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AN EXPERIMENTAL AND KINETIC CALCULATION OF THE PROMOTION EFFECT OF HYDROCARBONS ON THE NO–NO_2 CONVERSION IN A FLOW REACTOR

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Experimental and detailed chemical kinetic modeling work has been performed to investigate the role of hydrocarbon oxidation in NO–NO_2 conversion. An atmospheric pressure, quartz flow reactor was used to examine the dependence of NO oxidation to NO_2 by hydrocarbon type, reaction temperature, and residence time. The five hydrocarbons examined were methane, ethylene, ethane, propene, and propane. In the experiment, probe measurement of the species concentrations was performed in the flow reactor using a mixture of NO(20 ppm)/air/hydrocarbon(50 ppm) at residence times from 0.16 to 1.46 s and temperatures from 600 to 1100 K. In the chemical kinetic calculation, the time evolution of NO, NO_2, hydrocarbons, and reaction intermediates were evaluated for a series of the hydrocarbons and the temperatures. The chemical mechanism consisted of 639 reversible reactions and 126 species.

Experimental results indicate that, in general, ethylene and propane effectively oxidize NO to NO_2 while methane is less effective. The calculation indicates the important chemical kinetic features that control NO–NO_2 conversion for each hydrocarbon type. The dependence of NO–NO_2 conversion with hydrocarbon type and temperature is qualitatively reproduced by the calculation. The calculation indicates that all five hydrocarbons oxidize NO to NO_2 predominantly through NO + HO_2 ⇄ NO_2 + OH and that the contribution of oxidation by RO_2 and $HORO_2$ is minor. Highest effectiveness comes from hydrocarbons that produce reactive radicals (i.e., OH, O atom) that promote hydrocarbon oxidation and lead to additional HO_2 production. On the other hand, if hydrocarbons produce radicals, such as methyl and allyl, which resist oxidation by O_2, then these radicals tend to reduce NO_2 to NO. Experimental results show that the effectiveness of hydrocarbons varies appreciably with temperature and only within the low-temperature range. Propane shows the greatest NO–NO_2 conversion for the lowest temperatures. This ability is primarily due to the hydroperoxy-propyl plus O_2 reactions as indicated by the sensitivity analysis results.

Introduction

The main route to nitrogen dioxide (NO_2) formation in combustion systems is through the oxidation of nitric oxide (NO). This process was originally investigated in order to explain the high proportion of NO_2 found in NO_x emissions from the exhaust of some gas turbine engines [1]. Moreover, the understanding of the NO–NO_2 conversion mechanism is relevant to a number of issues including NO_2 emission from unflued space heaters, development of NO_x control technologies, behavior of NO/NO_2 in the atmosphere, formation and reduction chemistry of NO_x, and the probe sampling techniques for NO_x concentration measurements. Originally, the NO–NO_2 conversion was thought to proceed through the rapid oxidation of NO by oxidative radicals without much attention to the effect of fuels on the conversion [2–4]. Although, in later studies, it was revealed that the conversion was greatly promoted by small quantities of fuels such as hydrocarbons, H_2, CO, and methanol [5–9]. In our former experiment and model calculation of the NO–NO_2 conversion in the mixing of hot combustion gas with cold air and nine different fuels [6], the results indicated that NO–NO_2 conversion appeared only in the low-temperature range and showed a strong dependence on fuel type. Thus, the interaction between the NO–NO_2 reactions and the oxidation reactions of the fuel in the low-temperature range must be understood in order to explain the effect of fuel type on the NO–NO_2 conversion and consequently to predict the NO–NO_2 emission levels from combustion systems.

The objective of the present study is to compare the experimental results obtained from a flow reactor with the calculated results of a detailed chemical model in order to understand the important controlling features of hydrocarbon oxidation kinetics on

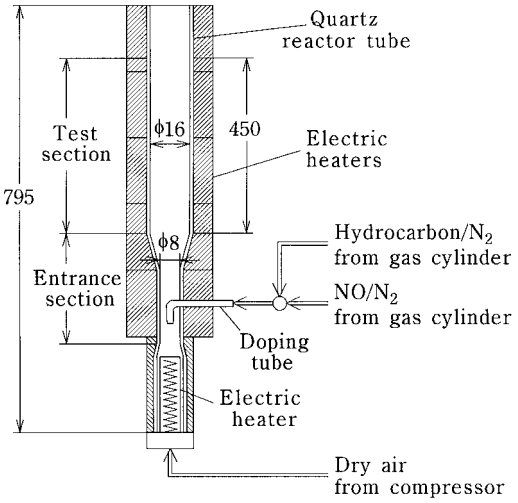

FIG. 1. Schematic of the flow reactor.

the NO–NO_2 conversion. The study is original as this effort represents a first attempt to compare the NO–NO_2 conversion dependence by hydrocarbon type and reaction temperature through a combined effort of experiment and detailed chemical kinetic modeling. Previous experiment and detailed chemical kinetic modeling studies have been conducted for methane [10,11] and ethylene [12] on NO–NO_2 conversion, and our findings confirm those previous investigations. The present study focuses on the NO–NO_2 conversion found in C_1 to C_3 hydrocarbons, that is, methane, ethylene, ethane, propene, and propane. This problem is interesting not only in the area of NO_x chemistry but also in low-temperature hydrocarbon oxidation chemistry that has been investigated extensively in studies of engine knock, cool flames, and ignition phenomena [13–15]. In the experiment, a probe measurement of species concentrations was performed in an atmospheric pressure flow reactor using a mixture of NO(20 ppm)/air/hydrocarbon (50 ppm). In the chemical kinetic calculations, the temporal evolution of NO, NO_2, hydrocarbons, and reaction intermediates for a series of hydrocarbon types and reaction temperatures is shown. The important chemical kinetic features that control the NO–NO_2 conversion for each hydrocarbon type are discussed.

Experimental

Experimental Apparatus

The experiment was performed using a constant-temperature quartz flow reactor shown schematically in Fig. 1. Dry air was supplied to an electric heater at the bottom end of the flow reactor and the air was heated to a desired reaction temperature. Just above the electric heater, an NO-hydrocarbon (balance N_2) mixture was doped as a counterflow jet into the heated air stream. In the flow reactor, the initial NO (20 ppm)/air/hydrocarbon (50 ppm) mixture flowed up through the entrance section (mostly 8 mm i.d.) and into the test section (16 mm i.d., 450 mm length) as a reacting flow at constant temperature. The types of hydrocarbons selected were methane, ethylene, ethane, propene, and propane, and the reaction temperatures were controlled from 600 to 1100 K. Nearly uniform distribution of the species concentrations and temperature across the test section was confirmed before measurements were taken. Samples were withdrawn by a quartz sampling probe at 11 axial positions (which corresponded to residence times from 0.16 to 1.46 s) in the test section. To attain iso-kinetic sampling, the sampling probe was designed to have a larger sample inlet diameter than the diameter of the downstream sample tube. The samples were analyzed by a chemiluminescent NO–NO_x analyzer continuously and by three gas chromatographs with thermal conductivity detectors and a flame ionization detector with batch method. The species detected by the gas chromatographs were oxygen, nitrogen, hydrogen, carbon monoxide, carbon dioxide, and five hydrocarbons selected for the experiment.

Experimental Results and Discussion

According to the experimental results, the NO_x concentration remains essentially constant with residence time for all the experimental conditions investigated, and thus the decrease (increase) in the NO concentration corresponds to the increase (decrease) in the NO_2 concentration. When the hydrocarbons were not doped into the mixture, the NO_2 concentration was below 1 ppm and did not vary with residence time. From these results, it is clear that only the NO–NO_2 conversion occurs within the flow reactor and that the formation of considerable levels of NO_2 is due to the role of hydrocarbon oxidation in the NO–NO_2 conversion.

The variations of the NO–NO_2 conversion with hydrocarbon type that are shown as the NO_2/NO_x ratio against the residence time are discussed at first. At the reaction temperature of 700 K, only propane promotes the NO–NO_2 conversion as shown in Fig. 2. In this case, it was found that only propane was consumed up to 30%, which resulted in the NO_2/NO_x ratio above 0.9. At 800 K, four hydrocarbons except methane promote the NO–NO_2 conversion, while, among them, ethylene and propane effectively oxidize NO to NO_2, and ethane is less effective (see Figs. 4 and 5). Although at 1000 K, all five hydrocarbons promote the NO–NO_2 conversion, and the NO_2/NO_x ratios decrease gradually in the later

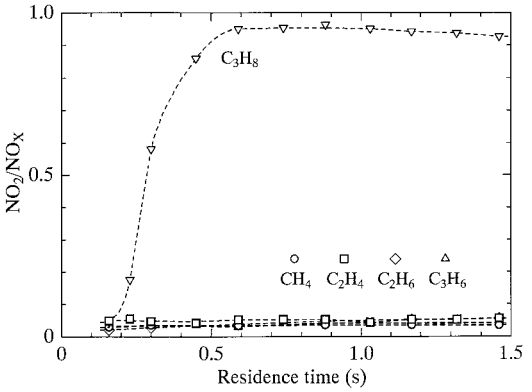

FIG. 2. NO_2/NO_x ratios against residence time obtained by the flow-reactor experiment for five hydrocarbons at 700 K.

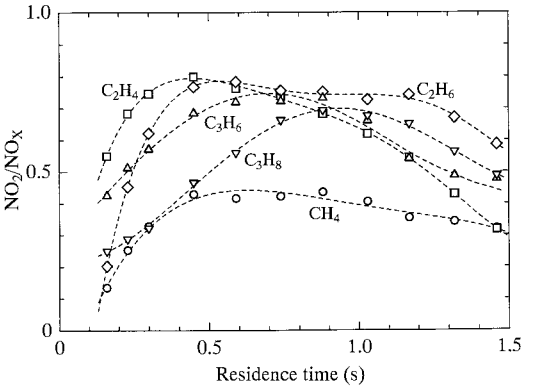

FIG. 3. NO_2/NO_x ratios against residence time obtained by the flow-reactor experiment for five hydrocarbons at 1000 K.

stage of the NO–NO_2 conversion due to the reduction of NO_2 to NO as shown in Fig. 3. In this case, it was found that the concentrations of five hydrocarbons decreased monotonically against the residence time. It is suggested from these experimental results that methane promotes the NO–NO_2 conversion most weakly and that the simple relationship is not found between the amount of hydrocarbon consumption and the level of the NO_2/NO_x ratio.

The effectiveness of hydrocarbons varies appreciably with reaction temperature and only within a low-temperature range (see Fig. 6). Propane shows the greatest NO–NO_2 conversion for the lowest temperatures, and even methane and ethane show fairly large NO–NO_2 conversion for the higher temperatures. The variations of the hydrocarbon consumption with the reaction temperature obtained in the experiment showed that the consumption was accelerated with increasing the reaction temperature.

Chemical Kinetic Calculations

Numerical Model

The numerical calculations were performed using the CHEMKIN-II/SENKIN computer programs [16,17]. The SENKIN code was used to compute the time evolution of a homogeneous reacting gas mixture in an adiabatic system at constant pressure. The detailed chemical kinetic model used in the numerical calculations was based on a hierarchical structure of hydrocarbon oxidation kinetics starting from hydrogen and building up to propane. The main portion of the detailed kinetics mechanism was taken from our previous modeling work on hydrogen [18], methane [19], ethylene [20], ethane [19], propane [21], and ethanol [22] flame chemistry. The chemical model was extended to include NO_x chemistry and was primarily taken from GRI-MECH2.11 [23], Dean and Bozzelli [24], and Atkinson [25]. The nitrogen compounds used in the mechanism are N atom, NO, NO_2, NO_3, HNO, HONO, $HONO_2$, HNO_2, HNO_3, NH, NH_2, NH_3, NNH, N_2, N_2O, CN, HCN, NCO, HCNO, HNCO, HOCN, H_2CN, HCNN, CH_3NO, CH_3NO_2, CH_3ONO, CH_3ONO_2, and $C_3H_5NO_2$. The chemical kinetic calculations performed for propane at temperatures less than ca. 800 K by the foregoing mechanism showed no fuel conversion. A low-temperature chemistry submechanism was added to the foregoing mechanism to achieve the amount of reactivity observed in the experiments. These reactions were taken from Bozzelli and coworkers [26,27] and involve the addition of molecular oxygen to hydroperoxy-propyl radicals that eventually lead to OH radical formation and chain branching. Thermodynamic properties of the chemical compounds were obtained from the CHEMKIN Thermodynamic Database [28] or calculated by group additivity techniques as described by Benson [29] and fitted to a polynomial form using THERM [30]. The complete listing of the chemical kinetic mechanism and thermodynamics used in the modeling portion of the study can be obtained from the authors [31]. The detailed chemical kinetic model consisted of 639 reversible reactions and 126 species.

Detailed Chemical Kinetic Calculations—Results

In this section, the calculated results are compared to the experimental results. The NO_2/NO_x ratio against the residence time at 800 K is shown in Fig. 4. The experiments indicate a small amount of NO is oxidized for methane and ethane, whereas the model suggests relatively little to no conversion for

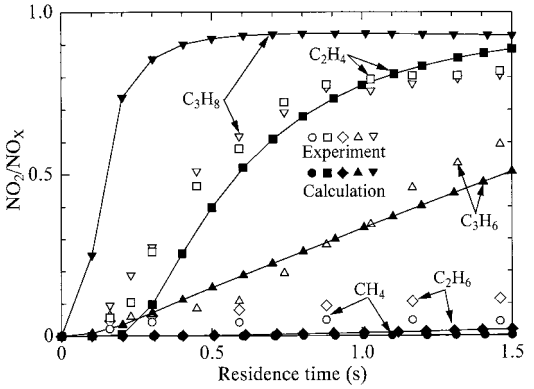

FIG. 4. Comparison between the flow-reactor experiment and the chemical kinetic calculation. NO_2/NO_x ratios against residence time for five hydrocarbons at 800 K.

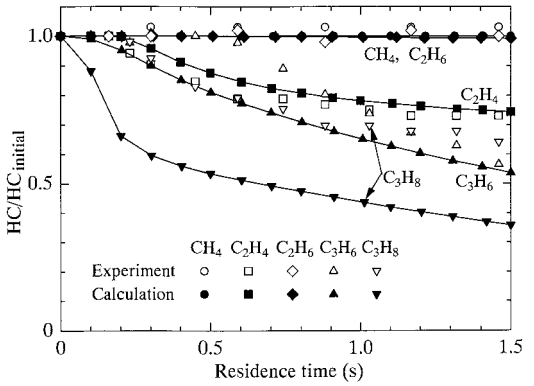

FIG. 5. Comparison between the flow-reactor experiment and the chemical kinetic calculation. Nondimensional hydrocarbon concentrations against residence time for five hydrocarbons at 800 K. (Hydrocarbon concentrations are nondimensionalized to the initial hydrocarbon concentrations.)

these fuels. The ethylene experimental data show a fairly rapid rise in NO conversion at early residence times and slowly levels out with time. The calculation shows similar behavior, although the NO_2/NO_x ratio increases a little more rapidly at longer residence times. The propene experimental data show a fairly linear increase in NO_2 formation with time that is reproduced by the model calculation. Propane exhibits nearly the same measured NO_2/NO_x profile as ethylene, although the calculation shows a greater oxidation of NO at the early residence times than indicated by the experiment. There are a number of possibilities that could account for this discrepancy. The overpredicted oxidation of NO could be due to the inadequate understanding of the propyl plus O_2 chemical activation reaction process and

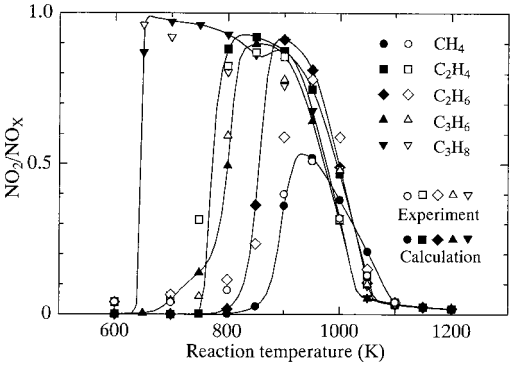

FIG. 6. Comparison between the flow-reactor experiment and the chemical kinetic calculation. NO_2/NO_x ratios at the residence time of 1.46 s against the reaction temperature for five hydrocarbons.

inaccurate thermochemical assignments to the propyl-O_2 and hydroperoxy-propyl adducts.

Figure 5 shows the hydrocarbon consumption with residence time at 800 K. The hydrocarbon concentration has been nondimensionalized to the initial hydrocarbon concentration of 50 ppm. Experimental results for methane and ethane are reproduced by the calculation and show very little hydrocarbon consumption with residence time. The experimental ethylene consumption profile is also well reproduced by the calculation. The propene experimental data show a longer induction time prior to the start of its oxidation than indicated by the calculation. At longer residence times, the propene experimental consumption profile exhibits a linear change in concentration with residence time that is a similar characteristic exhibited by the calculation. The modeling results for propane show an over oxidation of the fuel in comparison with the experimental data, and the causes for this disagreement have been previously discussed in connection to the over oxidation of NO with residence time.

The calculated change in the NO_2/NO_x ratio with temperature is compared to measurement in Fig. 6. The NO_2/NO_x ratios for five hydrocarbons are reasonably reproduced by the model. The model was able to reproduce qualitatively the low-temperature NO–NO_2 conversion behavior for propane, and the mechanism for this behavior is discussed in the next section.

Computer simulations were also performed for HO_2 and NO_2 loss within the reactor. We assumed the wall destruction of HO_2 and NO_2 as the rate-limiting case (i.e., HO_2 and NO_2 diffusion to the wall surface is fast) for HO_2 and NO_2 loss within the reactor. An HO_2 and NO_2 sticking coefficient of (no higher than) 1.0×10^{-4} and 1.0×10^{-6}, respectively, were determined as appropriate values based on these experimental measurements. Our

calculations show that these reasonable sticking coefficient values result in no loss of HO_2 and NO_2 to the reactor walls.

Detailed Chemical Kinetic Calculations—Analysis

Reaction flux calculations indicate that all five hydrocarbons oxidize NO to NO_2 predominantly through the NO + HO_2 ⇄ NO_2 + OH mechanism for the operating conditions examined in this study. Alkyl, alkenyl, or hydroxyalkyl plus molecular oxygen addition and subsequent stabilization of the adduct does not produce any appreciable concentration of these peroxy species that would otherwise convert the NO to NO_2 via (RO_2 or $HORO_2$) + NO ⇄ (RO + HORO) + NO_2. This particular NO–NO_2 conversion step was found to contribute less than 15% to NO–NO_2 conversion at the lowest temperature examined. Our numerical computations strongly suggest that the effectiveness of hydrocarbon type toward NO–NO_2 conversion depends on the hydrocarbon's propensity to produce reactive radicals like OH to sustain fuel oxidation while simultaneously producing HO_2 radicals for subsequent NO–NO_2 conversion. The production source of HO_2 is determined to occur primarily through the reaction steps of Alkyl + O_2 ⇄ Olefin + HO_2 (e.g., alkyl = iC_3H_7, nC_3H_7, C_2H_5), Alkyl-O_2 ⇄ Olefin + HO_2, HCO + O_2 ⇄ CO_2 + HO_2, and H + O_2 + M ⇄ HO_2 + M for the fuels studied at one atmosphere.

Methane does not readily promote NO–NO_2 conversion in comparison to other alkane fuels as suggested in Figs. 4 and 6. This is primarily due to the slow nature of methane oxidation that produces a limited amount of HO_2 radicals and the role of methyl radicals in reducing NO_2 via CH_3 + NO_2 ⇄ CH_3O + NO. The CH_3 radical, produced predominantly from CH_4 + OH, is difficult to oxidize by molecular oxygen as direct abstraction of H atom by O_2 is ca. 62 kcal/mol endothermic, and CH_3 + O_2 ⇄ CH_3O + O has an energy barrier of ca. 30 kcal/mol [19], thereby making this reaction enthalpically unfavorable at these temperatures. Instead, methyl radical is initially oxidized by CH_3 + O_2 ⇄ CH_2O + OH. A rate constant of 3.51×10^{11} $\exp(-7368\ K/T)$ $cm^3\ mol^{-1}\ s^{-1}$ is used in the mechanism and is in agreement with Grela et al. [32]. This reaction initially sustains the early stages of methane oxidation and allows the HO_2 concentration to become established through the reaction steps of CH_2O + OH ⇄ HCO + H_2O, HCO + O_2 ⇄ CO + HO_2, CO + OH ⇄ CO_2 + H, and H + O_2 + M ⇄ HO_2 + M. The HO_2 reacts with NO to make NO_2 and OH, whereupon the OH is recycled back to oxidize additional methane, formaldehyde, and CO. The NO_2 can further oxidize methyl through CH_3 + NO_2 ⇄ CH_3O + NO. This reaction allows the net production of OH radical to increase via $CH_3O(+M)$ ⇄ CH_2O + H(+M), H + O_2 + N_2 ⇄ HO_2 + N_2, H + O_2 ⇄ OH + O, and NO + HO_2 ⇄ NO_2 + OH. As the temperature is raised, the amount of NO_2 formed increases as methane becomes further oxidized but is limited in conversion due to the slow HO_2 production rate and fast NO_2 reduction to NO by CH_3. The NO-to-NO_2 oxidation process then declines at the highest temperatures as H + O_2 ⇄ OH + O dominates over H + O_2 + M ⇄ HO_2 + M, thereby limiting HO_2 formation, and the additional O atom formed aids in NO_2 reduction via NO_2 + O ⇄ NO + O_2.

Ethylene readily promotes the conversion of NO to NO_2, as shown in Figs. 4 and 6, due to the main oxidation pathways producing HO_2 and reactive radicals like OH and O atom for further ethylene conversion to products. Ethylene is primarily consumed by the OH radical to make C_2H_3 and H_2O. The C_2H_3 is oxidized by two competing pathways [34], and the net reaction schemes can be expressed as:

$$\begin{gathered} C_2H_3 + O_2 \rightleftarrows CH_2O + HCO \\ CH_2O + OH \rightleftarrows HCO + H_2O \\ (2\times)\ HCO + O_2 \rightleftarrows CO + HO_2 \\ \hline C_2H_3 + 3O_2 + OH \rightleftarrows 2CO + H_2O + 2HO_2 \end{gathered} \quad (1)$$

$$\begin{gathered} C_2H_3 + O2 \rightleftarrows CH_2HCO + O \\ CH_2HCO + O_2 \rightleftarrows CH_2O + CO + OH \\ CH_2O + OH \rightleftarrows HCO + H_2O \\ HCO + O_2 \rightleftarrows CO + HO_2 \\ \hline C_2H_3 + 3O_2 \rightleftarrows 2CO + H_2O + HO_2 + O \end{gathered} \quad (2)$$

In reaction sequence 1, two HO_2 molecules may form per ethylene consumed, thus making this pathway effective in promoting NO to NO_2. Reaction sequence 2 is an important chain-propagating pathway that sustains ethylene oxidation and indirectly allows ethylene to convert NO to NO_2 at lower temperatures than ethane. The unique synergistic effect of reaction sequences 1 and 2 in ethylene is different from the oxidation kinetics found in ethane. In ethane, the C_2H_5 + O_2 ⇄ C_2H_4 + HO_2 reaction primarily controls radical production, and HO_2 is an unreactive radical that does not contribute to the consumption of ethane via C_2H_6 + HO_2 ⇄ C_2H_5 + H_2O_2. This limits the extent of ethane consumption, thereby constraining the rate of NO-to-NO_2 conversion in the 750–850 K temperature range. These are the important chemical kinetic differences between ethylene and ethane at the low temperatures. The highest temperatures examined in the ethylene case showed the conversion of NO to NO_2 declining for the same reasons as discussed previously for the methane case.

Ethane shows a greater NO–NO_2 conversion relative to methane as indicated in Figs. 4 and 6. This is primarily due to the ease of producing HO_2 from C_2H_5 + O_2 ⇄ C_2H_4 + HO_2 and the subsequent

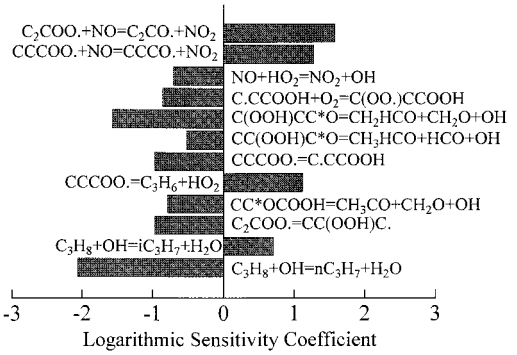

FIG. 7. Propane sensitivity analysis at 650 K. The logarithmic sensitivity coefficient determined by perturbing reaction's pre-exponential term by a factor of 1.3 and calculating the new NO value relative to the baseline, unperturbed case. A negative (positive) coefficient indicates the reaction promotes (reduces) NO–NO_2 conversion.

radical production that occurs as C_2H_4 is consumed. Ethane is primarily oxidized by OH to make C_2H_5 and H_2O. The ethyl radical reacts with O_2 and either collisionally stabilizes to the peroxy compound, $C_2H_5O_2$, or forms C_2H_4 + HO_2 through the chemically activated reactions of C_2H_5 + O_2 ⇄ C_2H_4 + HO_2 or C_2H_5 + O_2 ⇄ $C_2H_5O_2$ followed by $C_2H_5O_2$ ⇄ C_2H_4 + HO_2. The C_2H_5 + O_2 ⇄ C_2H_4 + HO_2 reaction exhibits an overall exothermicity of ca. 12 kcal/mol and has no energy barriers greater than the entrance channel's incoming energy. The favorable thermodynamics portrayed in C_2H_5 + O_2 ⇄ C_2H_4 + HO_2 opposed to CH_3 + O_2 ⇄ CH_2 + HO_2 allows for rapid HO_2 production in ethane oxidation while simultaneously consuming C_2H_5, thus limiting its participation in NO_2 reduction kinetics via C_2H_5 + NO_2 ⇄ CH_3CH_2O + NO. These are important differences when considering the NO–NO_2 promotion effect between ethane and methane fuels.

The NO–NO_2 conversion in propene oxidation lies between ethylene and ethane as shown in Figs. 4 and 6. The conversion is not as great as ethylene primarily due to NO_2 reduction via aC_3H_5 (allyl) + NO_2 ⇄ CH_2CHCH_2O + NO, yet the conversion temperature range is wider than ethane due to the greater carbon content of propene introduced into the reactive flow. Propene is initially consumed by O_2 to produce aC_3H_5 and HO_2. The NO + HO_2 ⇄ NO_2 + OH reaction provides the initial source of OH radicals for propene consumption. Propene is primarily removed by OH to make aC_3H_5 and H_2O. Allyl is a resonantly stabilized radical that is difficult to oxidize by O_2. This may be explained by noting the rate-determining energy barriers for allyl-O_2 isomerization to products typically exceeds the allyl + O_2 incoming energy by at least 12 kcal/mol [34], and the ca. 20 kcal/mol bond strength of allyl-O_2 suggests allyl-O_2 dissociation will tend to dominate over any product formation processes. Allyl's ability to resist O_2 oxidative attack allows aC_3H_5 to react with NO_2 via aC_3H_5 + NO_2 ⇄ CH_2CHCH_2O + NO analogous to CH_3 + NO_2 ⇄ CH_3O + NO. The CH_2CHCH_2O radical produced by this NO_2 reduction step then decomposes to acrolein and H atom and makes this a reactive chain sequence. The acrolein is consumed by OH to form CH_2CHCO and CHCHCHO. The CH_2CHCO decomposes to C_2H_3 + CO, and CHCHCHO reacts with O_2 to make C_2H_2 + CO + HO_2. Acrolein is also removed by O atom to produce CH_2HCO (vinoxy) and HCO radicals. Interestingly, the acrolein oxidation sequence yields radicals typically found in ethylene oxidation [33]. The consumption of C_2H_3 and CH_2HCO by O_2 yields CH_2O, HCO, and radicals like OH, O atom, and HO_2. The reaction of C_3H_6 + OH ⇄ C_3H_6OH followed by HOC_3H_6 + O_2 ⇄ $HOC_3H_6O_2$ and $HOC_3H_6O_2$ + NO ⇄ HOC_3H_6O + NO_2 is of secondary importance to NO–NO_2 conversion. Propene reactions with O atom to form C_2H_5 + HCO or CH_3CO + CH_3 products are of minor importance in the overall propene oxidation chemistry for this study, although these reactions provide additional sources of HO_2 and CH_3 radicals.

Propane shows the greatest NO–NO_2 conversion for the lowest temperatures and widest temperature range of all five fuels studied both experimentally and computationally. The ability of propane to convert NO to NO_2 at the lower temperatures is primarily due to the hydroperoxy-propyl plus O_2 reactions that lead to the production of oxygenates and two OH radicals. The OH radicals further consume propane through C_3H_8 + OH ⇄ iC_3H_7 + H_2O and C_3H_8 + OH ⇄ nC_3H_7 + H_2O. The generated propyl radicals react with O_2, and this leads to two possible general outcomes. The reaction could produce HO_2 via chemically activated routes of iC_3H_7 + O_2 ⇄ C_3H_6 + HO_2 and nC_3H_7 + O_2 ⇄ C_3H_6 + HO_2, iC_3H_7 + O_2 ⇄ $iC_3H_7O_2$ followed by $iC_3H_7O_2$ ⇄ C_3H_6 + HO_2, and nC_3H_7 + O_2 ⇄ $nC_3H_7O_2$ followed by $nC_3H_7O_2$ ⇄ C_3H_6 + HO_2, or the reaction could form the stabilized hydroperoxy-propyl (or C_3H_6OOH) adduct. The degree of reactivity exhibited in propane is essentially controlled by the competition of chemically activated reactions producing HO_2 and olefin (i.e., C_3H_6) versus the partial equilibrium established in the C_3H_7 + O_2 ⇄ $C_3H_7O_2$ ⇄ C_3H_6OOH reaction sequence as determined from reaction flux analysis and suggested by the sensitivity analysis results for NO in Fig. 7. The stabilized hydroperoxy-propyl adduct readily reacts with O_2 and establishes a partial equilibrium with $O_2C_3H_6OOH$. The $O_2C_3H_6OOH$ species undergoes internal H atom abstraction to make $HOOC_3H_5OOH$ [e.g., C(OO.)CCOOH ⇄ C(OOH)CC.OOH] followed by beta-scission of the

O–O bond leading to a ketohydroperoxide [e.g., C(OOH)CC*O] and OH radical. The ketohydroperoxides primarily undergo O–O bond scission that leads to further OH radical production, chain branching, and propane consumption. The decomposition of the ketohydroperoxides increases NO–NO_2 conversion as indicated by the negative sensitivity coefficients shown for the C(OOH)CC*O $\rightleftarrows$ $CH_2HCO + CH_2O + OH$, CC(OOH)C*O $\rightleftarrows$ $CH_3HCO + HCO + OH$, and CC*OCOOH $\rightleftarrows$ $CH_3CO + CH_2O + OH$ reactions. Sensitivity analysis shows hydroperoxy-propyl plus O_2 reactions, and the ketohydroperoxide decomposition reactions play an important promoting role in the NO–NO_2 conversion for propane.

The sensitivity analysis results for $NO + HO_2 \rightleftarrows NO_2 + OH$ showed a relatively small sensitivity coefficient in spite of its importance in promoting NO–NO_2 conversion. Reaction flux analysis indicates that this reaction dominates HO_2 consumption, and therefore, a small perturbation in the rate constant A-factor leads to a minor effect on the NO conversion. The reactions of $nC_3H_7O_2$ or $iC_3H_7O_2$ with NO exhibit larger in magnitude sensitivity coefficients than $NO + HO_2 \rightleftarrows NO_2 + OH$ because these reactions reduce the net production of alkylperoxy species and, in effect, indirectly limit OH and HO_2 radical production, thereby slowing the NO-to-NO_2 conversion rate as well.

Conclusions

The flow-reactor experiment indicated the following results:

1. In general, ethylene and propane effectively oxidize NO to NO_2 while methane and ethane are less effective.
2. High NO_2/NO_x ratios are obtained only within a relatively low reaction temperature range from 650 to 1000 K, though the hydrocarbon consumption is accelerated with increasing the reaction temperature. At higher reaction temperatures, the reduction of NO_2 to NO is observed at longer residence times.

The chemical kinetics modeling indicated the following results:

1. The kinetic calculation reproduces the experimental results qualitatively for the dependence of NO–NO_2 conversion with hydrocarbon type and reaction temperature.
2. Highest level of NO–NO_2 promotion comes from hydrocarbons that produce reactive radicals (i.e., OH, O atom) that further consume the parent hydrocarbon while at the same time producing HO_2 radicals for NO–NO_2 conversion via $NO + HO_2 \rightleftarrows NO_2 + OH$ (propane and ethylene).
3. If parent hydrocarbons (i.e., CH_4, C_3H_6) produce daughter radicals (i.e., CH_3, aC_3H_5) that are resistant to oxidation by O_2, then the daughter radicals will reduce NO_2 to NO via the reaction $R + NO_2 \rightleftarrows RO + NO$ ($R = CH_3$, aC_3H_5). This reaction limits NO-to-NO_2 conversion. The $R + NO_2 \rightleftarrows RO + NO$ reaction type was found to be important in the methane and propene studies.
4. If the parent fuel can be oxidized to C_2H_4 or C_2H_3, then NO will be readily promoted to NO_2 as reactive radicals (i.e., OH, O atom) and HO_2 are produced when C_2H_3 is oxidized by O_2 (propene and ethane).

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COMMENTS

Anders B. Bendtsen, Technical University of Denmark, Denmark. You are not using the heat of formation of CH_3O_2 suggested by Bromly [1]. Do you have a comment of the effect of using a lower heat of formation for CH_3O_2 on the initial oxidation of NO through the reactions CH_3O_2 (+ M) $\rightarrow CH_3O_2$ (+ M) and $CH_3O_2 + NO \rightarrow CH_3O + NO_2$?

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Author's Reply. Calculations were performed at 950 K for the NO (20 ppm)/air/CH_4 (50 ppm) case by reducing the CH_3O_2 heat of formation value from Tsang's recommendation of 6.7 kcal/mol to Bromly's value of 2.7 kcal/mol (Ref. [11] in the paper). We find the change in the CH_3O_2 heat of formation value results in additional CH_3 consumption via $CH_3 + O_2 \leftrightarrow CH_3O_2$ (due to the shift in equilibrium) and a slightly greater NO-to-NO_2 conversion. The greater NO-to-NO_2 conversion is primarily due to the lower CH_3 concentration that limits the amount of NO_2 reduction to NO by $CH_3 + NO_2 \leftrightarrow CH_3O + NO$ than the gain from $CH_3O_2 + NO \leftrightarrow CH_3O + NO_2$. The predominant NO-to-$NO_2$ conversion mechanism is still $NO + HO_2 \leftrightarrow NO_2 + OH$.

One additional point should be made regarding heat of formation choices. The $CH_3 + O_2$ reaction has three possible products CH_3O_2, $CH_2O + OH$, and $CH_3O + O$. The most important products for the conditions of this study are CH_3O_2 and $CH_2O + OH$, where CH_3O_2 is intermediary to $CH_2O + OH$ from the chemical activation process of $CH_3 + O_2 \leftrightarrow CH_3O_2 \leftrightarrow CH_2OOH \leftrightarrow CH_2O + OH$. Any adjustment to the CH_3O_2 heat of formation will affect the rate-limiting $CH_3O_2 \leftrightarrow CH_2OOH$ barrier height (relative to the $CH_3 + O_2$ entrance channel energy) for $CH_3 + O_2 \leftrightarrow CH_2O + OH$. A lower heat of formation for CH_3O_2 will require a faster $CH_3 + O_2 \leftrightarrow CH_2O + OH$ rate constant. This is noted by the difference in the $CH_3 + O_2 \leftrightarrow CH_2O + OH$ rate expression assignments where Marinov has $3.51 \times 10^{11} \exp(-7368\ K/T)$ $cm^3/mol/s$ while Bromly has $3.31 \times 10^{11} \exp(-4500\ K/T)$. The difference in activation energy nearly reflects the difference in CH_3O_2 heat of formation values used. Modeling agreement was better with our choice of CH_3O_2 heat of formation and $CH_3 + O_2 \leftrightarrow CH_2O + OH$ rate expression than Bromley's values. Additional work is required here.