

Effect of Nitrogen on Multifront Detonation Parameters

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UDC 534.222.2+536.46+661.215.1

Translated from *Fizika Goreniya i Vzryva*, Vol. 34, No. 1, pp. 79–83, January–February, 1998.
Original article submitted November 11, 1996; revision submitted February 10, 1997.

A faster increase in the cell size and other very important multifront detonation parameters compared with that predicted by the kinetic calculations has been shown for nitrogen-diluted fuel-oxygen mixtures of hydrogen and typical hydrocarbons. Dilution of mixtures with other inert gases does not lead to a similar effect. This may be associated with the increase in the chemical reactivity of nitrogen under the action of the electric field of a detonation wave. A more correct method of calculating the ignition delays of various nitrogen-containing mixtures for detonation conditions is proposed.

INTRODUCTION

Many important multifront detonation parameters, which play the decisive role in explosion hazard problems, such as critical initiation energies, critical scales of gas charges, channel dimensions for limiting detonation, etc. (see, for example, [1–3]) are determined via the cell size a . In turn, the value of a can be calculated using the technique proposed by Westbrook, the author, and others [2, 4] within the framework of the models of detailed or averaged kinetics of chemical reactions in a combustible mixture.

The kinetic constants of the reaction rates for several hundreds of various elementary (direct and reverse) reactions proceeding in a given chemically active system are the basis of the model of detailed kinetics for hydrocarbon-fuel combustion. Knowledge of the kinetic constants for all the components makes it possible to calculate, at given initial pressure and temperature (for a fixed volume and uniform parameters throughout the volume at each moment of time), the entire kinetic scheme and the initial substance-to-reaction product transformation (see, for example, [5, 6]) and to separate the characteristic stages for a macrokinetic description of the system, i.e., the induction period and the effective duration of a chemical reaction. We note that detailed kinetic calculations are more complicated for

reactions in a flowing gas mixture.

The traditional macrokinetic parameter is the ignition delay τ of the mixture being examined (an analog of the calculated induction period). Usually, this parameter is presented, within the framework of the averaged-kinetics model, in the form of the Arrhenius formula (see, e.g., [6]):

$$\tau = \frac{A \exp(E/RT)}{\{[f]^{k_1} [o]^{k_2} [i]^{k_3}\}}, \quad (1)$$

where f is the fuel, o is the oxidant, i is the inert additive, E is the activation energy of the "limiting" (leading) reaction in the induction period, R is the universal gas constant, T is the temperature of the mixture in the induction zone, the molar concentrations of the components of the combustible mixture per unit volume are indicated in the square brackets, and k_i are the numerical coefficients (constants) which are determined in the mathematical processing of experimental data.

EXPERIMENTS AND BASIC RESULTS

In [3], the author expounded the basic results of the theoretical and experimental investigations devoted to the determination of a . In the present paper, the effect of the dilution of mixtures with inert gases on the cell size a is discussed. Figure 1 gives the summary (from [3, 7–17]) experimental data on the cell size of a multifront detonation upon dilution of stoichiometric fuel-oxygen mixtures (FOM)

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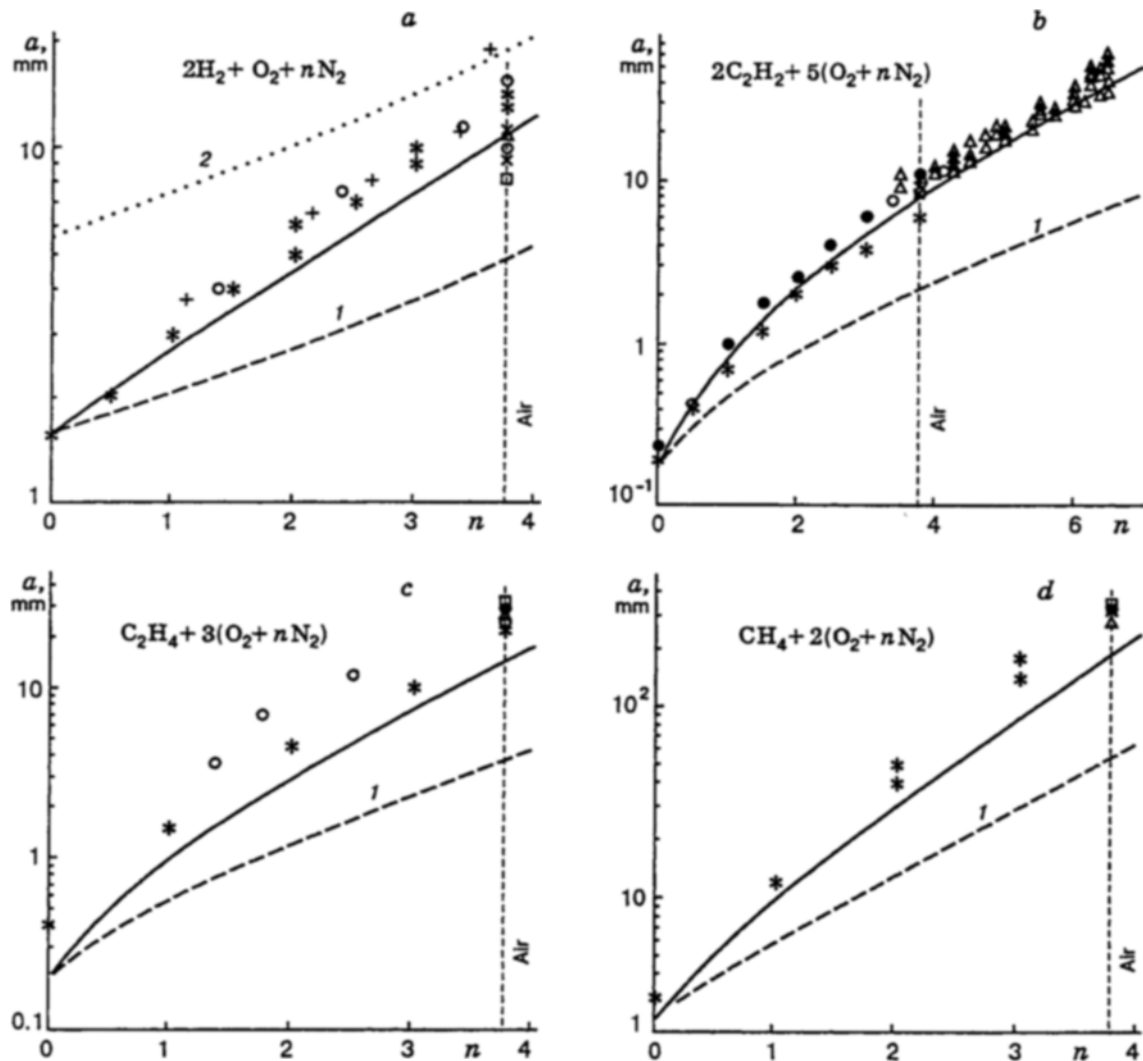


Fig. 1. Variations of the cell dimensions a upon dilution of mixtures with nitrogen: (a) $2\text{H}_2 + \text{O}_2 + n\text{N}_2$: points Δ , \circ , $+$, \square , and \times refer to the experimental data from [7-9], [14], and [15], respectively; (b) $2\text{C}_2\text{H}_2 + 5(\text{O}_2 + n\text{N}_2)$: points \times , \circ , Δ , and $+$ refer to the experimental data from [7], [8], [10], and [11], respectively; (c) $\text{C}_2\text{H}_4 + 3(\text{O}_2 + n\text{N}_2)$: points Δ , \circ , $+$, and \square refer to the experimental data from [7], [8], [11], and [13], respectively; (d) $\text{CH}_4 + 2(\text{O}_2 + n\text{N}_2)$: points Δ , \times , and \square refer to the results obtained by I. O. Moen [11] and reported in [1] and [16]; in all the diagrams, points $*$ and \bullet refer to the data obtained by the author (see also [3]).

with nitrogen ($p_0 = 0.1$ mPa, n is the molar concentration of N_2 relative to O_2 , and vertical lines refer to air: $n = 3.76$). The dashed curves are the calculated dependences $a(\text{N}_2)$ within the framework of the averaged-kinetics model for the induction period τ : only the curves which correspond to the "optimal" choice of the coefficients of formula (1) for a FOM selected from a large amount of τ data obtained by various researchers [3] are given:

$\text{H}_2\text{-O}_2$ [18]: $k_1 = k_3 = 0$, $k_2 = 1$, $A = 5.38 \cdot 10^{-5}$, and $E = 17,150$ cal/mole;

$\text{C}_2\text{H}_2\text{-O}_2$ [19]: $k_1 = k_2 = 0.5$, $k_3 = 0$, $A = 2.82 \cdot 10^{-5}$, and $E = 18,100$ cal/mole;

$\text{C}_2\text{H}_4\text{-O}_2$ [20]: $k_1 = k_3 = 0$, $k_2 = 1$, $A = 3.55 \cdot 10^{-6}$, and $E = 27,500$ cal/mole;

$\text{CH}_4\text{-O}_2$ [21]: $k_1 = k_3 = 0$, $k_2 = 1$, $A = 6.0 \cdot 10^{-6}$, and $E = 33,200$ cal/mole;

the oxygen concentration and τ are given in moles per liter and microseconds, respectively. The specific features of all the diagrams is the more rapid increase in the experimental values of the cell size as the mixtures are diluted with nitrogen compared with the calculated values. This feature is observed for the other characteristic parameters of multifront detonation with the dimension of length (or proportional to a) [3]: critical diameter of a free gas charge, chan-

nel dimensions for limiting detonation propagation, critical initiation energy, etc.

At the same time, the experimental dependences $a(N_2)$ do not go beyond the limits calculated with the use of the "minimum" and "maximum" (for example, curve 2 in Fig. 1a) delays, displacing toward the upper boundary as the content of N_2 in the mixture grows.

It is necessary to emphasize that as the mixtures are diluted, the unusual behavior of the cell size (and the other parameters proportional to a) is observed only for nitrogen. For the mixtures with argon or helium, the experimental values of $a(\text{Ar}, \text{He})$ are in agreement with the calculated ones up to very high concentrations of an inert gas, which markedly exceed the nitrogen concentration in stoichiometric fuel-air mixtures [3]. In other words, it is not justified reason to consider that the observed effect of $a(N_2)$ is due to the imperfection of the cell model [4]. The reason should be sought in the description of the kinetics of the induction period as applied to a multifront detonation wave (DW).

DISCUSSION OF RESULTS

The specifics of the detonation conditions (first of all, a strong spatial and time nonuniformity of the multifront DW parameters) makes it practically impossible to perform reliable experimental measurements of the detailed kinetics of chemical reactions occurring in the DW. Even under uniform conditions, which are typical of shock waves, most of the measurements were performed for averaged kinetics. The measurement results obtained under conditions which are different from the detonation ones were then extrapolated, with any degree of accuracy, to the region of interest. Because of this, for almost all fuels extrapolated to the region of gas dynamic parameters typical of detonation (temperature, density or concentration, and pressure), the "averaged" kinetic data for τ obtained by various researchers yield a pronounced scatter in the values of τ (see, for example, [3, 6, 22, 23]).

To "optimize" τ in the domain of detonation parameters, attempts at a repeat "averaging and reapproximation" of a set of kinetic data of various authors are known with a view to obtaining the new generalized constants for Eq. (1) (see, for example, [6, 23]). We note that calculation with the use of reapproximated coefficients in formula (1) does not eliminate the divergence of the experimental and calculated curves $a(N_2)$.

The next step is to calculate $a(N_2)$ with the use

of the available data on τ of the mixtures which are examined within the framework of a detailed kinetics. An analysis of the results calculated according to the detailed kinetics and given in [5] for a number of mixtures shows, for example, that in the dilution of a stoichiometric hydrogen-containing mixture with nitrogen and in the transition to a hydrogen-air mixture ($N_2/O_2 = 3.76$), the τ value increases by a factor of 9 (the calculated delay was determined as the period from the beginning of the process to the moment of fastest growth in temperature). At the same time, a calculation by means of formula (1) for the averaged kinetics shows that none of the known sets of kinetic constants for (1) gives the same increase for the "averaged" induction period [3]. Owing to this, the curves $a(N_2)$, which were calculated according to the delays from the detailed kinetics model, are somewhat steeper than the curves which correspond to the averaged kinetics, although they are, as before, lower than the experimental ones.

Formally, the situation with the faster increase in $a(N_2)$ can be improved, for example,

(a) by increasing the effective activation energy E (and by decreasing A for connection with the starting point, i.e., the "pure" mixture);

(b) by increasing the order of the "limiting" reaction.

Unfortunately, using this approach, it is necessary, for example, for the mixture $H_2-O_2-N_2$, either to "bring" E up to a value of ≈ 40 kcal/mole or to increase k_i above 2. Neither the first nor the second has sufficient physical substantiation or experimental support (although such "approaches" for other mixtures are known in the literature, such as an increase in E in [24] or the variation of k_i in [23]).

HYPOTHESIS ON NITROGEN REACTIVITY AND MODIFICATION OF FORMULAS FOR τ

According to the classical ideas, the nitrogen molecules remain inert up to very high temperatures (at $T = 3000^\circ\text{C}$ and at normal pressure, only 0.1% of molecules [25] were dissociated) and they play a role only in triple collisions (energy transfer). Nevertheless, at detonation temperatures an effective increase in the oscillatory degrees of freedom of molecular nitrogen can occur. According to [25], already at 1500°C nitrogen intensely interacts with acetylene, with the formation of the radical HCN. Moreover, nitrogen is able to convert, under the action of the electric field, to an active (excited) substance which actively interacts, for example, with atomic oxygen

and hydrogen even at room temperature [25]. The presence of the longitudinal electric field in the multifront DW was supported experimentally, in particular, by Pinaev and Sychev [26]. One can assume that having been produced under the conditions typical of multifront detonation, this excited nitrogen will be able to affect (via the concentration of active particles) the course of the chemical conversion of the initial substances to the final reaction products and, first of all, the induction period and, via this period, the basic dynamic parameters of multifront detonation, namely, cell size, critical initiation energies for a plane, cylindrical, or spherical cases of symmetry, critical charge diameters, etc. Unfortunately, the author failed to find in the literature a direct support of the hypothesis on the effect of electromagnetic fields on the induction period of nitrogen-containing mixtures.

It is worth noting that according to the existing ideas, for almost all kinds of fuels, the role of nitrogen reduces only to that of an inert additive, and it is incorporated in (1) indirectly, via the variation of $[O_2]$ in a mixture. Meanwhile, according to the assumption on nitrogen excitation in a detonation wave, a direct account of N_2 in (1) upon mixture solution is required.

In this paper, the effective activation energy E and the total order of the "limiting" reaction remained unchanged (in accordance with the experimental data). Since the concentrations of the mixture components can be expressed via one another, the effect of nitrogen can be taken into account mathematically with the use of a variable coefficient in front of $[O_2]$, which characterizes already the molar relations between nitrogen and oxygen in the mixture:

$$[N_2]^n [O_2]^m = [N_2/O_2]^n [O_2]^{n+m} = B [O_2]^{n+m}.$$

Attention should be given to the formal contradiction in formula (1), namely, to the trend of τ to infinity as the concentration of any component decreases to zero. To avoid this mathematical feature in the extrapolation to the FOM [nonzero amount of N_2 in the denominator of formula (1)], the coefficient B before $[O_2]$ was defined via a fraction of the FOM in a nitrogen-diluted mixture rather than the molar fraction of N_2 . For example, for a $2H_2 + O_2 + nN_2$ mixture, $B(n) = 3/(3+n)$ is added in the formula for τ from [18]: in the transition from a stoichiometric nitrogen-air mixture to a stoichiometric hydrogen-oxygen mixture, the value of B tends from $3/6.76 = 0.444$ to a correct asymptotic limit, i.e., to $3/3 = 1.0$. Similarly, $B(n) = 3.5/(3.5+2.5n)$ appears in the formula from [19] for a $C_2H_2 + 2.5(O_2 + nN_2)$

mixture, $B(n) = 4/(4+3n)$ is introduced into the formula for τ from [20] for $C_2H_4 + 3(O_2 + nN_2)$, and $B(n) = 3/(3+2n)$ appears in the formula of type (1) for τ from [21] for $CH_4 + 2(O_2 + nN_2)$, etc.

The solid curves in Fig. 1a-d refer to the calculation according to the proposed technique. Clearly, the refined technique for calculation of ignition delays in the presence of nitrogen in a mixture describes the experimental dependences $a(N_2)$ much more correctly compared with the previously used ones. We note that this approach has turned out to be more efficient for all the other mixtures considered.

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