J Eng Math (2007) 59:195–206
DOI 10.1007/s10665-007-9153-7

Travelling waves in autocatalytic chemical systems with decay: bounds on existence

J. H. Merkin

Received: 7 July 2006 / Accepted: 7 May 2007 / Published online: 13 July 2007

Abstract The existence of solutions to the travelling-wave equations governed by an autocatalytic reaction of order p ($p \geq 1$) and an autocatalytic decay step of order q ($q \geq 1$) are examined in the limit of large p. Two cases are treated, q of $O(1)$ and $q \sim p \gg 1$. In the first case, an upper bound k_{crit} is found for k for the existence of a solution, where k is a dimensionless measure of the strength of the decay step. In the second case, an upper bound on k is also found when $q < p$. For $q \geq p$, there is no upper bound on k and solutions exist for all (positive) values of k.

Keywords Autocatalytic reactions · High-reaction-order asymptotics · Propagating reaction fronts · Ranges of existence

1 Introduction

The coupling of chemical reactions with diffusion can, under appropriate conditions, lead to the propagation of locally applied stimuli in the form of travelling waves. Such waves are a fundamental aspect of many chemical and biological processes and an understanding of their basic properties is a necessary prerequisite for an appreciation of the complex structures that are often involved in such systems. The most basic form that can arise is a propagating reaction front which is essentially a local step-like change in concentration without returning to the original state; propagating reaction fronts convert the reacting medium from one state (usually the unreacted state) ahead to a different state (usually the fully reacted state) at the rear.

Autocatalytic chemical reactions, typically

$$A + pB \rightarrow (p+1)B \quad \text{rate } k_0 a b^p, \quad p \geq 1 \tag{1}$$

form the basis for the development of reaction fronts. Such reactions are, in spatially distributed systems and under some relatively unrestrictive initiation conditions, capable of sustaining permanent-form travelling waves. These are constant-speed, constant-form propagating reaction fronts that convert the substrate A (at some uniform concentration a_0 ahead of the front) fully into the autocatalyst B. In (1) we are assuming that $p \geq 1$, a and b are, respectively, the concentrations of A and B, and k_0 is a constant. The cases of quadratic autocatalysis ($p = 1$) and

J. H. Merkin (✉)
Department of Applied Mathematics, University of Leeds, Leeds, LS2 9JT, UK
e-mail: amtjhm@maths.leeds.ac.uk

cubic autocatalysis ($p = 2$) have previously been examined in considerable detail, see [1–4] for example, and the more general case has been treated in [5].

An important feature of at least some of the systems for which reaction (1) is a relevant model, is that the autocatalyst B is not indefinitely chemically stable but can decay to an inert product of reaction via some mechanism of the form

$$qB \rightarrow \text{product} \quad \text{rate } k_1 b^q, \tag{2}$$

where k_1 is a constant and we are taking $q \geq 1$. Reactions (1, 2) lead to the travelling-wave equations in dimensionless variables; see [2,6,7] for example:

$$a'' + ca' - ab^p = 0, \tag{3}$$

$$Db'' + cb' + ab^p - kb^q = 0, \tag{4}$$

where $D = D_B/D_A$ is the ratio of diffusion coefficients of the autocatalyst and substrate. The parameter $k = k_1 a_0^{q-p-1}/k_0$ measures the rate of autocatalyst decay by reaction (2) relative to its production by reaction (1). Primes denote differentiation with respect to the travelling co-ordinate y and c is the (constant) dimensionless propagation speed. We can assume that $c \geq 0$ without any loss in generality. The boundary conditions for Eqs. 3, 4 are, with $k > 0$,

$$a \to 1, \; b \to 0 \quad \text{as } y \to \infty, \qquad a \to a_s, \; b \to 0 \quad \text{as } y \to -\infty, \tag{5}$$

where a_s is a constant (dependent on k and D) which is determined as part of the solution to the travelling-wave problem. A travelling wave is then a non-trivial, i.e., $a \not\equiv 1, \; b \not\equiv 0$, solution to Eqs. 3–5. From this it then follows that $a_s < 1$.

Some specific cases have already been treated in detail. For quadratic autocatalysis and linear decay ($p = q = 1$) [6], minimum-speed (or linearly determined) travelling waves can exist only for $k < 1$, a result confirmed by numerical integrations of the corresponding initial-value problem. For $k \geq 1$, the effect of the termination step (2) is too strong for reaction-front initiation, the autocatalyst decays away and the system returns to its original state through diffusion. For quadratic autocatalysis with quadratic decay ($p = 1, \; q = 2$) [8], travelling waves exist for all (positive) values of k, the weaker termination step in this case is not able to overcome the production of autocatalyst by step (1). For cubic autocatalysis with quadratic decay ($p = q = 2$) and with linear decay ($p = 2, \; q = 1$) [9] there are upper bounds on k for the existence of travelling waves. In the first case, the situation is, in many respects, similar to the case $p = q = 1$, with existence requiring $k < 1$. The second case ($p = 2, \; q = 1$) is significantly different, the solutions to the travelling wave equations have two solutions for $0 < k < k_{\text{crit}}$, with a saddle-node bifurcation occurring at $k = k_{\text{crit}}$ and no solutions for $k > k_{\text{crit}}$. The value of k_{crit} was found to be relatively small, for $D = 1, \; k_{\text{crit}} = 0.0465$.

The general case was examined in [7], where some conclusions were drawn, perhaps a little conjecturally, basically following what was seen for the specific examples in [6,8,9]. There it was suggested that there are travelling-wave solutions for all k if $p < q$, travelling waves only for $k < 1$ if $p = q$ and, if $p > q$, there is a value k_{crit} of k (perhaps small) with travelling-wave solutions only for $k \leq k_{\text{crit}}$. No specific values for k_{crit} were given in [7], though some estimates were suggested.

In this paper we consider the problem given by Eqs. 3–5 in the limit of large p. We consider two cases, q of $O(1)$ and $q \sim p \gg 1$. Our calculations confirm the predictions in [7], at least in this limit. With q of $O(1)$, there is an upper bound k_{crit} on k of $O(p^{-3})$ for the existence of travelling waves, with an explicit expression for k_{crit} being obtained. With $q \sim p$, we find that there is a transition at $p = q$ from having bounds on k for existence ($q < p$) to having no restriction on k ($q > p$). The case without the decay reaction (2), where the asymptotic structure is simpler than that required here, has been treated in [10,11], our solutions agree with these previous calculations in the limit as $k \to 0$.

The approach that we adopt here has some similarities with high-activation-energy asymptotics in combustion theory, where it has been seen, see [12–14] for example, that such asymptotic solutions can give reliable qualitative (and in some cases even quantitative) insights about the nature of the flame, both its structure and propagation speed. In this asymptotic analysis, and in the situation described here, there is a relatively thin reaction zone, ahead of which is a diffusive region (in high-activation-energy asymptotics this is often referred to as the pre-heat zone). At the rear of the reaction zone is a much thicker decay region (termination region), where the final conditions are attained.

Asymptotics based on high powers of autocatalysis have been used with some success in understanding the structure of isothermal ‘flame balls’ (steady reaction–diffusion structures governed by autocatalytic reactions) [15,16] and in estimating the conditions where planar reaction fronts can become longitudinally unstable [11]. Finally, we note that the cases when $p, q < 1$ are qualitatively different to those referenced above and treated here. A full description of this case is provided in [17].

2 Asymptotic solutions for p large

We look for a solution of Eqs. 3, 4, subject to boundary conditions (5), valid for p large. We treat the two cases, namely q of $O(1)$ and $q \sim p$. For both cases we introduce the scalings

$$c = \bar{c}\, p^{-1}, \quad k = \bar{k}\, p^{-3}, \quad \bar{c},\ \bar{k} \ \text{of} \ O(1) \ \text{as} \ p \to \infty. \tag{6}$$

In both cases, the asymptotic solution has three regions, a thin reaction zone, with a thicker diffusive region ahead and a thicker decay region at its rear. We begin with the case when q is of $O(1)$.

2.1 q of $O(1)$

We start in the diffusive region where we scale $\xi = yp^{-1}$, giving an $O(p)$ thickness for this region. Since $b < 1$ in this region, we can neglect the autocatalytic reaction in the limit as $p \to \infty$. We look for a solution, after applying (6) and the above scaling for y, by expanding

$$\begin{aligned} &a(\xi; p) = a_0(\xi) + p^{-1} a_1(\xi) + \cdots, \quad b(\xi; p) = b_0(\xi) + p^{-1} b_1(\xi) + \cdots, \\ &\bar{c}(p) = c_0 + p^{-1} c_1 + \cdots \end{aligned} \tag{7}$$

At leading order we have

$$a_0(\xi) = 1 - \mathrm{e}^{-c_0\xi}, \quad b_0(\xi) = \mathrm{e}^{-c_0\xi/D}. \tag{8}$$

In (8) we have anticipated that a is small and $b \simeq 1$ in the reaction zone (to match with which we let $\xi \to 0$). At $O(p^{-1})$ we find

$$\begin{aligned} a_1(\xi) &= c_1 \xi\, \mathrm{e}^{-c_0\xi}, \\ b_1(\xi) &= \left(S_1 - \frac{c_1}{D}\xi\right) \mathrm{e}^{-c_0\xi/D} + \frac{D\bar{k}}{c_0^2 q(q-1)} \mathrm{e}^{-qc_0\xi/D}, \quad (q > 1) \\ &= \left[S_1 - \left(\frac{c_1}{D} + \frac{\bar{k}}{c_0}\right)\xi\right] \mathrm{e}^{-c_0\xi/D}, \quad (q = 1) \end{aligned} \tag{9}$$

for some constant S_1 to be determined.

We next consider the reaction zone, in which we leave y unscaled and write

$$a(y; p) = p^{-1} A(y; p), \quad b(y; p) = 1 - p^{-1} B(y; p) \tag{10}$$

and look for a solution by expanding

$$A(y; p) = A_0(y) + p^{-1} A_1(y) + \cdots, \quad B(y; p) = B_0(y) + p^{-1} B_1(y) + \cdots. \tag{11}$$

At leading order we obtain, on using (6, 7),

$$A_0'' - A_0 \mathrm{e}^{-B_0} = 0, \quad D B_0'' - A_0 \mathrm{e}^{-B_0} = 0, \tag{12}$$

where primes denote differentiation with respect to y. Eliminating the reaction terms gives $A_0'' = D B_0''$. If we now integrate twice and match with the solution in the diffusive region as $y \to \infty$, we obtain

$$A_0 = D(B_0 + T_0), \tag{13}$$

where

$$T_0 = D S_1 \quad \text{if } q = 1, \qquad T_0 = D S_1 + \frac{D^2 \bar{k}}{c_0^2 q (q-1)} \quad \text{if } q > 1. \tag{14}$$

Applying (13) in (12), integrating and matching with the diffusive region leads to

$$B_0'^2 = \frac{c_0^2}{D^2} - 2(B_0 + T_0 + 1)\mathrm{e}^{-B_0}. \tag{15}$$

Since $A_0 \to 0$ as $y \to -\infty$, $B_0 \to -T_0$. Expression (15) then gives

$$c_0^2 = 2D^2 \, \mathrm{e}^{T_0}, \tag{16}$$

where T_0 is given by (14).

We need to consider briefly the equations at $O(p^{-1})$. As above, we can eliminate the reaction terms and integrate once. Matching with the diffusive region then gives

$$A_1' + c_0 A_0 = D B_1' + c_0 B_0 - \frac{D\bar{k}}{c_0 q}, \quad \text{for } q \geq 1. \tag{17}$$

Equation 17 shows that

$$B_1 \sim \left(\frac{c_0 T_0}{D} + \frac{\bar{k}}{c_0 q} \right) y + \cdots \quad \text{as } y \to -\infty. \tag{18}$$

Finally we consider the decay region. Here $a \equiv 0$ (so that we can ignore the autocatalytic reaction) and we scale y by $Y = y p^{-2}$, leaving b unscaled. We look for a solution by expanding

$$b(Y; p) = b_0(Y) + b_1(Y) p^{-1} + \cdots \tag{19}$$

on $-\infty < Y < 0$. We find at leading order, using (7) and (10) to match with the reaction zone at leading order,

$$b_0(Y) = \mathrm{e}^{\bar{k} Y / c_0} \quad (q = 1), \; b_0(Y) = \frac{1}{\left(1 - \frac{\bar{k}(q-1)Y}{c_0}\right)^{1/(q-1)}} \quad (q > 1). \tag{20}$$

In (20), $b_0(Y) \to 0$ as $Y \to -\infty$ as required.

On matching at $O(Y)$ with the reaction zone, using (18), we find that

$$T_0 = -\frac{D\bar{k}(q+1)}{q c_0^2} \quad (q \geq 1). \tag{21}$$

Applying (21) in expression (16) gives the relation

$$c_0^2 = 2D^2 \exp\left(-\frac{D\bar{k}(q+1)}{q c_0^2} \right) \tag{22}$$

and it is expression (22) that determines the (leading-order) wave speed c_0 in terms of D and the decay parameter $\bar{k}$. We note that, if $\bar{k} = 0$, $c_0 = \sqrt{2} D$, or $c \sim \sqrt{2} D p^{-1} + \cdots$ for p large, in agreement with previous results. We can write (22) in the form

$$\bar{k} = \frac{q}{D(q+1)} \, c_0^2 \left(\log(2D^2) - \log(c_0^2) \right). \tag{23}$$

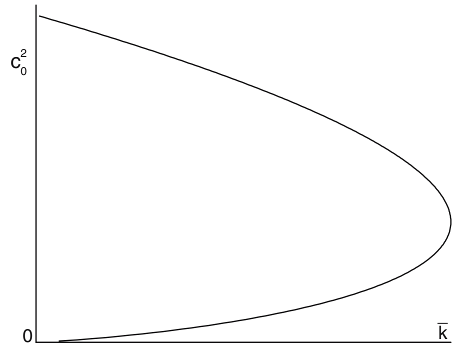

Fig. 1 A representative plot of c_0^2 against $\bar{k}$ obtained from expression (23) to show that there is a critical value $\bar{k}_{\mathrm{crit}}$ of $\bar{k}$ for the existence of solutions. The value of $\bar{k}_{\mathrm{crit}}$ is given in (24)

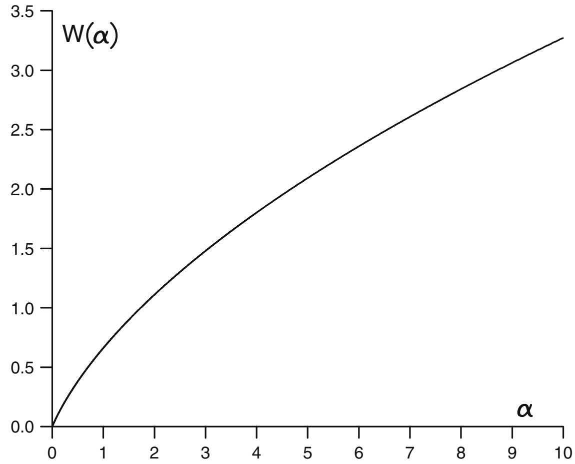

Fig. 2 A graph of $W(\alpha)$ obtained from the initial-value problem (40, 41)

If we now regard $\bar{k}$ as a function of c_0^2, we see that $\bar{k} \to 0^+$ as $c_0^2 \to 0$, $\bar{k} = 0$ at $c_0^2 = 2D^2$ and that $\bar{k}$ has a turning point (local maximum) at $c_0^2 = 2D^2\,\mathrm{e}^{-1}$, giving a critical value $\bar{k}_{\mathrm{crit}}$ of $\bar{k}$

$$\bar{k}_{\mathrm{crit}} = \frac{2qD\,\mathrm{e}^{-1}}{(q+1)}, \qquad \text{so that } k_{\mathrm{crit}} = \frac{2qD\,\mathrm{e}^{-1}}{(q+1)}\,p^{-3} + \cdots \quad \text{as} \quad p \to \infty. \tag{24}$$

A representative plot of c_0 against $\bar{k}$ obtained from (23) is shown in Fig. 1. The figure shows the existence of two solution branches for $\bar{k} < \bar{k}_{\mathrm{crit}}$ and a saddle-node bifurcation at $\bar{k} = \bar{k}_{\mathrm{crit}}$ and no solutions for $\bar{k} > \bar{k}_{\mathrm{crit}}$. This is the behaviour seen in [6] for $p = 2$, $q = 1$. For these values (and $D = 1$), expression (24) estimates $\bar{k}_{\mathrm{crit}} = 0.046$, only slightly less than the value of 0.0465 calculated in [6] by solving the travelling-wave equations (3–5). In [7] upper bounds on k_{crit} were obtained for the existence of a solution for general values of p and q. These gave $k_{\mathrm{crit}} < \mathrm{e}^{-1}p^{-1}$ (for $D = 1$) in the limit of large p and q of $O(1)$. This bound is considerably higher, of $O(p^{-1})$, than the result, of $O(p^{-3})$, provided by (24).

We next consider the case when q is large, of $O(p)$.

2.2 $\boldsymbol{q} \sim p \gg 1$

To deal with the case when $q \sim p \gg 1$, we put

$$q = q_0\,p, \quad \text{with } q_0 \text{ of } O(1) \text{ as } p \to \infty \tag{25}$$

and we still scale c and k by (6).

As above, we start in the diffusive region, with the same scaling $\xi = yp^{-1}$ for y and look for a solution by expanding as in (7). Now, since $b < 1$ in this region, both reaction terms can be neglected in the limit as $p \to \infty$. For this case, we note that $a_0(\xi)$ and $b_0(\xi)$ are still given by (8), $a_1(\xi)$ is as given in (9), but now

$$b_1(\xi) = \left(T_1 - \frac{c_1\xi}{D}\right)\mathrm{e}^{-c_0\xi/D} \tag{26}$$

for some constant T_1 to be found.

In the reaction zone, y is left unscaled (as before) and a and b are scaled as in (10), with a solution sought by expanding as in (11). At leading order we still obtain Eq. (12), from which we eliminate the reaction terms and integrate to obtain, on matching with the diffusive region,

$$A_0 = D(B_0 + T_1). \tag{27}$$

Applying this in (12) now gives

$$B_0'^{\,2} = \frac{c_0^2}{D^2} - 2(B_0 + T_1 + 1)\,\mathrm{e}^{-B_0}. \tag{28}$$

From (27), $B_0 \to -T_1$ as $y \to -\infty$, so that (28) gives

$$c_0^2 = 2D^2\,\mathrm{e}^{T_1} \tag{29}$$

analogous to (16). Since, with $\overline{k} > 0$, the wave speed is less than in the purely autocatalytic system (for which $c_0^2 = 2D^2$ [10,11]), we can expect T_1 to be negative. As above, we need to consider briefly the equations at $O(p^{-1})$. These give, following closely the argument given to derive Eq. 17,

$$A_1' + c_0 A_0 = D B_1' + c_0 B_0. \tag{30}$$

From (30) we find that

$$B_1 \sim \frac{c_0 T_1}{D}\, y + \cdots \quad \text{as} \quad y \to -\infty. \tag{31}$$

We finally consider the decay region which, since both reactions are small in this region, needs to be dealt with in a different way to that used previously. It is the solution in this region that determines T_1 and hence, from (29), the relationship between c_0 and $\overline{k}$. Before considering the solution in this region in detail, it is useful to consider how $b(y) \to 0$ at the rear of the wave. Thinking particularly of the situation $q \sim p \gg 1$, the main balance as $y \to -\infty$ in Eq. 4 is $cb' - kb^q \simeq 0$, giving $b \simeq \left((q-1)\frac{k}{c}\,|y|\right)^{-1/(q-1)}$. We can express this, using the scalings for $c,\ k$ and q in (6, 7) and (25), as

$$b \sim \left(q_0 \frac{\overline{k}}{c_0}\, \frac{|y|}{p}\right)^{-1/q_0 p} \qquad \text{as} \quad y \to -\infty, \quad p \ \text{ large}. \tag{32}$$

Expression (32) gives an insight into the nature of the solution in the decay region and suggests that, for this region, we write

$$b = \exp\left(p^{-1}\psi(\eta; p)\right), \quad \text{where} \quad \eta = y p^{-1}. \tag{33}$$

Note that this region has a scaling different to the previous case, now having a thickness of $O(p)$.

If we substitute (33) in (4) and then look for a solution by expanding in inverse powers of p, we find that the leading-order term $\psi_0(\eta)$ satisfies the equation

$$D\psi_0'' + c_0\psi_0' - \overline{k}\,\mathrm{e}^{q_0\psi_0} = 0 \quad (-\infty < \eta < 0), \tag{34}$$

where primes now denote differentiation with respect to η, subject to, on matching with the reaction zone,

$$\psi_0(\eta) \sim T_1\left(1 - \frac{c_0}{D}\,\eta \cdots\right) \quad \text{as} \quad \eta \to 0^- \tag{35}$$

with T_1 and c_0 related by (29). We note that, from Eq. 34,

$$\psi_0(\eta) \sim -\frac{1}{q_0}\log\left(\frac{q_0\overline{k}}{c_0}\,|\eta|\right) \quad \text{as} \quad \eta \to -\infty \tag{36}$$

which, on using (33), gives the form for b in (32).

We can convert the problem given by (34–36) into an initial-value problem. It is, perhaps, easier to deal with if we first transform from $-\infty < \eta < 0$ to $0 < \overline{\eta} < \infty$ by making the transformation $\overline{\eta} = -\frac{c_0}{D}\,\eta$. We then put $\psi_0 = T_1 - q_0^{-1}\,u(\overline{\eta})$. This results in the problem

$$\begin{aligned} &u'' - u' + \alpha\,\mathrm{e}^{-u} = 0 \quad \text{on} \quad 0 < \overline{\eta} < \infty, \\ &u \sim -q_0 T_1\,\overline{\eta} + \cdots \quad \text{as} \quad \overline{\eta} \to 0^+, \\ &u \sim \log\left(\frac{q_0\overline{k}D}{2D}\,\overline{\eta}\right) + (q_0 - 1)T_1 \quad \text{as} \quad \overline{\eta} \to \infty, \end{aligned} \tag{37}$$

where primes now denote differentiation with respect to $\overline{\eta}$, and where

$$\alpha = \frac{q_0\overline{k}}{2D}\,\mathrm{e}^{(q_0-1)T_1}, \tag{38}$$

on using expression (29). We next write Eq. 37_a in phase plane variables (u, w), where $w \equiv u'$, to obtain

$$\frac{\mathrm{d}w}{\mathrm{d}u} = \frac{(w - \alpha\,\mathrm{e}^{-u})}{w} \quad (0 < u < \infty). \tag{39}$$

Finally, we make the change of independent variable $x = \alpha\,\mathrm{e}^{-u}$ in (39). This results in the equation

$$\frac{\mathrm{d}w}{\mathrm{d}x} = \frac{x - w}{xw} \quad (x > 0). \tag{40}$$

Now, as $\overline{\eta} \to \infty$, $u \to \infty$ corresponding to $x \to 0$, and, for x small, expression $(37)_c$ and Eq. 40 give

$$w \sim x - x^2 + 3x^3 + \cdots \quad \text{as } x \to 0. \tag{41}$$

To proceed, we solve (40) numerically as an initial-value problem, starting with (41), for increasing values of x, giving the solution $w(x)$. Now, $\overline{\eta} \to 0$ corresponds to $u \to 0$ and hence to $x = \alpha$. Thus, in effect, we have calculated $w = W(\alpha)$ for increasing α. A graph of $W(\alpha)$ calculated in this way is shown in Fig. 2. However, as $\overline{\eta} \to 0$, $w \to -q_0T_1$, from $(37)_b$, so that

$$T_1 = -\frac{W(\alpha)}{q_0}. \tag{42}$$

Figure 2 suggests that $W'(\alpha) > 0$ and, in fact we can show that

$$W(\alpha) > 0, \quad W'(\alpha) > 0 \qquad \text{for all } \alpha > 0. \tag{43}$$

Proof Clearly from (41), $w(x) > 0$ and hence $W(\alpha) > 0$ for x or α sufficiently small. To establish the result that $w(x) > 0$ for all (positive) x, we assume that there is an $x_1 > 0$ at which $w(x_1) = 0$. Hence there must be some $0 < x_0 < x_1$ at which

$$w(x_0) > 0, \quad w'(x_0) = 0, \quad w''(x_0) \leq 0. \tag{44}$$

Equation 40 gives, at $x = x_0$, $w''(x_0) = x_0^{-2} > 0$, leading to a contradiction with (44) and hence $w(x) > 0$ for all $x > 0$. The right-hand side of (40) is then bounded and thus has a solution for all $x > 0$. Now $w'(x)$ can be zero only at discrete values of x. Suppose $x = x_0 > 0$ is the smallest of these. Then, since $w'(0) > 0$ from (41), $w(x_0)$ satisfies the conditions in (44), with again $w''(x_0) = x_0^{-2} > 0$ contradicting (44). This establishes the result that $w'(x) > 0$ for all $x > 0$, and thus gives (43). □

Equation 40 gives

$$w(x) \sim x^{1/2}\left(\sqrt{2} - 2x^{-1/2} + \cdots\right) \quad \text{as } x \to \infty, \tag{45}$$

so that $W(\alpha) \sim \sqrt{2\alpha}$ for α large.

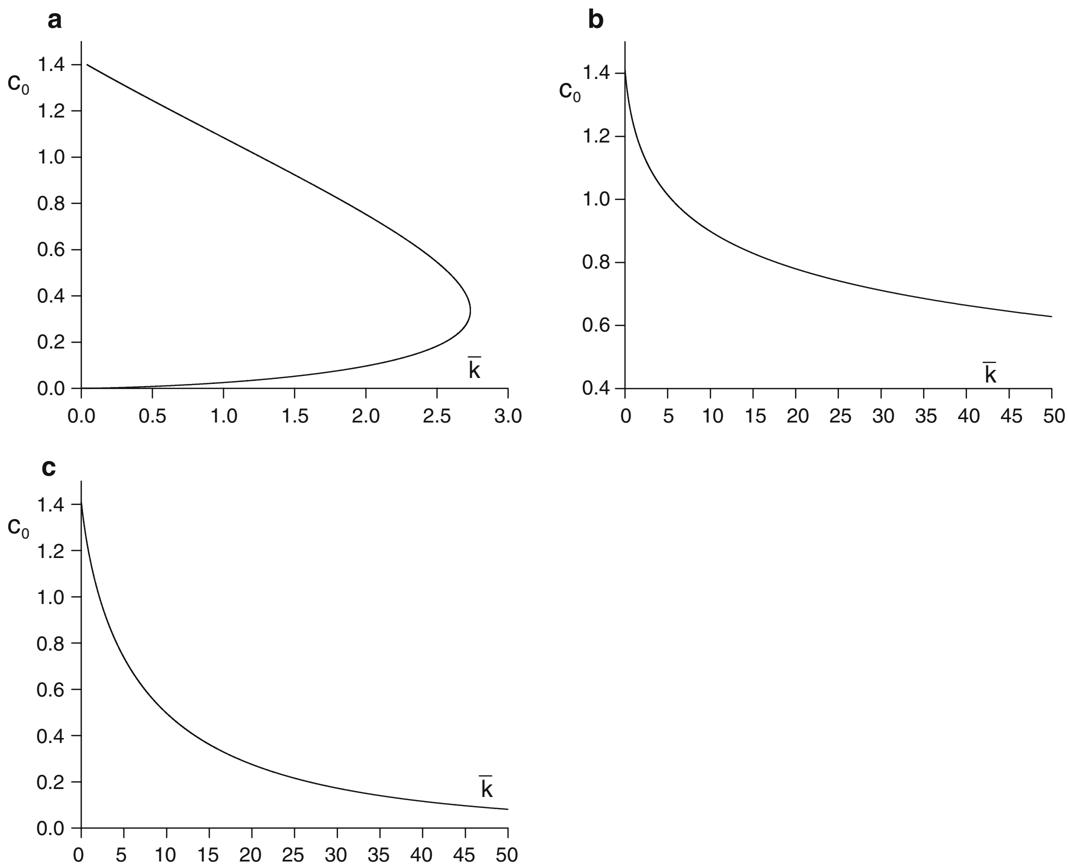

Fig. 3 Plots of c_0 against $\bar{k}$ obtained from expressions (46) with $D = 1.0$ for (**a**) $q_0 = 0.5$, showing a critical value (upper bound) on $\bar{k}$ for the existence of a solution, (**b**) $q_0 = 1.0$ and (**c**) $q_0 = 2.0$, the curves being monotone decreasing with solutions for all $\bar{k} \geq 0$

From expressions (38) and (42)

$$\bar{k} = \frac{2D\alpha}{q_0} \exp\left[\frac{(q_0 - 1)}{q_0}\, W(\alpha)\right], \quad c_0^2 = 2D^2 \exp\left[-W(\alpha)/q_0\right] \tag{46}$$

so that a saddle-node bifurcation, i.e., a critical value for $\bar{k}$, occurs where $\mathrm{d}\bar{k}/\mathrm{d}\alpha = 0$, that is, where

$$1 + \frac{(q_0 - 1)}{q_0}\, \alpha\, W'(\alpha) = 0. \tag{47}$$

Since, from (43), $W'(\alpha) > 0$, expression (47) shows that a critical value for $\bar{k}$ requires $q_0 < 1$ (or $q < p$). For $q_0 \geq 1$ (or $q \geq p$), the graph $\bar{k}$ against α, and hence against c_0, is monotone.

We can use expression (46) to obtain plots of c_0 against $\bar{k}$ for given values of q_0 and D. Having determined $W(\alpha)$ by solving the initial-value problem (40, 41) for a given value of α, we apply this in (46) to obtain both c_0 and $\bar{k}$ for that value of α. By doing this for increasing values of α we obtain ranges of values for c_0 and $\bar{k}$, which we can then plot. Typical examples (all with $D = 1.0$) are shown in Fig. 3 for $q_0 = 0.5$ (Fig. 3a), showing the existence of a critical value of $\bar{k}_{\text{crit}} \simeq 2.735$ for $\bar{k}$ with two solution branches for $\bar{k} < \bar{k}_{\text{crit}}$, and for $q_0 = 1.0$ and $q_0 = 2.0$ (Fig. 3b, c), where the curves are monotone decreasing.

For α small, (41) has $W(\alpha) \simeq \alpha$ with (46) then giving

$$\bar{k} = \frac{2D}{q_0}\, \alpha + \cdots, \quad c_0^2 = 2D^2 \left(1 - \frac{\alpha}{q_0} + \cdots\right).$$

Eliminating α shows that

$$c_0 = \sqrt{2}D\left(1 - \frac{\bar{k}}{4D} + \cdots\right) \quad \text{for } \bar{k} \text{ small.} \tag{48}$$

Expression (48) gives the behaviour of c_0 for $\bar{k}$ small, on the upper solution branch when $q_0 < 1$. This linear behaviour can clearly be seen in Fig. 3a. For α large, $W(\alpha) \sim \sqrt{2}\,\alpha^{1/2} + \cdots$, so that

$$c_0^2 \sim 2D^2 \exp\left(-\frac{\sqrt{2}\alpha^{1/2}}{q_0}\right), \quad \bar{k} \sim \frac{2D\alpha}{q_0} \exp\left(\frac{(q_0 - 1)\sqrt{2}\alpha^{1/2}}{q_0}\right).$$

Eliminating α then gives

$$\bar{k} \sim Dq_0 \left[\log(2D^2) - \log(c_0^2)\right]^2 \left(\frac{2D^2}{c_0^2}\right)^{q_0 - 1} \quad (q_0 \neq 1). \tag{49}$$

Expression (49) shows the nature of the lower branch solution for $q_0 < 1$, with $c_0 \to 0$, $\bar{k} \to 0$ and, for $q_0 > 1$, shows how $c_0 \to 0$ as $\bar{k} \to \infty$. Note that, for $q_0 = 1$,

$$c_0^2 \sim 2D^2 \exp\left[-\left(\frac{\bar{k}}{D}\right)^{1/2}\right], \quad \text{for } \bar{k} \text{ large.} \tag{50}$$

The more rapid decrease of c_0 with $\bar{k}$, given by (50), for $q_0 = 1$ compared to the much slower decrease with $\bar{k}$, given by (49), can be seen by comparing Fig. 3b, and c.

We can also use expressions (46) to calculate the critical values of $\bar{k}$. From Eq. 40 and expression (47), the critical value occurs at $\alpha = \alpha_c$ when $W(\alpha_c) = \alpha_c(1 - q_0)$, with α_c being determined from the numerical solution of Eq. 40. Then, $\bar{k}_{\text{crit}}$ and the corresponding $c_{0,\text{crit}}$ can be calculated from

$$\bar{k}_{\text{crit}} = \frac{2D}{q_0}\alpha_c \exp\left[-\frac{(1 - q_0)^2}{q_0}\,\alpha_c\right], \quad c_{0,\text{crit}}^2 = 2D^2 \exp\left[-\frac{(1 - q_0)}{q_0}\,\alpha_c\right]. \tag{51}$$

A graph of $\bar{k}_{\text{crit}}$ against q_0 is shown in Fig. 4a (for $D = 1.0$), with the corresponding values of $c_{0,\text{crit}}$ shown in Fig. 4b. For q_0 small, α_c will be small, with from (41) $\alpha_c - \alpha_c^2 \simeq \alpha_c(1 - q_0)$, giving $\alpha_c \simeq q_0$. Expressions (51) then give $\bar{k}_{\text{crit}} \simeq 2D\,\mathrm{e}^{-1}$ in agreement with (24). For $q_0 \simeq 1$, α_c will be large, $W(\alpha_c) \simeq \sqrt{2}\,\alpha_c^{1/2}$, giving $\alpha_c \simeq 2/(1 - q_0)^2$ and

$$\bar{k}_{\text{crit}} \sim \frac{4D}{(1 - q_0)^2}\,\mathrm{e}^{-2}, \quad c_{0,\text{crit}}^2 \sim 2D^2\,\mathrm{e}^{-2/(1 - q_0)} \quad \text{for } 0 < (1 - q_0) \ll 1. \tag{52}$$

Expression (52) shows how $\bar{k}_{\text{crit}}$ becomes large, with the corresponding $c_{0,\text{crit}}$ becoming small, as $q_0 \to 1$ from below. Expression (52) for $\bar{k}_{\text{crit}}$ is shown by the broken line in Fig. 4a.

3 Discussion and conclusions

We have considered the effects that a decay or termination step (2) can have on a travelling wave arising from the autocatalytic reaction (1) for high orders of autocatalysis, $p \gg 1$. We treated two cases, namely when the decay step q is of $O(1)$ and when q is large, of $O(p)$. In the first case we found that the decay step always has a major influence and limits the existence of travelling waves to a finite range of k (a measure of the strength of the decay rate) to $0 \leq k \leq k_{\text{crit}}$. There is a saddle-node bifurcation at $k = k_{\text{crit}}$, with two solution branches for $0 < k < k_{\text{crit}}$ and no solutions for $k > k_{\text{crit}}$. We gave an estimate (24) for k_{crit}, which showed that k_{crit} was very small, of $O(p^{-3})$, for p large. The previous upper bounds on k_{crit} given in [7] are somewhat of an overestimate, being of $O(p^{-1})$ for p large, over those obtained from our large p analysis. Thus, for high values of p, the effect of the termination step (2) is to severely limit the range of existence of travelling-wave solutions.

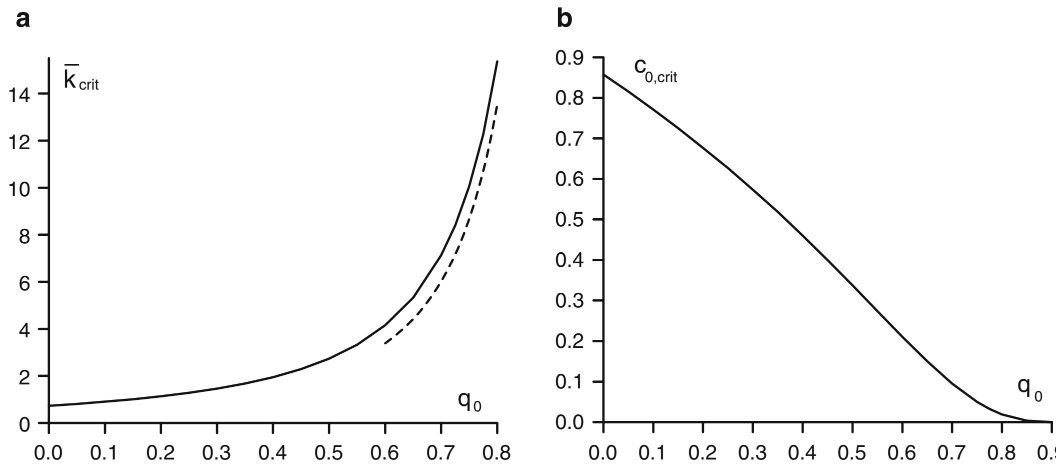

Fig. 4 Plots of (**a**) $\overline{k}_{crit}$ and (**b**) $c_{0,crit}$ against q_0 for $D = 1.0$, obtained from expression (51). Expression (52) for $\overline{k}_{crit}$ is shown by the broken line

When the decay and autocatalyst orders are comparable, $q \sim p \gg 1$, we found two possibilities. For $q < p$ the situation is analogous to the previous case, with there being a critical value k_{crit} for k and travelling-wave solutions only for $0 \le k \le k_{crit}$ (Fig. 3a). The values of k_{crit} depend on q (more precisely on q_0 where $q_0 = q/p$) (see Fig. 4a), with the values of k_{crit} become large as $q \to p$ (or $q_0 \to 1$). Our analysis gives

$$k_{crit} \sim \frac{4e^{-1}}{(p-q)^2 p} \quad \text{for} \quad p \gg 1, \ (p-q) \ll 1. \tag{53}$$

For $q > p$ (or $q_0 > 1$) there is no restriction on k for the existence of a travelling wave (Fig. 3c).

When $q = p$ (or $q_0 = 1$) there is a transition from having a restriction on $k (q < p)$ to having no restriction $(q > p)$ for the existence of a solution. Our analysis suggests that travelling waves exist when $p = q$ for all k (Fig. 3b), at least in the limit as $p \to \infty$. This result is contrary to what is seen when $p = q = 1$ [6] and when $p = q = 2$ [9]. A possible explanation for this difference could arise in the argument given in [6,9] to establish the necessary condition $k < 1$. This argument puts $a = 1 - \overline{a}$ in Eq. 4, then integrating results in, with $p = q$,

$$(1-k)\int_{-\infty}^{\infty} b^p \, dy = \int_{-\infty}^{\infty} \overline{a}\, b^p \, dy > 0. \tag{54}$$

Since both integrals in (54) are strictly positive, having $k > 1$ is then required. However, in the large-p limit, the integral on the left-hand side of (54) does not exist since $b \sim (-y)^{-1/p}$ as $y \to -\infty$, see expression (32), and so invalidates the above argument. The question still remains as to whether solutions exist when $p = q$ only in the limit as $p \to \infty$ or whether there is some finite (large) value of p where solutions can exist when $k = 1$.

The basic structure of the travelling wave for p large is a thin reaction zone, where the autocatalytic reaction (1) is the dominant mechanism, and a much thicker decay or termination region, where the decay step (2) is dominant. This is also the structure of the travelling wave in general when k is small. To obtain a solution of (3–5) valid for $k \ll 1$, we expand

$$a(y;k) = a_0(y) + k\, a_1(y) + \cdots, \quad b(y;k) = b_0(y) + k\, b_1(y) + \cdots \quad c(k) = c_0 + k\, c_1 + \cdots. \tag{55}$$

At leading order we obtain the travelling-wave equations for the autocatalytic reaction

$$a_0'' + c_0 a_0' - a_0 b_0^p = 0, \quad D b_0'' + c_0 b_0' + a_0 b_0^p = 0, \tag{56}$$

subject to the boundary conditions

$$a_0 \to 1, \ b_0 \to 0 \quad \text{as} \quad y \to \infty, \qquad a_0 \to 0, \ b_0 \to 1 \quad \text{as} \quad y \to -\infty, \tag{57}$$

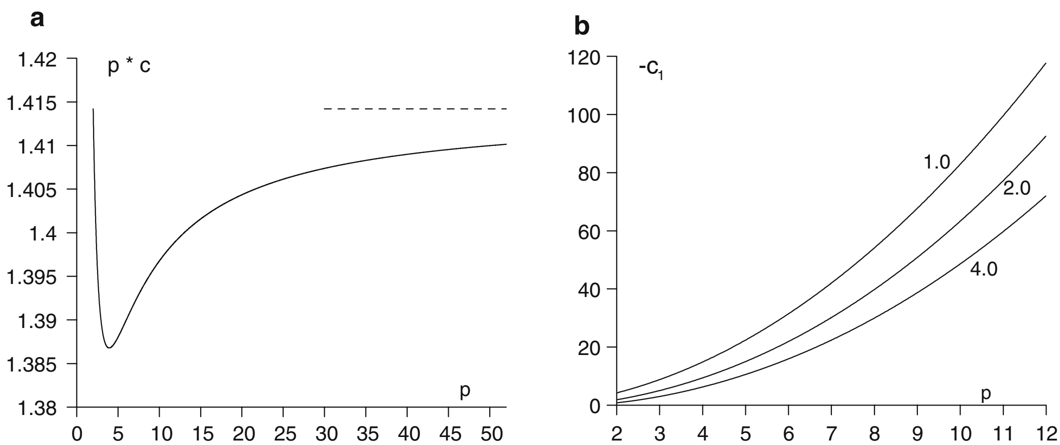

Fig. 5 (**a**) Plot of $p\,c_0$ against p for $D = 1.0$ obtained from Eqs. (56, 57). The asymptotic limit $p\,c_0 \to \sqrt{2}$ as $p \to \infty$ is shown by the broken line. (**b**) Plots of $-c_1$ against p for different values of q obtained from the compatibility condition (64). $c \simeq c_0 + c_1 k$ for k small

where primes again denote differentiation with respect to y. Boundary conditions (57) show the singular nature of the solution as $k \to 0$, since we really require $b \to 0$ as $y \to -\infty$, as given in (5), when $k > 0$. This condition is not allowable from equations (56). A plot of c_0 against p for $D = 1.0$ is given in [5]. In Fig. 5a values of $p\,c_0$ are plotted against p (again for $D = 1.0$) obtained from a numerical integration of (56, 57). The asymptotic limit of $p\,c_0 \to \sqrt{2}$ as $p \to \infty$ is shown by the broken line. Figure 5a shows that this asymptotic limit is approached only relatively slowly as p increases.

At $O(k)$ we have

$$a_1'' + c_0 a_1' - (b_0^p a_1 + p a_0 b_0^{p-1} b_1) = -c_1 a_0',$$

$$Db_1'' + c_0 b_1' + (b_0^p a_1 + p a_0 b_0^{p-1} b_1) = -c_1 b_0' + b_0^q. \tag{58}$$

Equations (58) show that $b_1 \sim y/c_0$ as $y \to -\infty$. Hence

$$b \sim 1 + \frac{ky}{c_0} + \cdots, \quad a \to 0, \quad \text{as } y \to -\infty. \tag{59}$$

Expressions (59) lead to an outer (decay) region of thickness $O(k^{-1})$ in which we put $Y = ky$. The leading-order problem in this region on $-\infty < Y < 0$ is, still with $p = q$,

$$c_0 b' - b^q = 0, \quad b \sim 1 + \frac{ky}{c_0} + \cdots \text{ as } Y \to 0^-, \quad b \to 0 \text{ as } Y \to -\infty. \tag{60}$$

The required solution is, following (19),

$$b = \mathrm{e}^{Y/c_0} \quad (q = 1), \qquad b = \left(1 - \frac{(q-1)Y}{c_0}\right)^{-1/(q-1)} \quad (q > 1). \tag{61}$$

The structure of this outer region depends on the ratio of diffusion coefficients D only through the leading-order wave speed c_0.

To calculate c_1 we need to consider (58). Now the equations in (58) have a complementary function (a_0', b_0') which satisfies homogeneous boundary conditions. Hence a compatibility condition is required for the non-homogeneous problem (58) and this will determine c_1. To derive this condition we require the adjoint problem for $U(y)$, $V(y)$ given in [18], namely

$$\frac{\mathrm{d}}{\mathrm{d}y}\left(\mathrm{e}^{c_0 y} U'\right) - b_0^p \mathrm{e}^{c_0 y}(U - V) = 0,$$

$$\frac{\mathrm{d}}{\mathrm{d}y}\left(\mathrm{e}^{c_0 y} V'\right) - p a_0 b_0^{p-1} \mathrm{e}^{c_0 y}(U - V) = 0, \tag{62}$$

on limiting attention to the case $D = 1$ for simplicity, subject to

$$U, V \to 0 \;\text{ as }\; y \to \pm\infty. \tag{63}$$

Applying (62, 63) in (58) then leads to the compatibility condition

$$c_1 \int_{-\infty}^{\infty} \mathrm{e}^{c_0 y}(a_0' U + b_0' V)\mathrm{d}y = \int_{-\infty}^{\infty} \mathrm{e}^{c_0 y}\, b_0^q\, V \mathrm{d}y = 0. \tag{64}$$

It is from condition (64) that we determine c_1. The adjoint problem (62, 63) has to be solved numerically, with (64) then being used to calculate c_1. Graphs of $-c_1$ against p are shown in Fig. 5b for $q = 1, 2, 4$. The graphs show that $-c_1$ increases as p is increased (for a given value of q) and that $-c_1$ decreases as q is increased (for a given value of p). We recall that $c \simeq c_0(p) + kc_1(p, q)$ for k small and that c_0 decreases as p is increased. This suggests that the range of existence of a solution (requiring $c > 0$) will decrease as p is increased and that this range of existence might be larger for a given value of p if q is increased. These conclusions are fully in line with the results from our large p analysis, see Fig. 4a for example.

References

1. Billingham J, Needham DJ (1991) The development of travelling waves in quadratic and cubic autocatalysis with unequal diffusion rates. I. Permanent form travelling waves. Phil Trans R Soc Lond A334:1–24
2. Billingham J, Needham DJ (1991) A note on the properties of a family of travelling-wave solutions arising in cubic autocatalysis. Dyn Stabil Syst 6:33–49
3. Needham DJ, Merkin JH (1992) The effects of geometrical spreading in two and three dimensions on the formation of travelling wavefronts in a simple, isothermal chemical system. Nonlinearity 5:413–452
4. Billingham J, Needham DJ (1992) The development of travelling waves in quadratic and cubic autocatalysis with unequal diffusion rates. I. Large time development in quadratic autocatalysis. Quart Appl Math 50:343–372
5. Merkin JH, Needham DJ (1993) Reaction-diffusion waves in an isothermal chemical system with general orders of autocatalysis and spatial dimension. Z Angew Math Phys (ZAMP) 44:707–721
6. Merkin JH, Needham DJ, Scott SK (1989) The development of travelling waves in a simple isothermal chemical system I. Quadratic autocatalysis with linear decay. Proc R Soc Lond A 424:187–209
7. Needham DJ, Merkin JH (1991) The development of travelling waves in a simple isothermal chemical system with general orders of autocatalysis and decay. Phil Trans R Soc Lond A337:261–274
8. Merkin JH, Needham DJ (1991) The development of travelling waves in a simple isothermal chemical system IV. Quadratic autocatalysis with quadratic decay. Proc R Soc Lond A434:531–554
9. Merkin JH, Needham DJ (1990) The development of travelling waves in a simple isothermal chemical system II. Cubic autocatalysis with quadratic and linear decay. Proc R Soc Lond A430:315–345
10. Metcalf MJ, Merkin JH, Scott SK (1994) Oscillating wave fronts in isothermal chemical systems with arbitrary powers of autocatalysis. Proc R Soc Lond A447:155–174
11. Balmforth NJ, Craster RV, Malham SJA (1999) Unsteady fronts in an autocatalytic system. Proc R Soc Lond A455:1401–1433
12. Buckmaster J (1976) The quenching of deflagration waves. Combust Flame 26:151–162
13. Simon PL, Kalliadasis S, Merkin JH, Scott SK (2003) Inhibition of flame propagation by an endothermic reaction. IMA J Appl Math 68:537–562
14. Lazarovici A, Kalliadasis S, Merkin JH, Scott SK (2002) Flame quenching through endothermic reaction. J Eng Math 44:207–228
15. Jakab E, Horváth D, Merkin JH, Scott SK, Simon PL, Tóth A (2002) Isothermal flame balls. Phys Rev E 66:016207-1–8
16. Jakab E, Horváth D, Merkin JH, Scott SK, Simon PL, Tóth A (2003) Isothermal flame balls: effects of autocatalyst decay. Phys Rev E 68:036210-1–9
17. Leach JA, Needham DJ (2003) Matched asymptotic expansions in reaction-diffusion theory. Springer Monographs in Mathematics
18. Merkin JH (2005) The effect of an electric field on reaction fronts in autocatalytic systems. J Math Chem 38:657–670