Effect of chemically active additives on the velocity of detonation waves and on the limit of gaseous detonation

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A one-dimensional model of gaseous detonation waves with heat energy losses was used to explain the narrowing of detonation limits in the presence of small amounts of efficient inhibitors by the example of hydrogen oxidation, and it was found that chemical energy losses due to chain termination should be taken into account along with heat and friction energy losses.

The distinction between two regimes of gaseous combustion (deflagration and detonation) is that the chemical energy of a metastable mixture in deflagration (subsonic combustion) is transformed into thermal and kinetic energies of expanding reaction products, whereas in detonation (a supersonic mode of combustion, in which the wave travels at a velocity of thousands of meters per second) a part of chemical energy is converted into the energy of compression of the reaction products (shock wave). The suppression of gaseous detonation is of practical importance. Physical methods like detonation arresters are insufficiently effective.[1] It was found[2] that small amounts of gaseous inhibitors lead to the marked narrowing of the detonation limits. As a rule, gaseous detonation is caused by branching chain processes (BCP) of fuels oxidation. Thus, the properties of BCP will strongly determine the velocity of a detonation wave (DW) and detonation limits.[2,3] However, the majority of studies (*e.g.*, refs. 4, 5) dealt with physical aspects of DW propagation, and the kinetics of a chemical reaction was represented by the Arrhenius equation. This is not true in BCP.[3,6] It is evident that the strong narrowing of detonation, which was observed[2] in the presence of ~2% inhibitor, cannot be explained on the basis of the one-step Arrhenius kinetics. It was also found[7] that $C_2F_4Br_2$ additives (up to 30% of H_2) decrease the detonability of 29.5% H_2 + air mixtures, although the additive content is too high to have only chemical nature. An effort was made[8] to describe detonation limits using a one-dimensional theory applied to a detailed mechanism of H_2 oxidation. However, a numerical simulation involving a wide variety of elementary steps did not reveal the determining chemical factors. For example,[8] the important role of the termolecular reaction $H + O_2 + M$ was specified. However, the rate constants for $M = Ar$, He and N_2 were taken to be equal, though this is not the case.[9]

The aim of this work was to explain the effect of small amounts of effective inhibitors on the DW velocity and on the detonation limits on the basis of the Zel'dovich–von Neumann–Doring one-dimensional DW model taking into account the kinetics of BCP. This consideration corresponds to the test conditions of initiating detonation in a mixture by a shock wave or another detonation wave.[7,10]

The consideration of chain termination *via* an inhibitor and the neglect of heat and friction energy losses (henceforth, losses) seemingly give rise to the classical DW velocity without losses:[10]

$$D_0^2 = (k^2 - 1)Q \tag{1}$$

where D_0 is the DW velocity without losses; $k = C_p/C_v$ is the ratio between the heat capacities at constant pressure and volume, respectively; Q is the specific heat. Because chain termination *via* an inhibitor causes a decrease in the reaction rate and, evidently, a decrease in the heat released, an increase in the inhibitor concentration leads to D_0 arbitrarily close to the sonic speed. However, the experimentally observed DW velocity at the limit is supersonic.[2,7] It means that the DW propagation with losses should be taken into account. Therefore, a one-dimensional DW model with heat losses is examined. The kinetics of a chemical reaction is represented by the simple oxidation of H_2.[11] We will follow the consideration.[10]

The gas-dynamic equations of mass, impulse and energy conservation, respectively, with heat losses take the forms:

$$\begin{aligned} &D/v_0 = (D - w)/v;\\ &p - p_0 = -D^2(v - v_0)/v_0^2;\\ &H - H_0 + 0.5(p - p_0)(v_0 + v) = -\int M\mathrm{d}x, \end{aligned} \tag{2}$$

where v is the specific volume, $D - w$ is the DW velocity in the coordinate system associated with the leading front of DW, p is the pressure, H is the enthalpy behind the DW front, M is a function that describes heat losses, x is a coordinate, and the subscripts '0' indicate the initial state. Note that a consideration of only heat losses leads to a linear relationship between p and v. This simplifies the following treatment and makes it more illustrative because the problem can be solved in an implicit form. Separating the chemical part of enthalpy $H = k/(k - 1)pv + \beta Q$, where β is the fraction of an unreacted component (fuel or oxidant), taking k ahead of and back of the DW front to be equal, and neglecting both the temperature dependence of Cp and the initial pressure p_0, we can transform equation (2) to the differential form (see ref. 10):

$$R[\mathrm{d}T'(x)/\mathrm{d}x] = \frac{Q(k - 1)[v_0 - 2v(x)](\psi - M/Q)}{k[v_1 - v(x)]} \tag{3}$$

where $v_1 = k/(k + 1)/v_0$, $T'(x)$ is the temperature, R is the gas constant, and ψ is the rate of chemical reaction with the opposite sign. Considering the origin of the coordinates just beyond the front of a shock wave and taking the corresponding initial values $v = (k - 1)/(k + 1)v_0$ and $\beta = 1$ at this point, we examine the behaviour of $T'(x)$ in the immediate vicinity of the front for $v(x) = (k - 1)/(k + 1)v_0$.

First, the rate of BCP is calculated. On the basis of a simple mechanism of H_2 oxidation in stoichiometric and rich mixtures with no regard for the reactions of termolecular chain break and chain origination, we have:[11]

$$\begin{aligned} &\mathrm{d}n(t)/\mathrm{d}t = n(t)\{2k_2[O_2]_t[O_2]_0 - k_1[\mathrm{inh}]\},\\ &\mathrm{d}[O_2]_t/\mathrm{d}t = -k_2n(t)[O_2]_t[O_2]_0 \end{aligned}$$

where $n(t)$, $[O_2]_t$ are the concentrations of H atoms and O_2 molecules, related to the initial concentration of O_2 $[O_2]_0$, [inh] is the concentration of the inhibitor of the same dimension as $[O_2]_0$; k_1, k_2 are the rate constants of elementary reactions of H with inhibitor and O_2, respectively. Thus, the chain termination *via* an inhibitor is considered to be most rapid. Next, the consumption of the inhibitor is ignored. We divide the first equation by the second, eliminating t, and denote by definition $[O_2]_t = \beta$. The subsequent integration results in

$$n(\beta) = 2(1 - \beta) + k_1[\mathrm{inh}]\ln(\beta)/(k_2[O_2]_0) \tag{4}$$

The rate of consumption of O_2 is $W = -k_2\beta[O_2]_0n(\beta)$. Using equation (4) (the temperature dependence of k_1 is ignored because the activation energies of reactions of H atoms with, *e.g.*, halogenated compounds as inhibitors, are much lower than E[2]), considering $\ln(\beta) = -(1 - \beta)$, and replacing $[O_2]_0$ by P, we obtain:

$$W = -2\beta(1 - \beta)(\mathrm{e}^{-E/RT} - k_1[\mathrm{inh}]/2k_0P) \tag{5}$$

Substitution of (5) into (3) gives

$$R[\mathrm{d}T'(x)/\mathrm{d}x] = \\ = \frac{Q(k-1)[v_o - \dfrac{2(k-1)v_0}{k+1}]\{2\beta(1-\beta)[\mathrm{e}^{-E/RT'(x)} - \dfrac{k_1[\mathrm{inh}]}{k_0P}] - \dfrac{M}{Q}\}}{k\,\dfrac{kv_0 - (\mathrm{k}-1)v_0}{k+1}} \quad (6)$$

We examine the behaviour of W in the immediate vicinity of the front of a shock wave, where only a small fraction of components reacts. The factor $\mathrm{e}^{-E/RT'(x)}$ changes the most rapidly. This change is an order of magnitude, when $T'(x)$ increases by a small quantity, as compared with T_0, at the front of the shock wave. Thus, we expand the exponent in the series: $E/RT'(x) = = E/RT_0 - E[T'(x) - T_0]/RT_0^2$ in (6), assuming $T'(x) - T_0 = T(x)$, $\delta = \beta(1-\beta)$ and $f_0 = \mathrm{e}^{-E/RT_0}$ equation (6) takes the form

$$R\,\frac{\mathrm{d}T(x)}{\mathrm{d}x} = k^{-1}(k-1)(3-k)(2f_0Q\delta\,\mathrm{e}^{ET(x)/RT_0^2} - \delta Q\frac{k_1[\mathrm{inh}]}{k_0P} - M) \quad (7)$$

Equation (7) is integrated by changing variables $T(x) = \ln[t(x)]RT_0^2/E$:

$$R^2T_0^2\frac{\mathrm{d}t(x)}{\mathrm{d}x}\,\frac{1}{t(x)E} = \frac{(k-1)(3-k)\{2f_o\delta t(x)Qk_0P - \delta Qk_1[\mathrm{inh}] - Mk_0P\}}{kk_0P} \quad (8)$$

Equation (8) shows that, as distinct from the classical treatment,[10] the new term responsible for chemical energy losses $\delta Qk_1[\mathrm{inh}]/(k_0P)$ occurs along with heat losses. Let $H = \delta Qk_1[\mathrm{inh}]/(k_0P) + \mathrm{M}$ be the sum of chemical and heat losses. Upon integrating (8) in view of $t(0) = 1$, we obtain:

$$\mathrm{e}^{ET(x)/RT_0^2} = \frac{1}{2f_0\delta\dfrac{Q}{H} - (2f_0\delta\dfrac{Q}{H} - 1)\mathrm{e}^{\alpha}} \quad (9)$$

$$\alpha = -\frac{EH(k^2 - 4k + 3)x}{R^2T_0^2k}$$

According to ref. 10, the following inequality asserts the occurrence of a detonation regime (the heat-loss rate must be lower than the heat-production rate):

$$\frac{H}{2f_0\delta Q} < 1 \text{ or } \left(\frac{\delta Qk_1[\mathrm{inh}]}{k_0P} + M\right)\frac{1}{2f_0\delta Q} < 1 \quad (10)$$

The set of equations (2) can be easily transformed to the following form[10]

$$h(v_1,D) = Q(1-\beta_{00}) - \int_0^{x_1} H(x)\mathrm{d}x \quad (11)$$

where $h(v_1,D) = D^2/2(k^2-1)$ is the function that governs detonation without losses [see equation (1)], $H(x)$ describes the sum of chemical and heat losses; in this case, $v(x) = v_1$ at the point x_1; heat-production and heat-loss rates are equal; β_{00} is the fraction of the unreacted component at this point. Note that it is the point of tangency of the Hugoniot curve and the Rayleigh–Mikhelson line; equation (1) takes place at this point. Moreover, the simultaneous equality of the numerator and denominator of equation (3) to zero at this point is a necessary condition for the occurrence of a detonation regime.[10] Thus, at the temperature T_{00}, corresponding to the point of tangency, we have

$$\psi = M/Q \text{ or } 2\beta(1-\beta)(\mathrm{e}^{-E/RT_{00}} - k_1[\mathrm{inh}]/k_0P) = M/\mathrm{Q} \quad (12)$$

We consider that inhibitor is entirely consumed at this point, then

$$M/2Qf_0 = \beta_{00}(1-\beta_{00}) \quad (13)$$

It follows from equation (10) that $0.5M/Qf_0 < 1$. The following identity takes place: $M/Qf_{00} = (M/Qf_0)(f_0/f_{00})$:

$$M/2Qf_{00} = M\mathrm{e}^{-E/RT_0}/2Qf_0\mathrm{e}^{-E/RT_{00}} \quad (14)$$

It follows from equation (14) in terms of equation (12) and $f_0/f_{00} << 1$:[10] $0.5M/Qf_{00} << 1$ and then $\beta_{00} << 1$. Thus, β_{00} in equation (13) can be neglected.

The value $\int H(x)\mathrm{d}x$ is estimated. It is evident from (9) that $2f_0\delta Q/H - (2f_0\delta Q/H - 1)\mathrm{e}^{\alpha} < 1$ then $(1 - H/2f_0\delta Q)\mathrm{e}^{\alpha}$ and $\alpha < -\ln(1 - H/2f_0\delta Q)$

If $H/2f_0\delta Q$ is not too close to 1, the expansion in series can be used:

$$\alpha < H/2f_0\delta Q \quad (15)$$

Next, x can be expressed from α [equation (9)]. Replacing α by its upper boundary from equation (15) and substituting $f_0 = = \mathrm{e}^{-E/RT_0}$ we obtain

$$x = \frac{R^2T_0^2k\mathrm{e}^{E/RT_0}}{2\delta QE(k-1)(3-k)} \quad (16)$$

Let $\int H(x)\mathrm{d}x \sim Hx$, and x is taken from equation (16). Next, $\int H(x)\mathrm{d}x$ estimated in such a way is substituted into equation (11) taking into account that $\beta_{00} << 1$, $3-k \sim 2$, $k/(k+1) = C_\mathrm{p}/R$, $\delta \sim \delta_\mathrm{max} \sim 0.25$. After this transformation, equation (13) takes the form

$$\frac{D^2}{2(k^2-1)} = Q - \frac{C_\mathrm{p}RT_0^2(Qk_1[\mathrm{inh}]/4k_0P + M)\mathrm{e}^{E/RT_0}}{QE} \quad (17)$$

One of the most important outcomes of equation (17) is the fact that for [inh] = 0 we have the classical equation for a one-dimensional DW with heat losses.[10] It is seen that the chain break reaction (the chain termination *via* an inhibitor in this work), which depends on temperature only slightly, is responsible for chemical losses.

It is of interest to clarify whether only chemical losses are responsible for the existence of detonation limits. At the front of a shock wave (ignoring the initial temperature),[10] $T_0 = = D^2[1 - (k-1)^2/(k+1)^2]/C_\mathrm{p}$. Taking into account the above relation and $h(v_1,D_0) = D_0^2/2(k^2-1)$ and substituting $\mu = 2EC_\mathrm{p}/R[1-(k-1)^2/(k+1)^2]$, $g_1 = 2(k^2-1)C_\mathrm{p}RT_0^2/EQ$ in equation (17), we have

$$D^2 - D_0^2 = -g_1(Qk_1[\mathrm{inh}]/4k_0P + M)\mathrm{e}^{\mu/D^2} \quad (18)$$

The expansion of the exponent in a series is used again: $\mathrm{e}^{\mu/D^2} = \mathrm{e}^{\mu/D_0^2}\,\mathrm{e}^{-(D^2 - D_0^2)\mu/D_0^4}$. As follows from equation (18):

$$\frac{(D^2 - D_0^2)\mu}{D_0^4} = -\frac{g_1(Qk_1[\mathrm{inh}]/4k_0P + M)\mu\mathrm{e}^{\mu/D_0^2}\,\mathrm{e}^{-(D^2 - D_0^2)\mu/D_0^4}}{D_0^4} \quad (19)$$

Let $s = -\mu(D^2 - D_0^2)/D_0^4$, $g_2 = g_1(0.25Qk_1[\mathrm{inh}]/k_0P + M)\mu\,\mathrm{e}^{\mu/D_0^2}/D_0^4$. Equation (19) takes the form:

$$s = g_2\mathrm{e}^s \quad (20)$$

It is easy to verify that, if $g_2 = 0$, $D = D_0$. Equation (20) is differentiated with respect to g_2:

$$\mathrm{d}s/\mathrm{d}g_2 = \mathrm{e}^s/(1-s) \quad (21)$$

It can be seen in equation (21) that $s < 1$, because for $s = 1$ $\mathrm{d}s/\mathrm{d}g_2$ is equal to infinity. It can also be seen that a detonation regime cannot occur at any value of g_2: a detonation regime is impossible starting from some value of losses. For the maximum value $s = 1$, we have[10]

$$D^2 = D_0^2 - D_0^4/\mu, \quad D^2 \sim D_0^2(1 - RT/E), \quad D \sim D_0(1 - RT/2E)$$

Now, let $M = 0$. The foregoing is also true in this case: a detonation regime is impossible starting from some value of g_2; however, detonation occurs over a certain range of [inh]. Therefore, it is shown that the detonation limit occurs only due to chemical losses. Let $M = 0$, $[\mathrm{inh}]/P = X_0$. The substitution of the expression for g_1 in equation (19) gives:

$$\frac{(D^2 - D_0^2)\mu}{D_0^4} = -\frac{\mathrm{Cp}RT_0^2X_0k_1\mu\mathrm{e}^{\mu/D_0^2}\,\mathrm{e}^{-(D^2 - D_0^2)\mu/D_0^4}}{4k_0ED_0^4} \quad (22)$$

The expression for μ [equation (18)] and corresponding parameters are substituted into equation (22): $D_0 = 230000$ cm s^{-1}, $C_\mathrm{p} = 4R/m$ ($m = 12$ is the mean molecular weight of the $2\mathrm{H}_2 + \mathrm{O}_2$ mixture),[8] $R = 8.3\times10^7$ erg mol^{-1} K^{-1}, $T_0 = 2000$ K, $E = = 22.4\times10^{10}$ erg mol^{-1},[9] $k = 1.5$, $k_1 = 2.7\times10^{-11}$ cm^3 molec^{-1} s^{-1} in the case of an efficient inhibitor, $k_0 = 4\times10^{-11}$ cm^3 molec^{-1} s^{-1}.[9] The calculation is given below only for illustration due to a qualitative character of the treatment performed. The solution of (22) takes the form:

$$D = \pm1.08\times10^5[4.5 + 15.4\mathrm{LambertW}(-7.28X_0)]^{1/2}$$

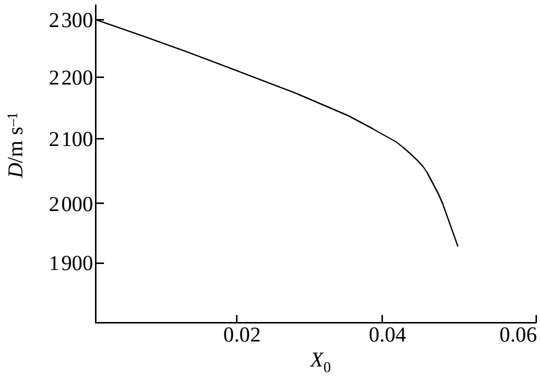

Figure 1 Calculated detonation velocity as a function of the fraction of an inhibitor.

Here, by definition, $\mathrm{LambertW}(x) + e^{\mathrm{LambertW}(x)} = x$. The positive branch of the solution is shown in Figure 1. As can be seen, the limit of detonation exists at $X_0 = 0.05$. Therefore, $[\mathrm{inh}]/P = 0.05$ or $[\mathrm{inh}]/0.05 = [O_2]_0$, *i. e.*, the linear dependence of the inhibitor concentration on the concentration of an oxidant at the limit of inhibited detonation can be expected for stoichiometric and rich $H_2 + O_2$ mixtures in the presence of an efficient inhibitor.

Thus, it was shown that a detonation limit can occur even only due to chemical losses. The losses caused by the chain termination reaction *via* an inhibitor are considered in this work. As low concentrations of an efficient inhibitor as several percents can suppress the detonation regime.[2] By this means chemical losses due to reactions of chain termination must be taken into account in the numerical modelling of the propagation of detonation waves. The above can also be true for the action of small additives of promoters (the substances that increase the degree of branching of reaction chains). Really, the denominator of the term of chemical losses is the rate of chain branching. The increase in denominator leads evidently to a reduction of chemical losses; therefore, we have a promoting effect.

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References

1 B. E. Gelfand, S. M. Frolov and M. A. Nettleton, *Prog. Energy Combust. Sci.*, 1991, **17**, 327.
2 V. V. Azatyan, H.-G. Wagner, G. K. Vedeshkin and R. G. Aivazyan, in *Gaseous and Heterogeneous Detonations: Science to Applications*, ENASH Publishers, Moscow, 1999, p. 331.
3 V. V. Azatyan, *Kinet. Katal.*, 1999, **40**, 818 [*Kinet. Catal*. (*Engl. Transl*.), 1999, **40**, 720].
4 M. H. Lefebvre and E. S. Oran, *Int. J. Shock Waves*, 1995, **4**, 277.
5 S. M. Frolov, A. N. Polenov and B. E. Gelfand, *Khim. Fiz.*, 1986, **5**, 978 (in Russian).
6 V. V. Azatyan and A. A. Shavard, *Izv. Akad. Nauk, Ser. Khim*., 1977, 2460 (in Russian).
7 A. A. Borisov, V. V. Kosenkov, A. E. Mailkov, V. N. Michalkin and S. V. Khomik, *Proceedings of the American Institute of Aeronautics and Astronautics*, 1993, 312.
8 G. L. Agafonov and S. M. Frolov, *Fizika Goreniya i Vzryva*, 1994, **1b**, 92 (in Russian).
9 V. T. Gontkovskaya and A. G. Merzhanov, *Chislennoe issledovanie kinetiki i mekhanizma okisleniya vodoroda* (*Numerical Simulation of Kinetics and Mechanism of the Combustion of Hydrogen*), 1982, Izd. AN SSSR, otd. OICP, Chernogolovka (preprint), p. 22 (in Russian).
10 Ya. B. Zel'dovich and A. S. Kompaneets, *Teoriya detonatsii* (*Theory of Detonation*), Gostekhizdat, Moscow, 1955, p. 268 (in Russian).
11 N. N. Semenov, *O nekotoryckh problemakh khimicheskoi kinetiki i reaktsionnoi sposobnosti* (*On Some Problems of Chemical Kinetics and Reaction Ability*), AN SSSR, Moscow, 1958, p. 685 (in Russian).

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