Autocatalytic Waves in the Nitric Acid–Formaldehyde System

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Abstract

Propagating reaction fronts generated in the autocatalytic oxidation of formaldehyde by nitric acid have been investigated. The experimental values of the wave velocity ν and those of the maximal reaction rate r_m at a given spatial coordinate have been described by the formulae $\nu = 2(Dk[CH_2(OH)_2]_0)^{1/2}$ and $r_m = 0.247 \times k[CH_2(OH)_2]_0^2$, respectively, (D and k are constants). Similarities and differences to other nitric acid oxidations have been discussed. © 1995 John Wiley & Sons, Inc.

Introduction

Propagating reaction fronts, i.e., traveling chemical waves, are part of the very active field of research into exotic reaction kinetics. Traveling waves are of interest because of their chemical [1] and biological [2] importance, as well as their intrinsic interest as an unusual phenomenon. The wave velocity and spatial profile of the wave depend upon the kinetics and mechanism of the chemical reactions taking place, and measurement of these parameters can support (or confute) a suggested mechanism. The autocatalytic oxidations of different substrates by nitric acid, whose mechanisms have a common core of reactions [3] but differ in fine details, are especially appropriate for comparative investigations of propagating reaction fronts. In these systems the active species are the nitrogen(IV) oxides N_2O_4 or NO_2 , formed by the reaction of nitrous and nitric acids. As nitric acid is reduced to nitrous acid during the reaction, autocatalytic kinetics occur. Here we report on experimental and theoretical studies of the waves generated in the nitric acid-formaldehyde system, and compare the results with those of other autocatalytic nitric acid systems. A study of the kinetics and mechanism of the homogeneous reaction has been reported by Horváth et al. [4], but they did not succeed in observing traveling waves by visual observation.

Experimental

Nitric acid and formaldehyde were AnalaR reagents, while dodecane and butyl nitrite were of GPR grade, used without further purification. Previous workers [4] found

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it necessary to keep stock solutions of formaldehyde at 70°C to prevent slow polymerization, and we have followed this practice; failure to do so leads to some loss of reproducibility. A spectrophotometer cell $(1 \times 1 \text{ cm})$ was filled with a reaction mixture of aqueous nitric acid and formaldehyde cooled to 25°C, and a thin layer of a 10% v/v butyl nitrite in dodecane was floated on the top. The cell was placed in a thermostatted cell holder in a Unicam spectrophotometer. Diffusion of the butyl nitrite into the top of the aqueous layer was followed by rapid acid catalyzed hydrolysis to butanol and nitrous acid, the nitrite initiating the autocatalytic oxidation of formaldehyde,

$$HNO_3 + H_2C(OH)_2 \longrightarrow HNO_2 + HCOOH + H_2O$$
.

This generated an autocatalytic reaction front moving downwards along the vertical axis of the cell. As the system investigated was colorless, the wave front was detected by spectrophotometric measurements of [HNO₂] at 395 nm rather than simple visual methods. To detect a wave propagating at a given height, a second cell masked with black tape except for a narrow slit was placed in the spectrophotometer beam. This gave a narrow beam of light with a vertical width of about 0.2 mm, much narrower than the wave being monitored. The sigmoid shaped HNO_2 concentration profile of the wave that was passing the slit was measured as a function of time. After the wave had passed the slit the cell was lifted upwards by a plastic spacer of known thickness Δs , and the time Δt elapsed until the reappearance of the wave at the slit was measured. From previous work on studies of traveling waves in the nitric acid oxidation of thiocyanate in which the wave is easily visible due to its dark red color we know that careful movement of the cell does not significantly disturb the wave. An alternative procedure (for which we are indebted to a referee) would be to keep the traveling wave cell stationary and move the cell masked to provide the narrow beam. Of course, this latter method also needs some tests since the optical axis changes in the experiments. The wave velocity ν was calculated from the formula $\nu = \Delta s / \Delta t$.

Results and Discussion

Horváth et al. [4] have suggested the following mechanism for the nitric acid-formaldehyde reaction:

(1a)
$$H^+ + NO_3^- + HNO_2 = N_2O_4 + H_2O_3$$

(1b)
$$r_1 = k_1 [\mathrm{H}^+] [\mathrm{NO}_3^-] [\mathrm{HNO}_2]$$

(1c)
$$r_{-1} = k_{-1}[N_2O_4]$$

(2a)
$$N_2O_4 + CH_2(OH)_2 \longrightarrow HCOOH + 2HNO_2$$

(2b)
$$r_2 = k_2[N_2O_4][CH_2(OH)_2].$$

Here formaldehyde is written in the hydrated form, $CH_2(OH)_2$. Applying the steadystate principle to N_2O_4 we obtain the following overall reaction and rate equation:

$$(3a) \qquad H^+ + NO_3^- + CH_2(OH)_2 + HNO_2 \longrightarrow 2HNO_2 + HCOOH + H_2O$$

(3b)
$$r = k[\text{HNO}_2][\text{CH}_2(\text{OH})_2]$$

where

(3c)
$$k = k_1 k_2 [\mathrm{H}^+]_0 [\mathrm{NO}_3^-]_0 / k_{-1}$$

In the derivation of (3) it is assumed that nitric acid is in large excess and so $[H^+]$ and $[NO_{3^-}]$ are nearly equal to their initial values (indicated by subscript 0) and that $k_{-1}/k_2 >> [CH_2(OH)_2]$. Equation (3) can also be derived by treating (1a) as a preequilibrium [4]. To obtain simpler formula we assume that the diffusion constant of HNO₂ and that of CH₂(OH)₂ are equal. According to the theory of reaction-diffusion waves [2] and the conservation of mass the spatiotemporal distribution of the autocatalyst HNO₂ can be described by the equations

(4a)
$$\frac{\partial [\text{HNO}_2]}{\partial t} = D \frac{\partial^2 [\text{HNO}_2]}{\partial x^2} + k([\text{CH}_2(\text{OH})_2]_0 - [\text{HNO}_2])[\text{HNO}_2]$$

(4b)
$$[HNO_2](x, 0) = \{[CH_2(OH)_2]_0 \text{ if } x > 0 \text{ and } 0 \text{ if } x < 0\}.$$

where t, x, D, and $[CH_2(OH)_2]_0$ denote time, space coordinate, the diffusion coefficient of HNO₂, and the initial concentration of the substrate, respectively. On substituting $[HNO_2](x,t) = \varphi(x + \nu t)$, which describes a constant-form wave propagating with a constant velocity ν along the axis x, we obtain the following equations for the spatial distribution of the autocatalyst:

(5a)
$$D\frac{d^2\varphi}{dz^2} - \nu \frac{d\varphi}{dz} + k([CH_2(OH)_2]_0 - \varphi)\varphi = 0$$

(5b)
$$\varphi(+\infty) = [CH_2(OH)_2]_0 \text{ and } \varphi(-\infty) = 0$$

where $z = x + \nu t$. According to the KPP theory [5] the full solution of (4) tends to the solution of (5) if the wave velocity is

(6)
$$\nu = V = 2(Dk[CH_2(OH)_2]_0)^{1/2}$$

Figure 1 shows a typical absorbance vs. time curve measured at the slit, that is, a fixed coordinate x along the vertical axis of the spectrophotometer cell. If we consider the reaction rate occurring at the point x then initially the rate is zero. As the wave approaches the rate observed at point x will increase, pass through a maximum and then fall to zero as the wave passes and all of the formaldehyde is consumed. The



Figure 1. A typical absorbance vs. time profile measured at the slit. $[CH_2(OH)_2]_0 = 0.14 \text{ mol } dm^{-3} \text{ and } [HNO_3]_0 = 7.5 \text{ mol } dm^{-3}$.

value of the maximum rate will correspond to the slope at the point of inflection for the sigmoid shaped curve of absorbance against time. We characterize the wave profile with the maximum reaction rate r_m at the coordinate x. We shall give r_m in concentration/time units dividing the absorbance values by the optical path length and the molar absorbance of HNO₂ at the given wavelength. In the present theoretical approach this quantity is proportional to the maximal slope of the spatial wave profile and, independently of the actual value of x, is given by the expression

(7a)
$$r_m = V \left(\frac{d\varphi}{dz}\right)_m = 2pk[\mathrm{CH}_2(\mathrm{OH})_2]_0^2$$

where

(7b)
$$p = 0.1233...$$

The main problem in fitting the theoretical formula to the experimental data is in determining the fractional conversion of nitrous acid to dinitrogen tetraoxide in eq. (1a). Reliable values of k_1 and k_{-1} for solutions of low ionic strength are available, but at the high nitric acid concentrations that are necessary to obtain reasonable rates in this system, up to 8 mol dm^{-3} , nitric acid is only partially jonized and activity coefficients are far from unity. Longstaff and Singer [6] have used measurements of the variation in spectrum of solutions of nitrous acid in nitric acid up to 12 mol dm⁻³ to calculate the fraction of nitrite present as N_2O_4 . In such experiments there can be problems with medium effects on the spectra over such a wide range of nitric acid concentrations, and they quote upper and lower limits. For 8.6 mol dm^{-3} nitric acid their results predict that $[N_2O_4]/[HNO_2]$ lies between 0.11 and 0.18. Horváth et al. [4] used recommended values of 0.015 mol⁻² dm⁶ s⁻¹ and 1000 s⁻¹ for k_1 and k_{-1} , and used the Hammett acidity function [7] h_0 in place of [H⁺]. This empirical approach predicts $[N_2O_4]/[NHO_2] = 0.041$ for 8.6 mol dm⁻³ nitric acid. Other approaches are also possible. As we compare our data with that of Horváth et al. [4], we have followed their procedure, though recognizing its limitations.

To fit our formula to the experimental data we have used a multivariable leastsquares method [8] treating the product $(h_0[NO_{3^-}]_0)$ and $[CH_2(OH)_2]_0$ as variables, using the stoichiometric concentrations of nitric acid and formaldehyde for the latter two quantities, and $k_1/k_{-1} = 1.5 \times 10^{-5} \text{ mol}^{-2} \text{ dm}^6$. Values of k_2 and D were determined from the fitting procedure. From the experimental velocity values we have obtained $k_2D = 1.5 \times 10^{-3} \pmod{\text{dm}^{-3}}^{-1} \min^{-1} \text{cm}^2 \text{ s}^{-1}$ which, together with the rate coefficient

(8a)
$$k_2 = 99 \;(\text{mol dm}^{-3})^{-1} \; \text{min}^{-1}$$

calculated from the experimental r_m data, have yielded the realistic

(8b)
$$D = 1.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$$

value for the diffusion coefficient of the autocatalyst. (In perchloric acid the diffusion coefficient of nitrous acid is $(0.71-2.2) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [9]). We remark that the trial and error fits in the homogeneous experiments [4] have yielded the value $k_2 = 240 \text{ (mol dm}^{-3})^{-1} \text{ min}^{-1}$. In Figures 1–5 the experimental and theoretical results are compared in different projections. The lines have been offset by constant amounts to show the data more clearly. It is interesting to note that the experimental values of the thickness of the wave front, defined by

(9)
$$\Delta x = \frac{[\mathrm{CH}_2(\mathrm{OH})_2]_0}{r_m} V,$$



Figure 2. Wave velocity vs. initial formaldehyde concentration curves. $[HNO_3]_0 = 8.5 (\Box, 1, c = 0.4)$; 8.0 (\blacklozenge , 2, c = 0.3); 7.5 (+, 3, c = 0.2); 7.0 (Δ , 4, c = 0.1); and 6.5 (\times , 5, c = 0) mol dm⁻³. Symbols-experimental and lines-theoretical values.

lie in the range of 2-8 mm. These large values are due to the relatively slow chemical reaction taking place in the system, and the calculations with the above parameters yield a range of 3-6 mm. It can be seen that mechanism (3) qualitatively describes well the main properties of the waves. The quantitative agreement still corresponds to the present standards of the wave investigations. Horváth et al. [4] comment on the significant scatter that they found in the homogeneous reaction, and this may be reflected in the scatter in our wave experiments. A part of the



Figure 3. Acidity dependence of the wave velocity. $[CH_2(OH)_2]_0 = 0.06 (\Box, 1, c = 0);$ 0.10 (\blacklozenge , 2, c = 0.1); 0.14 (+, 3, c = 0.2); 0.18 (\vartriangle , 4, c = 0.3); and 0.21 (×, 5, c = 0.4) mol dm⁻³. Symbols-experimental and lines-theoretical values.



Figure 4. The maximum reaction rate at a fixed spatial coordinate vs. initial formaldehyde concentration curves. [HNO₃]₀ = 8.5 (\Box , 1, c = 0.04); 8.0 (\blacklozenge , 2, c = 0.03); 7.5 (+, 3, c = 0.02); 7.0 (Δ , 4, c = 0.01); and 6.5 (\times , 5, c = 0) mol dm⁻³. Symbols-experimental and lines-theoretical values.

quantitative discrepancies may be explained by the experimental error caused mainly by the inevitable polymerization of formaldehyde. There may be problems due to the spontaneous decomposition of nitrous acid, though this should have been minimized by the presence of an immiscible layer floating on the surface. While there may be room for modifications of the mechanism that Horváth et al. propose [4], our traveling wave results broadly support their kinetics.



Figure 5. Acidity dependence of the maximum reaction rate at a given spatial coordinate. $[CH_2(OH)_2]_0 = 0.06 (\Box, 1, c = 0); 0.1 (\blacklozenge, 2, c = 0.005); 0.14 (+, 3, c = 0.01); 0.18 (\Delta, 4, c = 0.015); and 0.21 (×, 5, c = 0.02) mol dm⁻³. Symbols-experimental and lines-theoretical values.$

It is interesting to note that in some nitric acid-substrate systems [10-12] the wave velocity decreases with increasing values of the substrate concentration. This effect, however, which is a consequence of processes that temporarily or irreversibly consume the autocatalyst, is apparently absent in the present system. This study demonstrates that with very simple techniques traveling waves can be investigated even in systems where there is no visible absorption.

Bibliography

- R.J. Field and M. Burger, Eds., Oscillations and Traveling Waves in Chemical Systems, Wiley, New York, 1985.
- [2] J.D. Murray, Mathematical Biology, Springer-Verlag, Berlin-Heidelberg-New York, 1993.
- [3] G. Bazsa and I.R. Epstein, Comm. Inorg. Chem., 5, 57 (1986).
- [4] M. Horváth, I. Lengyel, and G. Bazsa, Int. J. Chem. Kinet., 20, 687 (1988).
- [5] A. N. Kolmogorov, I. G. Petrovsky, and N. S. Piscounov, Bull. MGU, Mathematics and Mechanics, 1, (1937).
- [6] J.V.L. Longstaff and K. Singer, J. Chem. Soc., 2610 (1954).
- [7] J.G. Dawber and P.A.H. Wyatt, J. Chem. Soc., 3589 (1960).
- [8] P. Valkó and S. Vajda, Solution of Scientific and Engineering Problems Using Personal Computers (in Hungarian), Müszaki Könyvkiadó, Budapest, 1986, pp. 166–178.
- [9] H.N. Heckner and G. Schmid, *Electrochim. Acta*, 16, 131 (1971).
- [10] G. Póta, I. Lengyel, and G. Bazsa, J. Phys. Chem., 95, 4379 (1991).
- [11] M.S. Garley, E. Jones, and G. Stedman, Phil. Trans. Roy. Soc. Lond A, 337, 237 (1991).
- [12] E. Jones, G. Póta, and G. Stedman, Catalysis Letters, 24, 211 (1994).

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