalaR grade were used in all experiments. The velocity measurements were carried out in a vertically mounted and thermostatted (25°C) 1 cm^2 spectrophotometer cell. The waves were initiated by adding a small amount of a 10% v/v solution of butylnitrite in dodecane to the top layer of the homogeneous solution of nitric acid + hydroxylamine. Acid catalysed hydrolysis of the alkylnitrite liberated the nitrous acid autocatalyst at the interface. The initial concentrations (denoted by subscript 0) always satisfied the relation $[HNO_3]_0 >> [NH_3OH^+]_0$, and therefore $[HNO_3] \approx [HNO_3]_0$ was always valid during a given experiment.

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Although the system was colourless, the wave front, which moved downwards, could be observed visually due to the differences in refractive index. Precision of the visual method was checked spectrophotometrically in masked cell [3] experiments.

3. Results and discussion

Briefly, there are two main processes in the nitric acid–hydroxylamine system at high acidity: the first process produces nitrous acid and the second consumes it. An application of the steady state principle to a recently published mechanism [4,5] proposed for the autocatalytic production of nitrous acid leads to the overall equation

$$NH_3OH^+ + 2HNO_3 \rightarrow 3HNO_2 + H_2O + H^+, \tag{1a}$$

whose rate, at a given concentration of nitric acid, is

$$r_1 = \frac{(k_1/2)[NH_3OH^+][HNO_2]}{\beta + [NH_3OH^+]}. \tag{1b}$$

The coefficients k_1 and β are defined in terms of the full mechanism [4,5]. Nitrous acid is consumed in the process

$$NH_3OH^+ + HNO_2 \rightarrow N_2O + 2H_2O + H^+, \tag{2a}$$

whose mechanism has also been discussed [6]. At a given nitric acid concentration the reaction has a simple second-order rate equation,

$$r_2 = k_2[NH_3OH^+][\,HNO_2]. \tag{2b}$$

The behaviour of the whole nitric acid–hydroxylamine system is determined by the balance between reactions (1) and (2). (In the description of the above processes we have taken into account that hydroxylamine exists essentially 100% in its singly protonated form at high acidity.)

On the basis of some general considerations [7], $[NH_3OH^+]$ in the wave front must be approximately equal to that in the still unreacted part of the system, and this reduces the reaction–diffusion equation for the concentration of nitrous acid to an analytically solvable linear differential equation. A study of this linear equation yields the following formula for the wave velocity c:

$$c^2 = 4D\left(\frac{3k_1/2}{\beta + [NH_3OH^+]_0} - k_2\right)[NH_3OH^+]_0, \tag{3}$$

where D is the diffusion coefficient of HNO_2. Eq. (3) is seen to be consistent with the velocity formulae obtained for similar autocatalytic systems [8,9]. On comparison with other nitric acid waves [10–14] we may assume that quantity β is much less than 10^{-2} mol dm^{-3}, the order of magnitude of $[NH_3OH^+]_0$ in the experi-

ments. Neglecting β in the denominator of eq. (3) we obtain the following velocity formula:

$$c^2 = 4D\{(3k_1/2) - k_2[NH_3OH^+]_0\}. \quad (4)$$

Obviously, eqs. (3) and (4) have a physical meaning only if $c^2 > 0$. This relation gives the concentration limits within which a travelling wave can exist in the system being studied, and corresponds to the borderline conditions investigated in the homogeneous system [5].

To reduce the error introduced mainly by the simplified description of the autocatalysis we have treated D and k_1 as adjustable parameters in the calculations. Fig. 1 shows that the experimental points lie reasonably close to the best fit theoretical lines calculated with $k_2 = 6.4$ (mol dm^{-3})$^{-1}$ s^{-1} [15], $D = 1.76 \times 10^{-6}$ cm^2 s^{-1} and $k_1 = 0.54$ s^{-1} ($[HNO_3]_0 = 3.96$ mol dm^{-3}), 1.09 s^{-1} ($[HNO_3]_0 = 4.67$ mol dm^{-3}) and 1.60 s^{-1} ($[HNO_3]_0 = 4.98$ mol dm^{-3}). Within the present standards of wave studies the fitted parameter values are seen to be good as the diffusion coefficient of HNO_2 in $HClO_4$ is reported to be (0.71–2.2) $\times 10^{-5}$ cm^2 s^{-1} (depending on the ionic strength) [16], and the experimental values of k_1 [17] (corrected to 25°C) are only 1.3 times less than those listed above.

In spite of being basically successful, these investigations raise two mechanistic problems. Firstly, an alternative value for k_2 of 12.2 (mol dm^{-3})$^{-1}$ s^{-1} has been reported [18], and this value could not be used here without additional assumptions. Secondly, the low value of β used here requires, because of the diffusion controlled limit on the rate coefficients, a slight modification of the original mechanism [4,5], in which N_2O_4 is proposed to react directly with NH_3OH^+ instead of with NH_2OH. These questions may indicate the need for more work on this system.

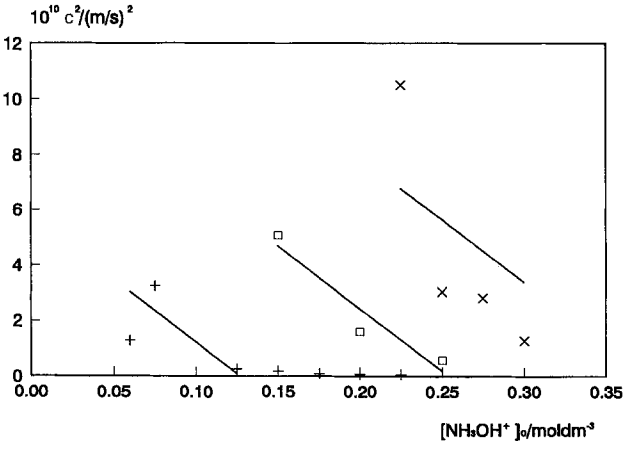

Fig. 1. Dependence of the wave velocity c on $[NH_3OH^+]_0$. Points: experimental values; lines: theoretical values. $[HNO_3]_0 = 3.96$ (+); 4.67 (□); 4.98 (×) mol dm^{-3}.

It is an important advantage, that the analytic treatment presented here is capable of linking this particular system to other nitric acid oxidations supporting autocatalytic waves. In the nitric acid–ferroin system [12,13] the HNO_2 autocatalyst is formed in essentially the same way as here but that system does not contain an HNO_2 consuming reaction. Thus, the first terms in the velocity formulae of the two systems are the same but the second term is absent in the case of ferroin substrate. At the given level of approximation, however, the wave velocity is described by essentially the same formulae in the nitric acid–iron(II) system [14] and the nitric acid–hydroxylamine one despite that HNO_2 is consumed only temporarily in the former but irreversibly in the latter. This once again emphasises that the wave velocity crucially depends on the processes taking place in the leading edge of the wavefront but does not reflect the differences between the kinetics of the two systems. A general theory concerning the detectability of kinetic differences via the measurement of the wave velocity would be useful, and there already exist encouraging results in this direction [19].

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