Berlin Institute of Technology • Fasanenstr. 89 • 10623 Berlin

Voevodsky Institute of Chemical Kinetics and
Combustion, Siberian Branch of the
Russian Academy of Sciences
Andrey Shmakov
Institutskaya 3
Novosibirsk 630090, Russia

Berlin, 30. April 2014

Confirmation of paper submission

Name:	Andrey Shmakov
Email:	shmakov@kinetics.nsc.ru
Co-author:	Denis Knyazkov
2nd co-author:	Oleg Korobeinichev
3rd co-author:	Tatyana Bolshova
Title of Paper:	Structure of premixed fuel-rich CH4/O2/N2/CO2 and C3H8/O2/N2/CO2 flames stabilized on a flat burner at atmospheric pressure
Program:	Laminar flames
Name of Institute:	Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences, Institutskaya 3, Novosibirsk 630090, Russia

Structure of premixed fuel-rich $CH_4/O_2/N_2/CO_2$ and $C_3H_8/O_2/N_2/CO_2$ flames stabilized on a flat burner at atmospheric pressure

A.G. Shmakov[1,2*], D.A. Knyazkov[1,2], O.P. Korobeinichev[1], T.A. Bolshova[1], A.M. Dmitriev[1,2], A.S. Lobasov[2,3], D.K. Sharaborin[2,3]

[1]Voevodsky Institute of Chemical Kinetics and Combustion, Novosibirsk, Russia
[2]Novosibirsk State University, Novosibirsk, Russia
[3]Kutateladze Institute of Thermophysics, Novosibirsk, Russia

Abstract

Species concentration profiles in the fuel-rich ($\varphi=1.2$) methane/air, propane/air and methane/air/CO_2, propane/air/CO_2 flames stabilized on a flat burner at 1 atm were studied using the molecular beam mass-spectrometry and numerical simulation. Mole fraction profiles of reactants, intermediates and final products were measured and simulated. The results of measurements indicate that the replacement of 15% of N_2 with CO_2 leads to decreasing maximum mole fraction of majority of intermediate species in the reaction zone. Analysis of the results of calculating the structure of the flame under study and of the literature data has shown the effect of reducing the concentration of intermediate combustion products with partial replacement of N_2 with CO_2 to be connected with the increase of the reaction rate $CO_2+H \rightarrow CO+OH$, resulting in the growth of the ratio of OH/H in the zone of reactions in rich flames. The increase of OH concentration results in acceleration of the transformation of intermediate carbon-containing species into the final combustion products, thus reducing the probability of soot formation.

1. Introduction

The reduction of pollutant emissions from combustion of fossil fuels is the world's largest problem. One of the alternative methods of solving this problem is using the technology of recirculation of flue gas, the main component of which is CO_2 [1]. Previous studies have shown that the replacement of N_2 with CO_2 influences significantly on combustion efficiency of hydrocarbons [2-11]. Some researchers have shown that the effect of CO_2 is to inhibit the oxidation of CH_4 [6-9]. However, opposite results to inhibiting effect of CO_2 on the CH_4 oxidation have been reported also [10,11]. The effects of CO_2 on combustion characteristics of hydrocarbon/air mixtures were extensively studied [2-11] but chemical structure of premixed hydrocarbon/air/CO_2 flames at atmospheric pressure was not investigated earlier. An important issue, in particular, is the influence of replacement of N_2 with CO_2 in the fresh combustion mixture on soot formation in the flame.

The goal of this work is to study the effect of replacement of part of N_2 with CO_2 in fuel-rich CH_4/air and C_3H_8/air mixtures on chemical kinetics in premixed flame stabilized on a flat burner at 1 atm by measurement and numerical simulation of its thermal and chemical structure.

2. Experimental and Modeling details

Fuel-rich ($\varphi=1.2$) methane/air ($CH_4/O_2/N_2=0.111/0.186/0.703$), propane/air ($C_3H_8/O_2/N_2=0.048/0.2/0.752$) and methane/air/$CO_2$ ($CH_4/O_2/N_2/CO_2=0.111/0.186/0.553/0.15$), propane/air/$CO_2$ ($C_3H_8/O_2/N_2/CO_2=0.048/0.2.602/0.15$) flames were stabilized on a flat burner 16 mm in diameter at 1 atm. The burner was kept at 95^oC. The linear velocity of the fresh mixture on the burner surface was 16.0 cm/s for the $CH_4/O_2/N_2$ flame, 40.2

cm/s for the $C_3H_8/O_2/N_2$ flame and 7.25 cm/s for the $CH_4/O_2/N_2/CO_2$ flame, 20.1 cm/s for the $C_3H_8/O_2/N_2/CO_2$ flame.

The concentration profiles of species were measured using mass spectrometer coupled with molecular-beam sampling system [12]. Sampling was performed using a quartz probe with the orifice diameter of 0.08 mm and inner angle of 40 degrees. The mass spectrometer was equipped with improved ion source with a narrow spread of electron energies (±0.25 eV) [13].

The uncertainty of determination of mole fraction of the flame reactants and major products (CO, CO_2, H_2O, H_2) was estimated to be ±15% of the maximum mole fraction values. For other species, mole fractions were determined to within a factor of about 2. Temperature profiles were measured using Pt/Pt+10%Rh thermocouple made of wires 0.02 mm in diameter and coated with SiO_2. To

Fig. 1. Mole fraction profiles of $C_2H_6+CH_2O$, C_2H_4 and C_2H_2 (symbols – experiment, lines - modeling) in fuel-rich (φ=1.2) $CH_4/O_2/N_2$ flame with (filled circle and solid line) and without (open circle and dashed line) addition of 15% CO_2.

take into account the thermal disturbances induced in flames by a sampling nozzle temperature profiles were measured by a thermocouple, the junction of which was placed at the distance 0.2 mm from the probe's orifice. The temperature was measured with an accuracy of ±25 K, the radiative heat losses of the thermocouple were taken into account. The flame structure was simulated using Premix code from the Chemkin-II collection of codes and detailed reaction mechanism for combustion of small hydrocarbons [14]. Experimentally measured temperature profiles were used as input data for the modeling.

3. Results and Discussion

3.1. $CH_4/O_2/N_2$ and $CH_4/O_2/N_2/CO_2$ flames structure.

Figure 1a shows the mole fraction profiles of the total content of $C_2H_6+CH_2O$ in the $CH_4/O_2/N_2$ and $CH_4/O_2/N_2/CO_2$ flames. In the experiment with the $CH_4/O_2/N_2/CO_2$ flame, the peak mole fraction of $C_2H_6+CH_2O$ was about 3 times lower compared to that in the pure $CH_4/O_2/N_2$ flame, whereas the model predicts that it slightly decreases at CO_2 addition. The model does not quantitatively predict mole fraction profiles of $C_2H_6+CH_2O$ and reproduces poorly the effect of CO_2 addition to the initial mixture on the $C_2H_6+CH_2O$ concentration in the flame.

Figure 1b shows measured and calculated mole fraction profiles of C_2H_4 in both $CH_4/O_2/N_2$ and $CH_4/O_2/N_2/CO_2$ flames. For the maximum concentration of C_2H_4 in the $CH_4/O_2/N_2$ flame, the calculation provides a satisfactory agreement with the experiment, whereas in the flame with addition of 15% of CO_2
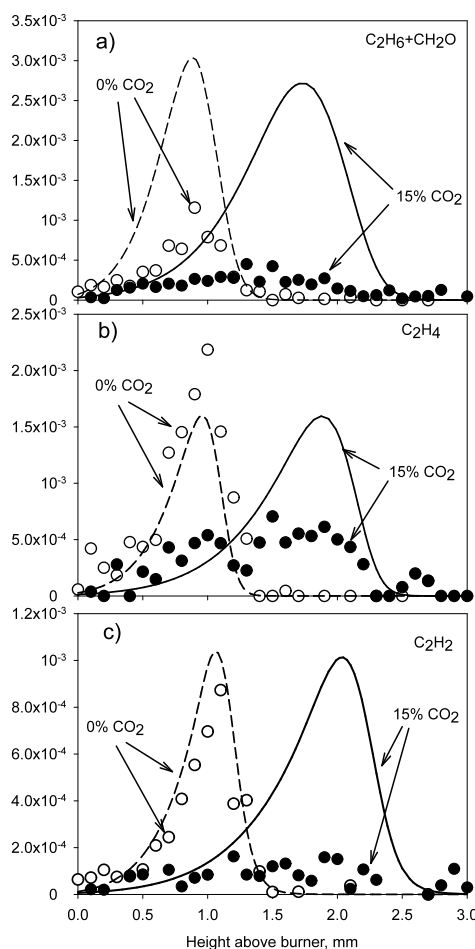
the model overpredicts the measured peak concentration of ethylene by 3 times. The experimental data show that addition of 15% of CO_2 results in decreasing the peak concentration of C_2H_4 by approximately 3 times, while modeling results do not demonstrate any changes in peak concentration of C_2H_4 with addition of CO_2. Thus, the chemical kinetic mechanism used for modeling does not reproduce the effect of addition of 15% of CO_2 to the unburnt mixture on peak concentration of C_2H_4 in the reaction zone of the flame.

One of the key intermediate C2 hydrocarbons in the flames studied is acetylene. According to experimental data (see Fig. 1c), its maximum mole fraction reaches 0.09% at a distance 1 mm from the burner in $CH_4/O_2/N_2$ flame. In the $CH_4/O_2/N_2/CO_2$ flame, it is also reached at a height 2 mm, but it is smaller in magnitude and comprises approximately 0.02%. With further increase in the height above the burner, the acetylene concentration in both flames decreases monotonically down to zero level. The kinetic mechanism used in the calculations satisfactorily reproduces the experimental profiles of acetylene in the $CH_4/O_2/N_2$ flame. However, in the $CH_4/O_2/N_2/CO_2$ flame, modeling yields values of concentration of acetylene five times higher than those measured in experiment.

3.2. $C_3H_8/O_2/N_2$ and $C_3H_8/O_2/N_2/CO_2$ flames structure

Figure 2 shows the mole fraction profiles of the total content of methyl (CH_3), methane (CH_4), acetylene (C_2H_2), C_2H_4, vinyl (C_2H_3), $C_2H_6+CH_2O$, propargyl (C_3H_3), allene and propyne (C_3H_4) in the $C_3H_8/O_2/N_2$ and $C_3H_8/O_2/N_2/CO_2$ flames. In the experiment with the $C_3H_8/O_2/N_2/CO_2$ flame, the peak mole fraction of CH_3 was about 2 times lower compared to that in the pure $C_3H_8/O_2/N_2$ flame, whereas the model predicts that its 1.6 times decreasing with CO_2 addition.

Similar changes are observed for CH_4 – its maximum concentration in the experiment was 3 times lower in the $C_3H_8/O_2/N_2/CO_2$ flame than in the pure $C_3H_8/O_2/N_2$ flame, however, the calculation predicts reduction of CH_4 only 1.2 times. Slight decrease of the peak concentration of C_2H_4 when CO_2 is added to the flame is observed both in the experiment (1.34 times) and in the calculation (1.24 times). Besides, a slight effect of reduction of the maximum concentration of C_3H_3 as CO_2 is introduced in the flame is observed in experiment (1.3 times), whereas in the calculation this reduction is much greater to be equal to 2.4 times. Even slighter changes in the peak concentrations as CO_2 was added were recorded for C_2H_3 and C_3H_4, their concentrations get reduced 1.2 and 1.1 times, accordingly, although the model predicts greater changes - 1.9 and 2.1 times, accordingly. Unlike the methane flames, where addition of CO_2 led to significant reduction of C_2H_2 concentration and $C_2H_6+CH_2O$ concentration, in propane flames the situation is reverse for these compounds: the peak concentrations of C_2H_2 и $C_2H_6+CH_2O$ increased 1.4 and 2.8 times, respectively. This change does not agree with the calculation results – the model predicts reduction of the maximum concentrations of these species 1.3 and 1.2 times, respectively.

Ethylene, vinyl, propargyl, allene, propyne and other unsaturated hydrocarbon species are considered as the species, which under certain conditions are potentially capable of producing PAH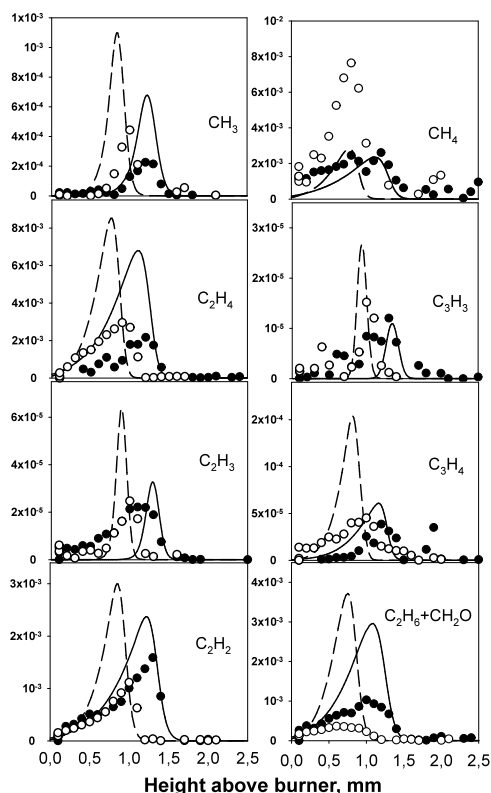 and soot in fuel-rich hydrocarbon flames through the reactions with other C_xH_y intermediates. Therefore, the reduction in concentration of the above mentioned species in the reaction zone of the flames indicates indirectly the tendency towards reduction of soot formation when CO_2 is added to the fresh hydrocarbon/air mixture. To elucidate the observed phenomena, additional analysis was performed.

Fig. 2. Mole fraction profiles of intermediate species (symbols – experiment, lines - modeling) in fuel-rich (φ=1.2) $C_3H_8/O_2/N_2$ flame with (filled circle and solid line) and without (open circle and dashed line) addition of 15% CO_2.

In order to estimate the impact of two different factors − of the thermal and chemical ones, which arise when CO_2 is introduced into the fuel mixture, on the oxidation processes of a hydrocarbon fuel, the structure of the flames investigated in this study was modeled. The concentration profiles of stable species, as well as of intermediates and radicals for methane- and propane- air flames (without CO_2 addition) were calculated using the experimentally measured temperature profiles in flames, in which 15% nitrogen was replaced with CO_2. Such approach allows the thermal effect from introducing CO_2 into the combustible mixture to be considered and at the same time the chemical effect of adding CO_2 to be eliminated. Comparison of the results of the calculation made using the approach described above with the concentration profiles of the species calculated for the flames with partial replacement of nitrogen with CO_2 (in such computations, transformation of introduced CO_2 into the fuel mixture is considered) allows the effect of adding CO_2 on the major intermediates in flame to be estimated. Shown in Fig. 3 are the concentration profiles of intermediates in the methane/air flame and in the methane/air+CO_2 flame, calculated by the same temperature profile measured in the methane/air + CO_2 flame. As seen from the above data, the presence of CO_2 in the fresh fuel mixture significantly reduces the maximum concentration of intermediates in the chemical reactions zone. Shown in Fig 3 are the concentration profiles of H and OH for the same conditions. As seen from the above data, the maximum concentration of H changes only slightly, while the maximum concentration of OH in the flame with CO_2 increases 1.7 times. The results of calculating the profile of the rate of reaction $CO_2+H\rightarrow CO+OH$ in the combustion zone in flames with addition of CO_2 and without it (by the temperature profile measured in the flame with CO_2) have shown that replacement of 15%

nitrogen with CO_2 increases the maximum value of the rate of this reaction 1.8 times (Fig.4). Similar conclusions can be made also for the propane/air flame, in which the maximum value of the reaction rate of reaction $CO_2+H\rightarrow CO+OH$ due to replacement of nitrogen with CO_2 increases 1.5 times. Thus, partial replacement of nitrogen with CO_2 in rich hydrocarbon/air
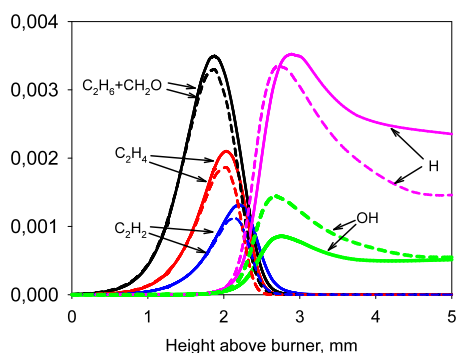
Fig. 3. Mole fraction profiles of C_2H_4, $C_2H_6+CH_2O$, C_2H_2, H and OH in fuel-rich $CH_4/O_2/N_2$ flame without (solid line) and with (dashed line) addition of 15% CO_2.
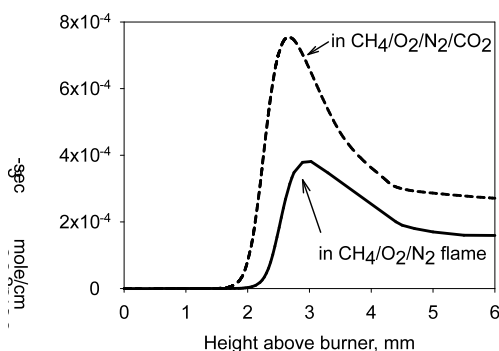

Fig. 4. Calculated rate of reaction $CO_2+H\rightarrow CO+OH$ in fuel-rich $CH_4/O_2/N_2$ flame without (solid line) and with (dashed line) addition of 15% CO_2. For modeling the temperature profile in $CH_4/O_2/N_2/CO_2$ for both flames was used.

fuel mixtures leads to the change in the H and OH concentrations in the zone of chemical reactions, resulting in the increase in the oxidation rate of the intermediate products of fuel transformation and in the lower probability of soot precursors formation.

4. Conclusions

The results of measurements indicate that the replacement of 15% of N_2 with CO_2 in $CH_4/O_2/N_2$ and $C_3H_8/O_2/N_2$ flames leads to reducing the post-flame temperature and decreasing maximum mole fraction of ethylene, vinyl, propargyl, allene, propyne and other intermediate hydrocarbon species in the reaction zone. Addition of CO_2 to fuel-rich methane and propane flames is shown to result in considerable reduction of mole fraction of soot precursors. Konnov's chemical kinetic mechanism, in general, adequately reproduces the experimental profiles for major flame species, however, noticeable discrepancies take place between measured and calculated mole fraction profiles for some combustion intermediates. Analysis of the results of calculating the structure of the flame under study and of the literature data has shown the effect of reducing the concentration of intermediate combustion products with partial replacement of N_2 with CO_2 to be connected with the increase of the reaction rate $CO_2+H\rightarrow CO+OH$, resulting in the growth of the ratio of OH/H in the zone of reactions in rich flames. The increase of OH concentration results in acceleration of the transformation of intermediate carbon-containing species into the final products of combustion, thus reducing the probability of soot formation.

Acknowledgements

References

1. P. Kutne, B.K. Kapadia, W. Meier, and M. Aigner, Proc. Combust. Inst. 33 (2011) 3383–3390.
2. O. Park et al, Proc. Combust. Inst. 33 (2011) 887-894.

3. A.A. Konnov and I.V. Dyakov, Comb. Sci. Technol. 179(4) (2007) 747-765.
4. F. Halter et al, Comb. Sci. Technol. 181 (2009) 813-827.
5. A.A. Konnov and I.V. Dyakov, Experimental Thermal and Fluid Science 29(8) (2005) 901-907.
6. T.L. Cong, P. Dagaut, Proc. Combust. Inst. 32 (2009) 427–435.
7. J. Gimenez-Lopez, V. Aranda, A. Millera, et al, Fuel Process. Technol. 92 (2011) 582–589.
8. Z. Cao, T. Zhu, Catalysis, kinetics and reaction engineering 20 (2012) 701-709.
9. T. Yuan, T. Liu, Y. Su, J. Huang, A Kinetic Analysis of CO_2 Addition in CH_4/O_2 Combustion, Proc. ECM-2013, June 25-28, 2013, Lund, Sweden, Paper P1-9, 6 pp.
10. H. Watanabe, T. Marumo, K. Okazaki, Energy Fuels 26 (2012) 938–951.
11. H. Hirotatsu, F. Arai, K. Okazaki, Combust. Flame 160 (2013) 2375–2385.
12. O.P. Korobeinichev, S.B. Il'in, V.V. Mokrushin, A.G. Shmakov, Combust. Sci. Technol. 117 (1-6) (1996) 51-67.
13. O.P. Korobeinichev, S.B. Ilyin, V.M. Shvartsberg, et al, Combust. Flame 118 (1999) 718-726.
14. F.H.V. Coppens, J. De Ruyck, A.A. Konnov, Combust. Flame 149 (2007) 409–417.