Formation and Destruction of Nitric Oxide in NO Doped Premixed Flames of C_2H_4, C_2H_6, and C_3H_8 at Atmospheric Pressure

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A study of the formation and destruction of NO in adiabatic laminar premixed flames of $C_2H_4 + O_2 + N_2$, $C_2H_6 + O_2 + N_2$, and $C_3H_8 + O_2 + N_2$ doped with NO (100 ppm in N_2) in a range of equivalence ratios at atmospheric pressure is presented. The heat flux method was employed to measure adiabatic burning velocities of these flames. Nitric oxide concentrations in the post flame zone at 10, 15, and 20 mm above the burner surface were measured using probe sampling. Burning velocities and NO concentrations simulated using a previously developed chemical kinetic mechanism were compared with the experimental results. The conversion ratio of NO seeded into the flames was determined. The kinetic mechanism accurately predicts burning velocities over the entire range of equivalence ratios. Significant discrepancies between the measured and calculated NO conversion in the flames were observed and discussed.

1. Introduction

The control of nitric oxide emissions from combustion systems could be achieved by different technologies including fuel staging, fuel reburning, selective catalytic, and noncatalytic reduction.[1] NOx control through reburning is a mature technology, which is based on injection of additional fuel downstream of the main combustion zone.[2] NOx formed in the main combustion zone is consumed in reactions with hydrocarbon radicals to form HCN and eventually N_2. The unreacted fuel from the rich reburning zone is then consumed in the burnout zone, where additional air is added.

The concepts of fuel staging and fuel reburning are based on a general understanding that reburning of nitric oxide occurs in rich mixtures without any substantial conversion in lean flames. The same assumption was often used in calibration of LIF signals of NO: although there was no direct experimental proof, it was generally accepted that small amounts of NO seeded into lean flames are not consumed (within ±10%). To validate this assumption, formation and conversion of NO in atmospheric methane flames doped with small amounts of NO (of the order of 100 ppm) has been studied through the range of equivalence ratios.[3] It was found that such a small amount of nitric oxide seeded into $CH_4 + O_2 + N_2$ and

$CH_4 + O_2 + Ar$ flames is consumed considerably not only under fuel-reach but also under fuel-lean conditions, whereas modeling performed using detailed kinetic mechanisms[4,5] predicted near-zero conversion of NO under the lean conditions. However, in other works, which were discussed in ref 3, NO conversion in NO-doped methane flames was observed only when either the concentration of NO added to the unburnt mixture was rather high (from about 0.1 to 2.8%) or under fuel-rich conditions, and these observations were in agreement with the results of kinetic modeling. Thus, our previous study[3] showed that the existing kinetic models containing nitrogen chemistry[4,5] are inadequate in predicting the conversion of nitric oxide in the lean methane flames doped with small amounts of NO.

The effects of nitric oxide seeding into the flames of hydrocarbons are much less investigated as compared to methane flames reviewed in ref 3. The LIF-technique and kinetic modeling were applied for studying flat premixed low-pressure flames of a number of hydrocarbons seeded with NO.[6,7] Williams and Pasternak[6] investigated the effect of nitric oxide additive (1%) on stoichiometric flames of methane, ethane, ethylene, and acetylene at 10 Torr. Spatial profiles of CH, [3]C_2, OH, NO, CN, NCO, and NH were measured. The experimental data showed that the methane, ethane, and ethylene flames demonstrate similar behavior for the nitrogen-containing intermediates. The acetylene flames were found to be quite different, producing three times more CN and NCO than those in flames of other fuels. This indicates a much greater NO reactivity in the acetylene flame. The species profiles were modeled with three different kinetic mechanisms: the Miller–Bowman mechanism[1] modified by the addition of several reactions and updating several reaction rates,[6] the mechanism of Lindstedt et al.,[8]

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and the GRI 2.11 mechanism. All of these models predicted the profiles in significant disagreement with the experimental data.

Atakan and Hartlieb[7] measured profiles of absolute NO concentration in fuel-rich propene flames at 50 mbar doped with 0.2%−1% of NO in order to study NO reburning. In all the flames, the NO mole fractions were found to be strongly reducing while moving away from the burner. In total, 64%, 34%, and 21% of the initial NO mole fractions were observed to remain in the exhaust zone of the flames for equivalence ratios φ = 1.5, 1.8, and 2.3, respectively. Modeling performed using a kinetic mechanism combined of those developed by Konnov (ver. 0.4) and by Miller and Melius[9] predicted the measured NO profiles accurately. Reaction flow analysis revealed that a variety of species and reactions contributes to the NO consumption in the different flame zones, the most important one being ketenyl (HCCO). Reactions involving CH and C atoms were found to be less important.

Rahinov et al.[10] investigated low-pressure methane and propane + air flames at 30 Torr to demonstrate simultaneous observation of CN, NH_2, HNO, and $^1CH_2$ using the intra-cavity laser absorption method. It was found that in rich (φ = 1.2) flames, seeding of nitric oxide in small amounts (0.2−2.2%) leads to a notable increase of concentrations of these radicals. Modeling performed with the GRI-mech. 3.0^5 satisfactorily reproduces the shape of the concentration profiles of CN and $^1CH_2$ and the absolute concentration of CN in the methane flame.

Nitric oxide seeding into the flames of hydrocarbons at atmospheric and higher pressures has been only studied by Schulz et al.[11] Premixed methane and *n*-heptane + air flames with equivalence ratios from φ = 0.9 to φ = 1.8, at pressures of 1−80 bar were seeded with 0−1300 ppm of NO. Direct comparison of NO LIF intensity with NO dopant concentration for different pressures and fuels clearly showed that small amounts of NO are consumed not only in rich but also in lean flames. It was concluded that evaluating the LIF signal increase on addition of small (0−200 ppm) quantities of NO for calibration purposes may be misleading.

Therefore, one can conclude that the studies of flames of hydrocarbons (other than methane) doped with NO at sub-atmospheric, atmospheric, and high pressures are rather limited. This work is a continuation of our previous study of effects of small additive of NO in methane flames.[3] The goal of the present work was again to study the impact of a small additive of NO on the burning velocity of C2 and C3 hydrocarbons and to ascertain how a NO additive transforms in the flames of C2 and C3 hydrocarbons. The authors of the study of formation and conversion of NO in atmospheric methane flames[3] were unaware of the original work.[11] Therefore, experiments on NO reburning in methane flames[3] and in flames of other hydrocarbons presented here were focused on rich mixtures, where significant consumption of NO was expected. As a result, some combinations of equivalence ratio and dilution ratio of the oxidizer, $D = O_2/(O_2 + N_2)$, have not been accessed experimentally. The flames of three fuels (ethylene, ethane, and propane) doped with NO and without additive are studied here. The burning velocity and probe sampling measurements of NO concentrations in the post-flame zone of laminar, premixed, nonstretched flames are presented. The experimental results are compared with the modeling in order to establish performance and deficiencies of the Konnov kinetic model.[4]

2. Experimental Details

Adiabatic flames were stabilized using the heat flux method on a perforated plate burner[3,12] at atmospheric pressure. Detailed descriptions of the method and experimental setup can be found elsewhere.[13−15] The temperature of the fresh gas mixture was controlled by a water cooling system of the burner's plenum chamber, and during the experiments it was maintained at 298 K. The gas supply system consisted of three channels for the fuel, oxygen, and nitrogen (or mixture of nitrogen and 100 ppm of NO). In the present work, C_2H_4, C_2H_6, and C_3H_8 flames with various dilution ratios $D = O_2/(O_2 + N_2)$ were studied. The dilution ratios of the flames studied were as following: for C_2H_4 mixtures, 0.18; for C_2H_6 mixtures, 0.19, 0.209, 0.23; for C_3H_8 mixtures, 0.18, 0.209, 0.23. Even minor modification of the dilution ratio leads to a significant change of the laminar burning velocity[14] and of the adiabatic flame temperature. For instance, the calculated flame temperature of propane flames at an equivalence ratio φ = 1.1 increases from 2068 K up to 2252 K when the dilution ratio is modified from D = 0.18 to 0.209. This may dramatically affect NOx chemistry even within the relatively narrow range of dilution ratios covered in the present work. All gases, including the N_2 + NO mixture, were supplied by Air Liquide. The stated purity of ethylene, ethane, propane, oxygen, and nitrogen were 99.995% or better. One should note that the amount of NO added was not constant with respect to a whole mixture and depended on the N_2 mole fraction in the mixture. NO/N_2 was unchanged and equal to 100 ppm.

The methodology of the measurements of laminar burning velocity was described in detail earlier.[13,14] A detailed analysis and quantification of burning velocity uncertainties was reported,[14] and the overall accuracy of the burning velocity measurements was estimated to be better than ±0.8 cm/s (double standard deviation with 95% confidence level). The absolute error of the equivalence ratio φ for a methane combustible mixture with φ = 1.4 was reported to be ±0.0076.[14] The accuracy of measuring the gas flows of the fuels presented in this work was not greater than those of methane (about ±0.38%). This results in the uncertainty of the equivalence ratio for ethylene, ethane, and propane mixtures to not be higher than for methane mixtures. Concentration measurements were made using a noncooled quartz probe. It had an inlet diameter of 0.9 mm, a 6 mm external diameter, and a wall thickness of 1 mm. The sampled gas was ducted to the gas analyzers through a conditioning unit, a membrane pump, and a filter. Moisture was separated in the conditioning unit by rapid chilling at a dew point of water of 5 °C, without dissolution of gases in the liquid phase. Consequently, the measured concentrations were compared to the modeling results recalculated to a dry basis. The probe used introduces gas-dynamic and thermal perturbations into the flame that may affect the measured species concentrations. A detailed analysis of the errors associated with the probe influence on the measurements results (due to flame perturbation by the probe, conversion of the sampled gas in the probe, etc.), as well as sampling methodology were reported earlier.[15] To eliminate the probe effects in concentration measurements, no attempts to resolve spatial concentration profiles were made and sampling was performed in the

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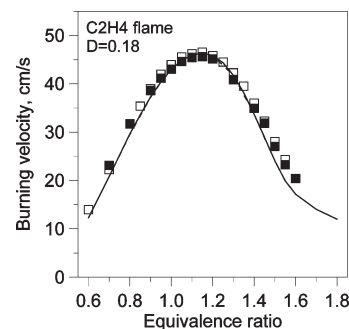
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postflame zone only. To measure the nitric oxide concentration, a Fisher Rosemount model 951A NO/NO_2 chemiluminescence analyzer was used. Before each set of measurements, the sampling and analyzing system was calibrated with a mixture of 100 ppm of NO in nitrogen. Instrumental errors of the analyzer and the calibration procedure were discussed earlier.[15] The uncertainty in the measurement of the NO concentration was evaluated[15] to be always better than 10%. Sampling was performed at heights of 10, 15, and 20 mm above the burner surface. Simultaneously with [NO] measurements, the measurements of the concentrations of CO, CO_2, and O_2 were also carried out. Comparing them with the simulated values, the range of equivalence ratios, where the flame is less affected by the ambient air entrainment, was established. The measurements of [NO] within this range only are presented in this work.

3. Modeling

The Konnov detailed reaction mechanism (Release 0.5) for the combustion of small hydrocarbons that was used for the modeling consists of 1207 reactions among 127 species.[4] This mechanism has been validated with experimental data available for the oxidation, ignition, and flame structure of hydrogen, carbon monoxide, formaldehyde, methanol, methane, ethane, propane, and some of their mixtures.[16] The Chemkin-II collection of codes,[17,18] including transport properties[19] from Sandia National Laboratories, were used. Multicomponent diffusion and thermal diffusion options were taken into account. Adaptive mesh parameters were GRAD = 0.1 and CURV = 0.5, as recommended in ref 18. Modeling of a flame structure was carried out taking into account downstream heat losses. For this purpose, the structure of the adiabatic flame was first modeled. Then, the calculated adiabatic temperature profile was modified downstream the flame front assuming a constant temperature gradient of 100 K/cm as $T_{x<0} = T_{ad}$, $T_{x>0} = T_{ad} - 100 \times x$, where x is the axial distance from the flame front in centimeters. The temperature decrease due to the heat losses to the environment with the gradient as large as 100 K/cm was observed experimentally by van Maaren et al.[20,21] These measurements were directly taken into account in approximation of the temperature profiles used in our calculations. Finally, the flame structure was simulated with the corrected temperature profile using the "burner-stabilized flame" option in the PREMIX code.

4. Results and Discussion

In the following, the experimental and numerical results obtained for the ethylene, ethane, and propane flames are presented. Measurements and modeling in the neat flames are compared with the measurements and modeling in the flames doped with NO. Similar to our previous study of methane

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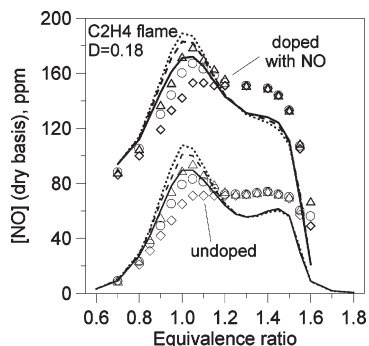
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Figure 1. Adiabatic burning velocities of $C_2H_4 + O_2 + N_2$ flames ($D = 0.18$) doped with NO and without NO additive at atmospheric pressure and initial gas temperature of 298 K. Open symbols, measurements in undoped flames;[22] filled symbols, measurements in NO-doped flames. Lines, modeling; solid lines, NO-doped flames; dashed lines, undoped flames.

flames,[3] for these fuels, the results on the burning velocity will be given first, then the concentrations of NO as functions of the equivalence ratio will be provided and, finally, in order to visualize clearly and to evaluate the conversion of NO, the dependencies of [NO] vs equivalence ratio will be presented in terms of the NO conversion ratio. The conversion ratio is determined in the same manner as it was done earlier:[3] conversion ratio $= 1 - ([NO]_{dop} - [NO]_{undop})/[NO]_{init}$, where $[NO]_{dop}$ and $[NO]_{undop}$ are the actual (wet basis) NO concentrations in doped with NO and undoped flames, respectively, $[NO]_{init}$ is the NO concentration in the initial combustion mixture corrected for changes in moles from the fresh mixture to the burnt gases ($[NO]_{init} = ([NO]_{fresh}[N_2]_{postflame})/[N_2]_{fresh}$, where NO_{fresh} is the NO concentration added to the fresh mixture, $[N_2]_{fresh}$ and $[N_2]_{postflame}$ are nitrogen concentrations in the fresh mixture and in the postflame zone, respectively, taken from the modeling data). Though this definition assumes subtraction of the two values of the same order of magnitude, thus increasing the relative uncertainty, it addresses, on the other hand, concerns on the possible modification of the sample composition in the probe. Any systematic error caused by, for example, surface reactions, would then be largely compensated. The absolute error in determining the values of the conversion ratio derived from the experiments is about ±0.06.

4.1. Ethylene Flames. Figure 1 shows adiabatic burning velocities measured in the flames of ethylene + oxygen + nitrogen mixtures seeded with NO and without additive as a function of the equivalence ratio of the mixture. Simulated burning velocities are also given in this figure. The dilution ratio of the mixture was kept at $D = 0.18$. Measurements of the burning velocity in the neat ethylene flames have been published earlier.[22] The experimental data and modeling results clearly demonstrate that within the experimental uncertainties the addition of NO does not influence the burning velocity of the flame. This is quite an expected result since it is generally accepted that small amounts of NO (of the order of 100 ppm) should not affect the burning velocities of hydrocarbons. It is important to emphasize, however, that good agreement of the present measurements in the NO-doped flames with the earlier measurements in the neat flames[22] confirms good reproducibility of the experiments and makes direct comparison of the NO formation and

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Figure 2. Concentration of NO at different distances from the burner in the postflame zone of $C_2H_4 + O_2 + N_2$ flames ($D = 0.18$) without additive[22] and doped with NO . Lines, modeling; symbols, experiment. Solid lines and diamonds, [NO] at 10 mm from the burner surface; dashed lines and circles, [NO] at 15 mm; short-dashed lines and triangles, [NO] at 20 mm.

consumption in these flames meaningful. The numerical calculations show that the chemical kinetic mechanism reproduces well the measured burning velocities of ethylene flames at least in the range of equivalence ratios in which the measurements were performed.

Measured and calculated concentrations of NO (dry basis) as functions of the equivalence ratio in C_2H_4 flames ($D = 0.18$) are presented in Figure 2. In this figure, the results for [NO] at 10, 15, and 20 mm above the burner surface in the flames without NO additive and doped with NO are given. The same tendency for the postflame concentrations of NO that was observed in methane flames[3] can be clearly seen in these ethylene flames: the increase of [NO] with the rise of the equivalence ratio from lean conditions to stoichiometry, typical maximum of [NO] at the near-stoichiometric conditions, and finally, the decrease of [NO] while moving from the stoichiometric to rich conditions. Generally, a good qualitative agreement between the experimental and numerical results can be observed over the range of equivalence ratios for the ethylene flames. However, some quantitative discrepancies between the modeling and experimental data can be distinguished. The model slightly overestimates the NO concentrations for both lean and near-stoichiometric conditions. For equivalence ratios higher than 1.2, the experimental NO concentrations exceed the simulated ones by about 15−25 ppm both in the neat[22] and doped flames.

Figure 3 shows the conversion ratios of NO in C_2H_4 flames, determined using the measured and predicted NO concentrations at different heights above the burner surface. It can be seen from this figure that modeling demonstrates a quite weak NO conversion in the lean and near-stoichiometric conditions and a significant increase of the NO conversion while moving from stoichiometric to rich mixtures. Similar results were also obtained numerically for methane flames.[3] However, contrary to the methane flames, the NO conversion in the C_2H_4 flame has a weak maximum at equivalence ratios between 0.9 and 1.05. The experimental data obtained for ethylene flames (Figure 3) show somewhat different behavior of the NO conversion ratio: in the lean and slightly rich mixtures, the NO conversion ratio is about 0.1; for the range of equivalence ratios φ from 1.05 to 1.2, it drops to the near-zero level; and finally, when $\varphi > 1.2$, it rises with increasing φ. Thus, the model predicts accurately (within the experimental uncertainties) NO conversion in the range of φ from about 0.95 to 1.3 only. A fairly high conversion of NO
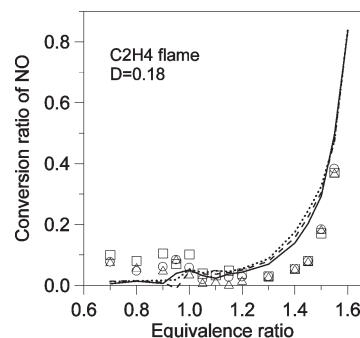
Figure 3. Conversion ratio of NO in $C_2H_4 + O_2 + N_2$ flames ($D = 0.18$) doped with NO. Lines, modeling; symbols, measurements. Solid line and diamonds, at 10 mm above the burner; dashed line and circles, at 15 mm; short-dashed line and triangles, at 20 mm.
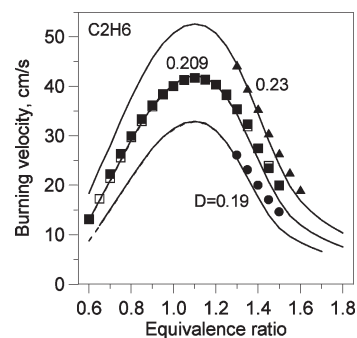

Figure 4. Adiabatic burning velocities of $C_2H_6 + O_2 + N_2$ flames with different dilution ratios doped with NO and without NO additive at atmospheric pressure and initial gas temperature of 298 K. Open symbols, measurements in undoped flames;[23] filled symbols, measurements in NO-doped flames. Lines, modeling; solid lines, NO-doped flames; dashed lines, undoped flames.

observed experimentally in the lean ethylene flame, as in the case of the methane flame,[3] is not predicted by the model. At the rich conditions, it overpredicts the experimental values.

4.2. Ethane Flames. Measured and calculated adiabatic burning velocities of ethane + oxygen + nitrogen flames doped with NO and without additive are shown in Figure 4. The results were obtained for mixtures with three dilution ratios of 0.19, 0.209, and 0.23. Similar to ethylene flames, the experimental and numerical results obtained in ethane flames demonstrate that within the experimental uncertainties the NO additive does not produce any noticeable change in the burning velocity of the flames. This is confirmed by direct comparison of the measurements performed in the neat ethane + air flames[23] with NO-doped flames with a dilution ratio of 0.209, Figure 4. The experimental data seem to favor again the model predictions at least in the range of equivalence ratios in which the measurements were performed.

Figures 5−7 present the measured and calculated concentrations of NO (dry basis) as functions of equivalence ratio in C_2H_6 flames doped with NO and without additive at 10, 15, and 20 mm above the burner surface. Figures 5−7 show the results for the mixtures with dilution ratios of 0.19, 0.209 and 0.23, respectively. Here again, the measured and calculated NO concentrations have the same behavior as was seen in the methane[3] and ethylene (see above) flames. The model
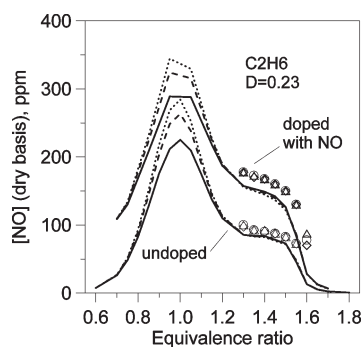
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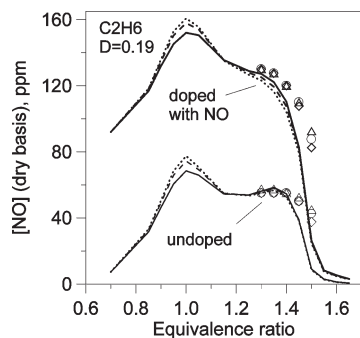
Figure 5. Concentration of NO at different distances from the burner in the postflame zone of $C_2H_6 + O_2 + N_2$ flames ($D = 0.19$) doped with NO and without additive. Lines, modeling; symbols, experiment. Solid lines and diamonds, [NO] at 10 mm from the burner surface; dashed lines and circles, [NO] at 15 mm; short-dashed lines and triangles, [NO] at 20 mm.
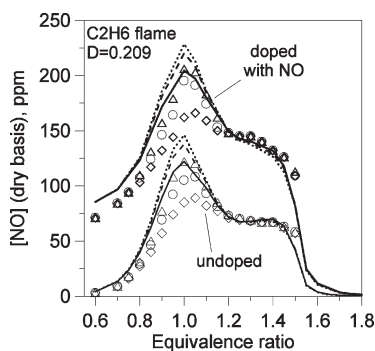

Figure 6. Concentration of NO at different distances from the burner in the postflame zone of the $C_2H_6 + O_2 + N_2$ flame ($D = 0.209$) without additive[23] and doped with NO. Lines, modeling; symbols, experiment. Solid lines and diamonds, [NO] at 10 mm from the burner surface; dashed lines and circles, [NO] at 15 mm; short-dashed lines and triangles, [NO] at 20 mm.

Figure 7. Concentration of NO at different distances from the burner in the postflame zone of the $C_2H_6 + O_2 + N_2$ flame ($D = 0.23$) doped with NO and without additive. Lines, modeling; symbols, experiment. Solid lines and diamonds, [NO] at 10 mm from the burner surface; dashed lines and circles, [NO] at 15 mm; short-dashed lines and triangles, [NO] at 20 mm.

qualitatively well predicts the experimental data, however, demonstrates some quantitative discrepancies with the measurements. In the flames of the mixtures with $D = 0.209$ (Figure 6), calculated NO concentrations are a bit higher than the measured ones under the lean and near-stoichiometric conditions. In the rich flames, a quite accurate agreement between calculated and measured [NO] is observed.
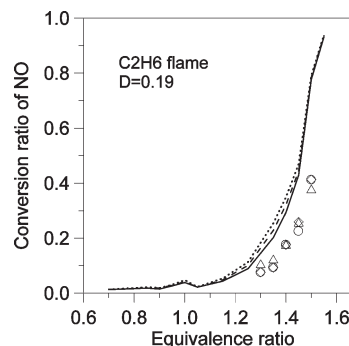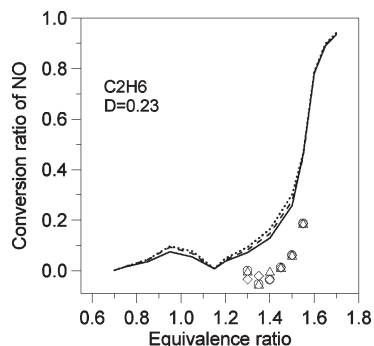

Figure 8. Conversion ratio of NO in the $C_2H_6 + O_2 + N_2$ flame ($D = 0.19$) doped with NO and without additive. Lines, modeling; symbols, experiment. Solid line and diamonds, [NO] at 10 mm from the burner surface; dashed line and circles, [NO] at 15 mm; short-dashed line and triangles, [NO] at 20 mm.
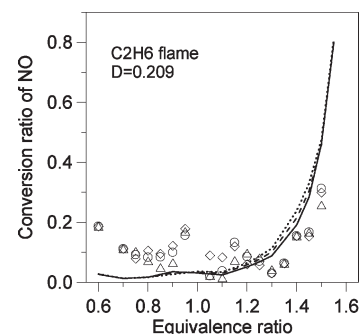

Figure 9. Conversion ratio of NO in the $C_2H_6 + O_2 + N_2$ flame ($D = 0.209$) doped with NO and without additive. Lines, modeling; symbols, experiment. Solid line and diamonds, [NO] at 10 mm from the burner surface; dashed line and circles, [NO] at 15 mm; short-dashed line and triangles, [NO] at 20 mm.

In the flames of the mixtures with $D = 0.19$ (Figure 5) and $D = 0.23$ (Figure 7), the kinetic mechanism is good in predicting NO concentrations in undoped flames within the equivalence ratios 1.3−1.4 and 1.3−1.55, respectively. However, in the corresponding NO-doped flames, the mechanism under-predicts the measured NO concentrations. In particular, for the flame with $D = 0.23$, the measured [NO] are 20−25 ppm higher than the calculated values.

Conversion ratios of NO in C_2H_6 flames determined using the measured and predicted NO concentrations (shown in Figures 5−7) at different heights above the burner surface are shown in Figures 8−10. Experimental data in the whole range of equivalence ratios are presented for the flame with $D = 0.209$ only (Figure 9). For these mixtures, one can see again that, similar to the methane and ethylene flames, the model underpredicts the values derived from the experiment in the ethane flames in the range of φ from 0.6 to about 0.95. For φ ranging from 1.05 to 1.25, the model reproduces the experimental data quite well. Under rich conditions, it slightly overestimates the experimental values. In the rich mixtures of ethane with $D = 0.19$ and 0.23 (Figures 8 and 10), the model also overpredicts the data derived from the experiments. Generally, for the ethane mixtures with all dilution ratios, the simulation gives similar dependencies of the NO conversion ratio versus the equivalence ratio. A weak maximum of the conversion ratio under the near-stoichiometric conditions is also predicted in these ethane mixtures as in the mixtures of ethylene. This maximum is more pronounced in the flame with $D = 0.23$.
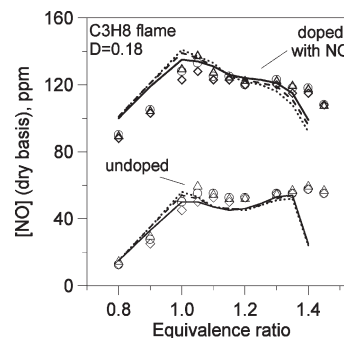
Figure 10. Conversion ratio of NO in the $C_2H_6 + O_2 + N_2$ flame ($D = 0.23$) doped with NO and without additive. Lines, modeling; symbols, experiment. Solid line and diamonds, [NO] at 10 mm from the burner surface; dashed line and circles, [NO] at 15 mm; short-dashed line and triangles, [NO] at 20 mm.
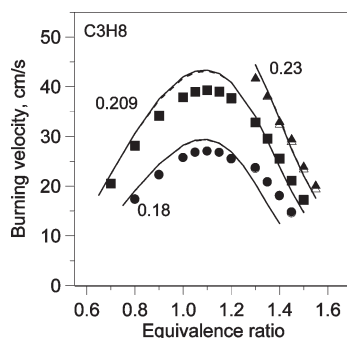

Figure 11. Adiabatic burning velocities of $C_3H_8 + O_2 + N_2$ flames with different dilution ratios doped with NO and without NO additive at atmospheric pressure and initial gas temperature of 298 K. Open symbols, measurements in NO-doped flames; filled symbols, measurements in undoped flames. Lines, modeling; solid lines, NO-doped flames; dashed lines, undoped flames.

4.3. Propane Flames. Study of formation and conversion of NO as well as its effect on the burning velocity of propane flames was performed for propane + oxygen + nitrogen mixtures with three different dilution ratios, D, of 0.18, 0.209, and 0.23. Figure 11 shows adiabatic burning velocities measured in the flames of these propane mixtures seeded with NO and without additive. Simulated burning velocities in these flames are also shown in Figure 11. It is clearly seen from the figure that NO additive has no influence on the burning velocity of the flames. The modeling results are in satisfactory agreement with the measured burning velocities of the propane flames, although the discrepancy is somewhat higher than for other fuels considered above.

Figures 12−14 show the experimental and calculated concentrations of NO (dry basis) versus the equivalence ratio in propane flames with $D = 0.18$, 0.209 and 0.23, respectively, doped with NO and without additive. In these figures, the experimental and numerical results for [NO] at 10, 15, and 20 mm above the burner surface are given. Generally, a good qualitative agreement between the experimental and numerical results is clearly observed over the range of equivalence ratios for all propane flames studied. However, some quantitative discrepancies between the modeling results and experimental data can be seen. The model well reproduces the measured NO concentrations over the range of equivalence ratios in the flames of all undoped propane mixtures (Figures 12−14). In the lean C_3H_8 mix-

Figure 12. Concentration of NO at different distances from the burner in the postflame zone of the $C_3H_8 + O_2 + N_2$ flame ($D = 0.18$) doped with NO and without additive. Lines, modeling; symbols, experiment. Solid lines and diamonds, [NO] at 10 mm from the burner surface; dashed lines and circles, [NO] at 15 mm; short-dashed lines and triangles, [NO] at 20 mm.
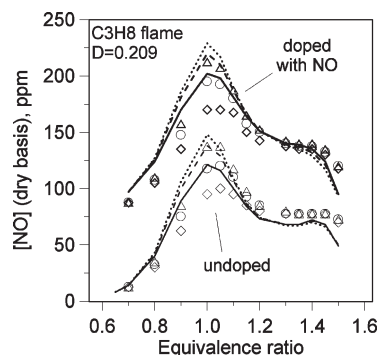

Figure 13. Concentration of NO at different distances from the burner in the postflame zone of $C_3H_8 + O_2 + N_2$ flames ($D = 0.209$) doped with NO and without additive. Lines, modeling; symbols, experiment. Solid lines and diamonds, [NO] at 10 mm from the burner surface; dashed lines and circles, [NO] at 15 mm; short-dashed lines and triangles, [NO] at 20 mm.
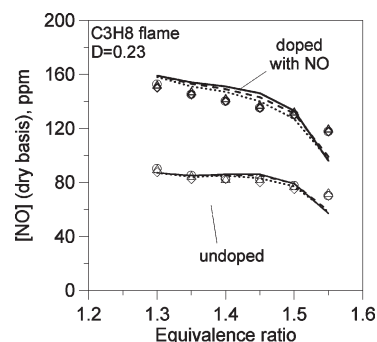

Figure 14. Concentration of NO at different distances from the burner in the postflame zone of $C_3H_8 + O_2 + N_2$ flames ($D = 0.23$) doped with NO and without additive. Lines, modeling; symbols, experiment. Solid lines and diamonds, [NO] at 10 mm from the burner surface; dashed lines and circles, [NO] at 15 mm; short-dashed lines and triangles, [NO] at 20 mm.

tures with $D = 0.18$ and $D = 0.209$ doped with NO (Figures 12 and 13), the NO concentrations determined numerically exceed the corresponding experimental values by ∼15 ppm. Under the near-stoichiometric and rich conditions, measured and calculated values of [NO] are in good agreement with each other. The model also satisfactory predicts the measured NO concentrations in rich propane mixtures with $D = 0.23$ (Figure 14).
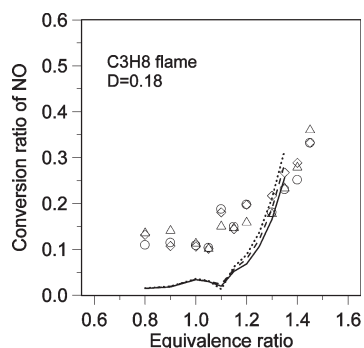
Figure 15. Conversion ratio of NO in the $C_3H_8 + O_2 + N_2$ flame (D = 0.18) doped with NO. Lines, modeling; symbols, experiment. Solid line and diamonds, [NO] at 10 mm from the burner surface; dashed line and circles, [NO] at 15 mm; short-dashed line and triangles, [NO] at 20 mm.
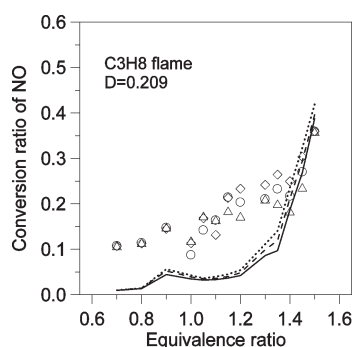
Figure 16. Conversion ratio of NO in the $C_3H_8 + O_2 + N_2$ flame (D = 0.209) doped with NO. Lines, modeling; symbols, experiment. Solid line and diamonds, [NO] at 10 mm from the burner surface; dashed line and circles, [NO] at 15 mm; short-dashed line and triangles, [NO] at 20 mm.
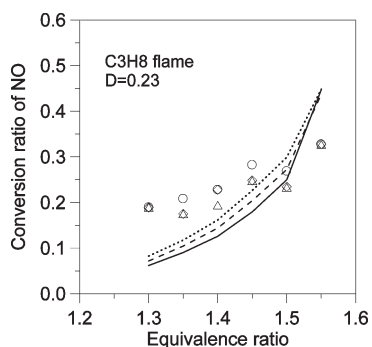
Figure 17. Conversion ratio of NO in the $C_3H_8 + O_2 + N_2$ flame (D = 0.23) doped with NO. Lines, modeling; symbols, experiment. Solid line and diamonds, [NO] at 10 mm from the burner surface; dashed line and circles, [NO] at 15 mm; short-dashed line and triangles, [NO] at 20 mm.

The conversion ratio of NO in C_3H_8 flames derived from the measured and predicted NO concentrations (shown in Figures 12−14) at different heights above the burner surface are plotted in Figures 15−17. In a wide range of equivalence ratios, the experimental and modeling data are presented for mixtures with two dilution ratios: for D = 0.18, from 0.8 to 1.45, and for D = 0.209, from 0.7 to 1.5, respectively. For these propane mixtures, one can see again that similar to what was observed for other fuels (methane, ethylene, ethane) under the near-stoichiometric and lean conditions,

the calculated consumption of the nitric oxide originally present in the fresh mixtures is not as high as it is observed in the measurements. Under the rich conditions, measured and simulated conversion ratio values of NO quantitatively agree with each other for all three mixtures.

5. Conclusions

Burning velocity and probe sampling measurements of the concentrations of nitric oxide in the postflame zone of laminar, premixed, nonstretched flames of $C_2H_4 + O_2 + N_2$, $C_2H_6 + O_2 + N_2$, and $C_3H_8 + O_2 + N_2$ doped with NO (100 ppm in N_2) and without additive were carried out. The experimental data were compared with simulation results obtained using the Konnov detailed chemical kinetic mechanism. The model was found to correctly reproduce laminar burning velocities in flames of all fuels studied.

With the use of measured and predicted NO concentrations, the conversion ratio of NO was determined. Summarizing the measured and calculated NO conversion ratios in all the flames studied, one can conclude that the model reproduces the experimental data obtained for all three fuels only qualitatively; quantitative disagreements between simulated and measured data take place. Similar to the methane flames,[3] in flames of ethylene, ethane, and propane a considerable consumption of NO (conversion ratio ∼0.1) was observed experimentally under the lean and near-stoichiometric conditions, whereas modeling showed near-zero NO conversion ratios in these mixtures. Quantitative disagreement between the calculated and measured NO conversion ratios was also found in rich ethylene and ethane flames (for φ > 1.3): the model overestimates experimental values under these conditions. A good agreement between the measurements and calculations in propane mixtures was found mostly for rich flames. In the lean and near-stoichiometric propane flames, the simulated conversion ratios are lower than those obtained from the experiment.

Therefore, combining the results obtained both in the present and in our earlier work,[3] one can conclude that the kinetic model is unable to properly predict nitric oxide conversion in the flames of methane, ethylene, ethane, and propane mixtures doped with NO. This finding indicates the important necessity of improvement of nitrogen chemistry in the kinetic mechanism. Of prime importance is clarifying the reasons causing the significant conversion of NO in fuel-lean mixtures. It also implies that, in agreement with the observations of Schulz et al.,[11] evaluating the LIF signal increase on the addition of small (0−200 ppm) quantities of NO for calibration purposes could be misleading.

The effect of lean reburning in flames is apparently nonfuel specific and is most probably common for hydrocarbons. Also, variation of the dilution ratio and thus the flame temperature has little bearing on this effect. Replacement of the main diluent, nitrogen, by argon did not significantly affect the conversion ratio of NO.[3] The role of different reactions involved in the NO conversion in flames has been analyzed, and it was concluded that some missing reactions between NO and radical species should be included in the mechanism to reproduce these general trends.[3] On the other hand, no indication of lean reburning or model deficiency was found in hydrogen flames.[24] One may assume, therefore, that

(24) Shmakov, A. G.; Korobeinichev, O. P.; Rybitskaya, I. V.; Chernov, A. A.; Knyazkov, D. A.; Bolshova, T. A.; Konnov, A. A. *Combust. Flame* **2010**, *157*, 556–565.

possible candidates could be reactions between NO and small excited radicals. Both in the Konnov mechanism[4] and in the GRI-mech.,[5] singlet methylene radical is the only representative of excited species. Other excited radicals, such as CH* should be tested for eventual model improvement, which is the objective of the authors.