
COMBUSTION, EXPLOSION,
AND SHOCK WAVES

Formation of Nitrogen Oxides in Detonation Waves

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Abstract—Based on detailed kinetic calculations and experimental data, it is demonstrated that the emission of nitrogen oxides from detonation burner units (DBUs) is significantly lower than that from powerful conventional burners with similar characteristics. Under certain conditions, realized largely in DBUs with rotating detonation, the main component of the nitrogen oxides may turn out to be N_2O .

Keywords: detonation, emission of nitrogen oxides, calculations, experiment.

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In the development of new energy-saving technologies based on pulse detonation combustion [1] or rotating detonation wave combustion [2], a persistent problem is the environmental performance of the process, especially regarding the emission of nitrogen oxides. The matter is that, in detonation burner units (DBUs), the operation process takes places in the mode of self-ignition at high pressures and temperatures in a running detonation wave. In this connection, it is often argued that the emission of nitrogen oxides from DBUs will be incomparably higher than that from existing powerful slow-combustion burner units with similar characteristics. However, there is another, opposite point of view: it is expected that, due to a very short time of combustion of fuel–air mixture in the DBUs and a rapid expansion of the detonation products, the emission of nitrogen oxides will be lower than that typical of existing burner units. The aim of the present work is to clarify this issue on the basis of detailed kinetic calculations and experimental studies of nitrogen oxide in a detonation wave.

The calculations were performed using a previously employed detailed kinetic mechanism of the oxidation and combustion of methane, supplemented by a group of H–C–N–O reactions leading to the formation of prompt and thermal nitrogen oxides [3] and a group of N_2O formation reactions.

The conditions for the formation of nitrogen oxides in the detonation wave were determined using a kinetic program intended for calculations at constant pressure. This program was applied under conditions where the temperature and pressure vary with time. The profiles were obtained from one-dimensional gasdynamic calculations, in which molecular heat and mass transfer were disregarded because of relatively

long characteristic times of these processes compared with the characteristic time of the chemical and gasdynamic processes behind the wave front.

In performing the kinetic calculations, the pressure $P(t)$ and temperature $T(t)$ profiles were approximated by piecewise step functions. In the kinetic program, pressure levels were specified in steps P_1, P_2, \dots, P_i (i is the number of steps). The initial temperature at the first step T_{01} was chosen such that, after mixture ignition, temperature would be the same as in the detonation wave. At each subsequent interval, the current initial temperature T_{0i} was kept constant, i.e., corresponding to that obtained in the gasdynamic calculation $T(t)$.

Figure 1 shows the yield of nitric oxide NO calculated by the above method. The sharp rise (almost vertical) of the NO concentration at the time of arrival of the detonation wave ($t \approx 0.2$ ms) corresponds to the formation of “rapid” nitric oxide, resulting from a sequence of reactions beginning presumably from the interaction of CH and CH_2 radicals with molecular nitrogen of the air. Note that, experimentally, rapid nitric oxide was observed only in laminar flames, so that models of its formation were also developed only for such flames, not for detonation waves. As can be seen from Fig. 1, at $t > 0.5$ ms (≈ 0.3 ms after detonation wave arrival), the NO concentration ceases to increase at a level of 276 ppm. At these times, the concentration of N_2O in the detonation products of a stoichiometric mixture was negligibly small.

To test model predictions, we measured the emission of nitrogen oxides NO_x at a laboratory pulse-detonation burner (PDBU) running on natural gas, containing 98.9% methane. The design and operation of the PDBU are described in detail in [4]. Briefly, the

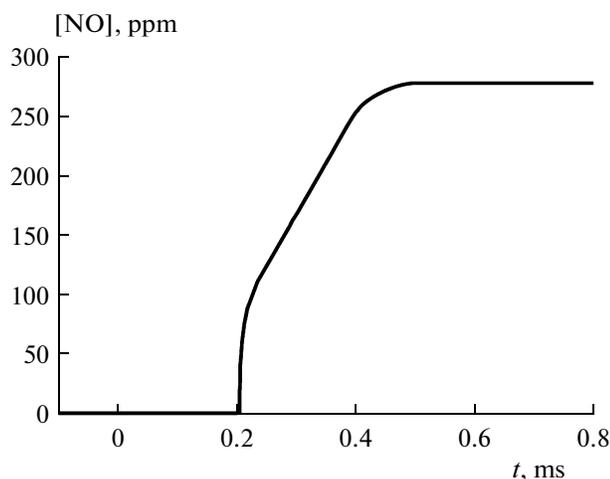


Fig. 1. Formation of NO as calculated within the framework of the detailed kinetic scheme.

PDBU detonation tube was 94 mm in diameter (close to the limiting diameter of detonation for a stoichiometric methane–air mixture) and 3600 mm in length. The deflagration-to-detonation transition occurred at a distance of 2000 mm to the open exit section of the tube, so that, at the end of the tube, where detonation products were sampled, the combustion of the mixture occurred in the detonation mode. Sampling was carried out using a probe with a check valve and a flute for dispersing the directed motion of detonation products. The probe was coaxially inserted into the PDBU at a depth of 500 mm from the exit section. The concen-

tration of nitrogen oxides in the detonation products was measured on Testo 335 gas analyzer (Testo AG, Germany).

For a detonation wave propagating in a stoichiometric natural gas–air mixture at $P_0 = 0.1$ MPa and $T_0 = 293$ K, the mean (based on a series of experiments) concentration of nitrogen oxides was found to be $[\text{NO}_x] \approx 210$ ppm, including $[\text{NO}] \approx 203$ ppm.

The calculated NO yield, 276 ppm, is in close agreement with the measured (203 ppm), especially given that, in experiment, the near-limit (spin) detonation regime was realized, with a mean velocity deficit of 100–200 m/s relative to the thermodynamic value for a stoichiometric methane–air mixture (≈ 1800 m/s). Indeed, due to a lower wave velocity, the measured temperature of the detonation products was lower than the calculated, and, consequently, the measured NO yield should be lower.

The calculated and measured NO yields should be compared to the similar characteristics of existing analogues, more specifically, powerful industrial burners with high-rate fuel supply and high combustion temperature. In such burner units, the air entering into the combustion chamber is preheated. The NO yield from such burner units is as high as 500–700 ppm [5]. Even with the most modern schemes of multistage combustion in burners, the emission of NO_x can be reduced only to 400 ppm, which is 1.5–2.0 times higher than that obtainable in PDBUs. Thus, the emission of nitrogen oxides from PDBUs turned out to be significantly lower than that from analogous high-power burner units.

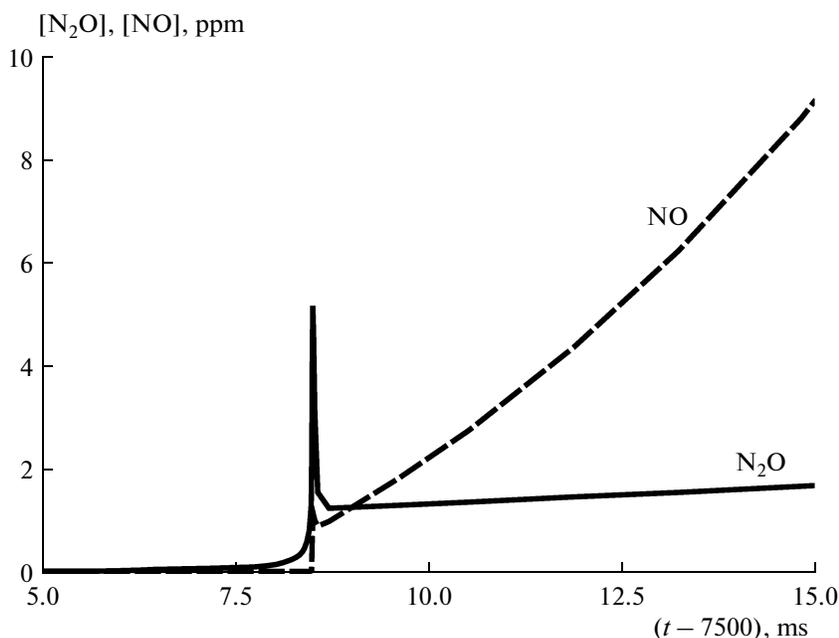


Fig. 2. Formation of N_2O and NO during the self-ignition of a $\alpha = 2$ methane–air mixture at $P_0 = 2.4$ MPa and $T_0 = 650$ K. The combustion temperature, 2043 K.

The performed kinetic calculations of the emission of nitrogen oxides in detonation waves revealed an interesting feature concerning the proportion between various nitrogen oxides in the detonation products. The detailed kinetic scheme included all known reactions of formation and consumption of N_2O (seven direct and respective reverse elementary reactions). Calculations within the framework of this kinetic program showed that, for the self-ignition of a lean methane–air mixture, with an oxidizer-to-fuel equivalence ratio of 2, there are conditions where the concentration of N_2O is higher than the NO concentration, $[N_2O] > [NO]$. Such conditions exist within a very short time (~ 0.1 ms). Figure 2 shows an example of such a situation.

It is seen that, for a short time (0.2 ms), the N_2O concentration is higher than that of NO, reaching 5 ppm. This suggests that, in DBUs with rotating detonation, characterized by short time scales of the process, the main component of the nitrogen oxides should be N_2O . For example, for a 0.2-m-high DBU annular chamber with rotating detonation wave, the axial velocity of detonation products is ~ 1000 m/s, i.e., the characteristic time of the process is 0.2 ms.

Recently, we learned that this effect (prevalence of N_2O in the detonation products) was observed experimentally at the Lavrent'ev Institute of Hydrodynamics of the Siberian Branch of the Russian Academy of Sciences. Thus, detailed kinetic calculations in con-

junction with experiments demonstrated that the emission of nitrogen oxides from DBUs is substantially lower than that from existing high-power burner units. Under certain conditions, applicable mainly to DBUs with rotating detonation, the main component of the nitrogen oxides may prove to be N_2O .

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