Shock-Induced Ignition of Methane, Ethane, and Methane/Ethane Mixtures Sensitized by NO2

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Supporting Information

ABSTRACT: Ignition delay times of stoichiometric CH4/NO2/O2/Ar, C2H6/NO2/O2/Ar, and CH4/C2H6/NO2/O2/Ar mixtures are measured with a shock tube to investigate the role of NO2 in ignition of methane, ethane, and natural gas (CH4/C2H6 = 9:1). All measurements are carried out at 1016–1981 K and 5–16 atm. Different NO2 concentrations (0, 25, 50, and 75% of fuel molar concentrations) are explored. The addition of NO2 promotes considerably the ignition of methane and natural gas but moderately for ethane. In addition, the promoting effect is temperature-dependent. Four assembled models are examined against the present measurements, and an updated kinetic model is proposed and validated in comparison to the experimental data. The current model is chosen for sensitivity and reaction pathway analyses, which reveal the role of NO2 in ignition of methane, ethane, and natural gas.

1. INTRODUCTION

Understanding the influence of NO2 on combustion kinetics of hydrocarbon fuels is important to properly model combustion in internal combustion engines and gas turbines with exhaust gas recirculation, partially as a result of the presence of NOx in recirculated exhaust gas. Oxidation of hydrocarbon fuels with NOx addition has long been investigated, including H2,1−3 CH4,4−18 C2 hydrocarbons,19−21 natural gas,22−27 and higher hydrocarbons.28,29 It has been shown that even a small amount of nitrogen oxides can have a significant effect on the combustion process.

In particular, several studies focused on the sensitization effect of NOx on hydrocarbon ignition.4,15−17,26 For example, Slack and Grillo1 explored methane ignition with NOx addition under a fuel-lean condition (equivalence ratio = 0.5) over a temperature range of 1310−1790 K. Herzler and Naumann26 studied natural gas in a high-pressure shock tube in the presence of NOx (20−250 ppm) at 16 bar, 1000−1700 K, and equivalence ratios of 0.25, 0.5, and 1.0 and found a pronounced effect of NO2 on the ignition delay time. Mathieu et al.16 examined ignition of methane in a shock tube with the addition of NO2 and N2O at 1−28 atm and equivalence ratios of 0.5−2.0 and proposed a model against their experimental data. Deng et al.18 investigated the promoting effect of NO2 on methane ignition at 1.2−10 atm, 933−1961 K, and equivalence ratio of 1.0, and the molar fraction ratios of NO2/CH4 were 30:70, 50:50, and 70:30. Their shock-tube study showed that NO2 addition promotes the reactivity of methane and reduces the global activation energy at all pressures explored and the promoting effect is more pronounced at higher NO2 concentrations. With a rapid compression machine, Gersen et al.15 measured ignition delay times of stoichiometric methane, ethane, and methane/ethane mixtures doped with 100 and 270 ppm of NO2 in a temperature range of 900−1050 K and a pressure range of 25−50 bar and found that the sensitization effect of NO2 was different for methane and ethane, but no explanation was offered.

Despite previous efforts on methane and ethane ignition with the addition of NOx, the data from rapid combustion machine or shock-tube experiments is sparse, with some results to be confirmed. In particular, the cause for the difference in NOx sensitization between methane and ethane ignition is still unclear, and chemical kinetics modeling of the methane–ethane–NOx system is highly desirable to resolve this issue.

In this work, a comparative study of NOx addition effects on ignition of natural gas and its main constituents, CH4 and C2H6, is performed with a shock tube. Ignition delay times for stoichiometric CH4/NOx/O2/Ar, C2H6/NOx/O2/Ar, and CH4/C2H6/NOx/O2/Ar mixtures are measured for a wide range of temperatures (1016−1981 K) and pressures (5–16 atm). Four chemical kinetic models are examined against experimental results, and a kinetic model is proposed with updated reaction rate constants. Sensitivity and reaction pathway analyses are performed to evaluate chemical kinetics of ignition of methane, ethane, and natural gas with NO2 addition and reveal the cause for the difference in the sensitization effect between methane and ethane ignition.

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2. EXPERIMENTAL SECTION

All experiments are performed with a stainless-steel shock tube. A detailed description of this shock tube was presented previously, and we briefly introduce it here. Before each experiment, the shock tube is evacuated to below 10 Pa by a mechanical vacuum pump, and then He and the test gas mixture are injected into the driver section and the driven section, respectively. Four piezoelectric pressure transducers, located at 971, 271, 11 mm away from the shock tube endwall, are applied to measure the incident shock wave speeds. The incident shock wave speed at the endwall is determined by linearly extrapolating the measured shock wave speeds at other locations to the endwall. Without considering chemical reactions, we use the chemical equilibrium program Gaseq to calculate the temperature \( T_0 \) and pressure \( P_0 \), and incident shock wave speed at the endwall as input parameters. Moreover, the thermodynamic properties of the relevant species, selected from the default thermodynamic database of Gaseq, are also provided as input in the calculation. The gas mixture is prepared in advance in a 15 L stainless-steel tank, and the fractions of the constituent gases are determined by Dalton's law of partial pressures. The prepared gas mixture is allowed to mix and diffuse for more than 24 h to become fully homogenized. The effect of \( N_2O_i \) is not considered here given the low initial pressure in the driven section, as discussed previously.

A photomultiplier, installed at 11 mm from the shock tube endwall, is used to obtain the OH* emission through a narrowband filter centered at 307 ± 10 nm. The pressure and OH* emission signals are used to determine ignition characteristics. The ignition delay time \( \tau \) is defined as the time interval between the arrival of the incident shock wave at the endwall and the extrapolation of the maximum slope of OH* emission to the baseline, as shown in Figure 1. There is a pressure rise \( (\frac{dP}{dt} = 8\% / ms) \) before the main ignition event, caused by the interaction between the reflected shock wave and the boundary layer. The uncertainty in the ignition delay time is estimated through the standard root-sum-squares method, and the overall uncertainty is approximately 20%.

To confirm the reliability of the present shock tube facility, a comparison experiment is carried out. Figure 2 shows a comparison between our measurements and literature ignition delay times for different mixtures and pressures. The reduction increases with an increasing NO2 concentration. For example, the reductions in \( \tau \) for \( N_{25} \), \( N_{50} \), and \( N_{75} \) are 72.6, 87.0, and 96.3%, respectively at 5 atm and 1300 K, respectively (Figure 3a). At 10 atm and 1500 K (Figure 3b), reductions of 74.4, 87.2, and 92.2% are observed for \( N_{25} \), \( N_{50} \), and \( N_{75} \), respectively. At 16 atm and 1500 K (Figure 3c), \( \tau \) is reduced by 76.8% (\( N_{25} \)), 87.9% (\( N_{50} \)), and 92.5% (\( N_{75} \)). The promoting effect of NO2 shows a strong temperature dependence, and it is more pronounced at low temperatures (below 1400 K) than at high temperatures (above 1400 K).

The effect of NO2 addition on natural gas ignition is shown in Figure 4 for three different pressures (5, 10, and 16 atm). The addition of NO2 in the \( \text{CH}_4/\text{C}_2\text{H}_6/\text{NO}_2/\text{O}_2/\text{Ar} \) mixture also markedly reduces ignition delay time, and a similar observation was made by Herzler and Naumann. For instance, the reductions in \( \tau \) are 67.3%, 78.5%, and 85.6% at 5 atm and 1300 K for \( N_{25} \), \( N_{50} \), and \( N_{75} \), respectively (Figure 4a). At 10 atm and 1300 K (Figure 4b), the corresponding reductions are 61.8, 76.3, and 84.2%. At around 16 atm and 1300 K (Figure 4c), the reductions are 67.3% (\( N_{25} \)), 79.0% (\( N_{50} \)), and 84.2% (\( N_{75} \)).

3. RESULTS AND DISCUSSION

3.1. Ignition Delay Time Measurements. Ignition delay times are obtained at different NO2 concentrations and different pressures for different mixtures (Figures 3–5). Figure 3 shows that, for CH4 ignition at 5, 10, and 16 atm, NO2 addition leads to a significant reduction in \( \tau \). The reduction increases with an increasing NO2 concentration. For example, the reductions in \( \tau \) for \( N_{25} \), \( N_{50} \), and \( N_{75} \) are 72.6, 87.0, and 91.8% at 5 atm and 1500 K, respectively (Figure 3a). At 10 atm and 1500 K (Figure 3b), reductions of 74.4, 87.2, and 92.2% are observed for \( N_{25} \), \( N_{50} \), and \( N_{75} \), respectively. At 16 atm and 1500 K (Figure 3c), \( \tau \) is reduced by 76.8% (\( N_{25} \)), 87.9% (\( N_{50} \)), and 92.5% (\( N_{75} \)). The promoting effect of NO2 shows a strong temperature dependence, and it is more pronounced at low temperatures (below 1400 K) than at high temperatures (above 1400 K).

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Table 1. Mixture Compositions Investigated in the Present Study

<table>
<thead>
<tr>
<th>Mixture Number</th>
<th>( \text{CH}_4 ) (%)</th>
<th>( \text{C}_2\text{H}_6 ) (%)</th>
<th>( \text{O}_2 ) (%)</th>
<th>( \text{Ar} ) (%)</th>
<th>( \text{NO}_2 ) (%)</th>
</tr>
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<tbody>
<tr>
<td>mix 1 ( N_0 )</td>
<td>1.982</td>
<td>0.000</td>
<td>3.964</td>
<td>94.054</td>
<td>0.000</td>
</tr>
<tr>
<td>mix 2 ( N_{25} )</td>
<td>1.982</td>
<td>0.000</td>
<td>3.964</td>
<td>93.559</td>
<td>0.496</td>
</tr>
<tr>
<td>mix 3 ( N_{50} )</td>
<td>1.982</td>
<td>0.000</td>
<td>3.964</td>
<td>93.063</td>
<td>1.487</td>
</tr>
<tr>
<td>mix 4 ( N_{75} )</td>
<td>1.982</td>
<td>0.000</td>
<td>3.964</td>
<td>92.586</td>
<td>2.835</td>
</tr>
<tr>
<td>mix 5 ( N_0 )</td>
<td>0.000</td>
<td>1.133</td>
<td>3.964</td>
<td>94.904</td>
<td>0.000</td>
</tr>
<tr>
<td>mix 6 ( N_{25} )</td>
<td>0.000</td>
<td>1.133</td>
<td>3.964</td>
<td>94.620</td>
<td>0.283</td>
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<tr>
<td>mix 7 ( N_{50} )</td>
<td>0.000</td>
<td>1.133</td>
<td>3.964</td>
<td>94.337</td>
<td>0.567</td>
</tr>
<tr>
<td>mix 8 ( N_{75} )</td>
<td>0.000</td>
<td>1.133</td>
<td>3.964</td>
<td>94.053</td>
<td>0.850</td>
</tr>
<tr>
<td>mix 9 ( N_{50} )</td>
<td>1.659</td>
<td>0.184</td>
<td>3.964</td>
<td>94.192</td>
<td>0.000</td>
</tr>
<tr>
<td>mix 10 ( N_{75} )</td>
<td>1.659</td>
<td>0.184</td>
<td>3.964</td>
<td>93.731</td>
<td>0.461</td>
</tr>
<tr>
<td>mix 11 ( N_{75} )</td>
<td>1.659</td>
<td>0.184</td>
<td>3.964</td>
<td>92.810</td>
<td>0.922</td>
</tr>
<tr>
<td>mix 12 ( N_{75} )</td>
<td>1.659</td>
<td>0.184</td>
<td>3.964</td>
<td>92.810</td>
<td>1.383</td>
</tr>
<tr>
<td>mix 13 ( N_{75} )</td>
<td>1.982</td>
<td>0.000</td>
<td>3.964</td>
<td>93.954</td>
<td>0.100</td>
</tr>
<tr>
<td>mix 14 ( N_{75} )</td>
<td>1.982</td>
<td>0.000</td>
<td>3.964</td>
<td>93.856</td>
<td>0.198</td>
</tr>
</tbody>
</table>

The percentages refer to molar ratios. \( N_0 \), \( N_{25} \), \( N_{50} \), and \( N_{75} \) denote the cases where the ratios between NO2 and fuels (in percentage) are approximately 0, 25, 50, and 75%, respectively.

Figure 1. Typical pressure and OH* emission histories at 5.2 atm and 1126 K. Ignition delay time \( \tau \) is indicated.

Figure 2. Comparison of the current and literature ignition data for NO2-sensitized methane.

Figure 3. Ignition delay times at 1.87% CH4/1.87% NO2/3.71% O2/92.55% Ar at different pressures for di

Figure 4. Ignition delay times at 1.87% CH4/1.87% NO2/3.71% O2/92.55% Ar at different pressures for di
(N50), and 85.9% (N75). The NO2-induced reduction in ignition delay time for the natural gas mixture is also temperature-dependent; the promoting effect is more pronounced at low temperatures (below 1300 K).

However, a drastically different behavior is observed for ethane mixtures (mixes 5–8 in Table 1), as illustrated by Figure 5. At P = 5, 10, and 16 atm, the addition of NO2 to ethane results in only a modest reduction in \( \tau \). Specifically, at 5 atm and 1140 K (Figure 5a), the reductions in \( \tau \) are 44.2, 58.1, and 64.9%, respectively, for N25, N50, and N75. At 10 atm and 1140 K (Figure 5b), the corresponding reductions are 52.8, 64.1, and 71.4%. At around 16 atm and 1140 K (Figure 5c), the reductions are 56.5% (N25), 67.4% (N50), and 73.5% (N75). The addition of NO2 to C2H6 has more pronounced effects at
low temperatures (below 1200 K) than at high temperatures (over 1200 K), and the difference in reductions between low and high temperatures increases with increasing pressure. However, in comparison to methane, the addition of NO$_2$ to ethane has only a modest effect on the ignition delay time. The influence of the pressure on ignition delay time reduction is weak (see Figures S1−S3 of the Supporting Information).

As motivated by a recent work, we also examine the effect of NO$_2$ concentrations (0−14865 ppm) on CH$_4$ ignition at 10 atm, and the result is shown in Figure 6a. The NO$_2$ addition leads to a significant reduction in the ignition delay time, consistent with a previous study. Because the current updated model (see details in section 3.3) reproduces the experimental results, we present a plot of simulated ignition delay times (on the logarithmic scale, log$_{10}$τ) as a function of the NO$_2$ concentration at 10 atm and different temperatures (Figure 6b). In the log$_{10}$τ versus concentration plot, two linear segments can be identified, separated at 2500 ppm. At lower concentrations (below 2500 ppm), increasing the NO$_2$ concentration results in a rapid reduction in ignition delay times, but this effect becomes weakened at higher concentrations (2500−14865 ppm).

3.2. Kinetic Model Evaluation. The chemical reaction kinetics in the post-reflected-shock region are simulated with Senkin in the Chemkin II package. Given the influence of boundary layers, the VTIM method (i.e., volume as a function of time) is applied to the cases where the ignition delay time is longer than 0.7 ms and a pressure rise rate of 8%/ms is used. A calculated ignition delay time is the interval between time zero and the instant defined at the temperature inflection point on an OH production curve, consistent with the experimental definition.

The data presented in this work are compared to the predictions by Aramco Mech 1.3 with four NO$_x$ submodels, denoted as Aramco-K by Konnov et al., Aramco-G by Gersen et al., Aramco-M by Mathieu et al., and Aramco-Y by Ye et al. The NO$_x$ submodel of Aramco-K consists of 36 species and 453 reactions, which was developed on the basis of in-flame NO$_x$ formation and reburning and validated against experiments on different substances. The NO$_x$ submodel of Aramco-
G includes 66 species and 479 reactions and is based on Rasmussen et al.38 The NO\textsubscript{x} submodel of Aramco-M involves 36 species and 305 reactions. The NO\textsubscript{x} submodel of Aramco-Y is based on Aramco-M, with the following amendment: the rate constant of reaction CH\textsubscript{3} + NO\textsubscript{2} ⇔ CH\textsubscript{3}O + NO is a factor of 1.5 smaller than that by Glaborg et al.39

The predicted ignition delay times are compared to our measurements in Figures 7−9. For CH\textsubscript{4} with different NO\textsubscript{2} additions (Figure 7), the measured ignition delay times at 10 atm are compared to the predictions of the four assembled models. The differences between the model predictions are small, and these four models underpredict the ignition delay time at temperatures over 1250 K. For N\textsubscript{2}O\textsubscript{5}, the Aramco-M model shows the best prediction at temperatures below 1250 K. For CH\textsubscript{4}/C\textsubscript{2}H\textsubscript{6} with different NO\textsubscript{2} additions (Figure 8), the four models underestimate the ignition delay time at over 1350 K. However, the Aramco-G, Aramco-M, and Aramco-Y models show better predictions at temperatures below 1350 K. For C\textsubscript{2}H\textsubscript{4} with different NO\textsubscript{2} additions (Figure 9), the differences between the predictions by these models are pronounced, in contrast with the cases of CH\textsubscript{4} and CH\textsubscript{4}/C\textsubscript{2}H\textsubscript{6}. Aramco-M and Aramco-Y underpredict the ignition delay time considerably, while Aramco-K and Aramco-G show appreciable overestimation.

To better predict the ignition delay time for CH\textsubscript{4}/NO\textsubscript{2}, C\textsubscript{2}H\textsubscript{6}/NO\textsubscript{2}, and CH\textsubscript{4}/C\textsubscript{2}H\textsubscript{6}/NO\textsubscript{2} mixtures, we choose Aramco-M as the base model for further development. The rate constants of several key reactions are updated to achieve better agreement with our measurements. Table 2 lists the modified rate constants for five selected reactions. As seen from Figures 3−9, the current updated model well reproduces our experimental data. The comparisons for pressures of 5 and 16 atm are provided in the Supporting Information.

### Table 2. List of the Updated Reaction Rate Constants

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A (cm\textsuperscript{3} mol\textsuperscript{-1} s\textsuperscript{-1})</th>
<th>$\pi$</th>
<th>$E_a$ (cal mol\textsuperscript{-1})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HONO + OH = NO\textsubscript{2} + H\textsubscript{2}O</td>
<td>1.55 × 10\textsuperscript{12}</td>
<td>0.00</td>
<td>0.0</td>
<td>40</td>
</tr>
<tr>
<td>CH\textsubscript{4} + NO\textsubscript{2} = CH\textsubscript{2}O + NO</td>
<td>2.50 × 10\textsuperscript{12}</td>
<td>0.00</td>
<td>0.0</td>
<td>41</td>
</tr>
<tr>
<td>CH\textsubscript{2}O + NO\textsubscript{2} = HCO + HONO</td>
<td>1.40 × 10\textsuperscript{-7}</td>
<td>5.64</td>
<td>922.0</td>
<td>42</td>
</tr>
<tr>
<td>NO\textsubscript{3} + NO\textsubscript{2} = NO\textsubscript{3} + NO + O\textsubscript{2}</td>
<td>2.35 × 10\textsuperscript{14}</td>
<td>0.00</td>
<td>2960.0</td>
<td>25</td>
</tr>
<tr>
<td>NO\textsubscript{2} + O = NO + O\textsubscript{2}</td>
<td>1.00 × 10\textsuperscript{14}</td>
<td>-0.52</td>
<td>0.0</td>
<td>15</td>
</tr>
</tbody>
</table>

Figure 10. Sensitivity analysis for the neat CH\textsubscript{4} mixture at (a) 1200 K and (b) 1700 K and for the N\textsubscript{2}O\textsubscript{5} mixture at (c) 1200 K and (d) 1700 K from the current model.
where $k_i$ is the pre-exponential factor of the $i$th elementary reaction and $\tau$ denotes the ignition delay time. A negative sensitivity coefficient indicates that the corresponding elementary reaction promotes ignition, while a positive value corresponds to an inhibiting effect.

Figure 10 presents the sensitivity analysis for neat methane and NO$_2$-added methane mixtures at 10 atm, and two temperatures of 1200 and 1700 K are considered. At high temperatures (1700 K; panels b and d of Figure 10), the differences in the sensitivity coefficient between these two tested mixtures are relatively small, except for the NO$_x$-related reactions: reactions R1717 (NO$_2$ + H ⇄ NO + OH) and R1773 (CH$_3$ + NO$_2$ ⇄ CH$_3$O + NO). Reactions R1 (H + O$_2$ ⇄ O + OH) and R148 (CH$_3$ + O$_2$ ⇄ CH$_3$O + OH) have the highest sensitivity coefficients for both mixtures, which produce reactive H atoms and OH radicals. The addition of NO$_2$ has opposite effects on reactions R1 and R148. The increase in the sensitivity coefficient for reaction R1 and decrease for reaction R148 are attributed to the following reasons: (i) CH$_3$ radicals react with NO$_2$ preferentially via reaction R1773, downgrading the role of CH$_3$ oxidation via reaction R148 and its self-recombination via reaction R189 [CH$_3$ + CH$_3$ (+M) ⇄ C$_2$H$_6$ (+M)], and (ii) CH$_3$ radicals are largely converted into reactive CH$_3$O radicals, which can decompose to H atoms via reaction R91 [CH$_3$O (+M) ⇄ CH$_2$O + H (+M)], accelerating reaction R1. CH$_3$ radicals can be also oxidized via reactions R144 (CH$_3$ + HO$_2$ ⇄ CH$_3$O + OH) and R147 (CH$_3$ + O$_2$ ⇄ CH$_3$O + O); thus, more reactive radicals are formed. CH$_3$ radicals play an important role in the oxidation of methane-based mixtures, and reaction R1773 decreases the contribution of reactions R144, R147, R148, and R189 in CH$_3$ radical consumption when NO$_2$ is present, assisting faster formation of reactive radicals.

At lower temperatures (1200 K; panels a and c of Figure 10), sensitivity coefficients differ considerably for neat and NO$_2$-added mixtures. With NO$_2$ addition, reaction R1 becomes the most promoting reaction instead of reaction R148, and this switch is probably due to the competition between reactions R148 and R1773, as described above. The sensitivity coefficient of reaction R31 (HCO + O$_2$ ⇄ CO + HO$_2$) increases markedly for the mixture containing NO$_2$ and becomes the third most sensitive reaction as a result of abundant HCO radicals in NO$_2$-added methane. Furthermore, reaction R1717 (NO$_2$ + H ⇄ NO + OH) is the most important reaction to inhibit fuel ignition for the mixture containing NO$_2$, with its sensitivity greater than that of reaction R189.

It is also interesting to note that the role of peroxide radicals is more important in methane oxidation at low temperatures (1200 K), similar to the study by Mathieu et al. As seen in Figure 9a, reaction R144 (CH$_3$ + HO$_2$ ⇄ CH$_3$O + OH) is the third most-sensitive reaction to promote methane ignition, whereas this reaction plays a lesser role at 1700 K. At this low
temperature, reactions R131 ($\text{CH}_4 + \text{HO}_2 \leftrightarrow \text{CH}_3 + \text{H}_2\text{O}_2$) and R1758 ($\text{NO} + \text{CH}_2\text{O}_2 \leftrightarrow \text{NO}_2 + \text{CH}_3\text{O}$) also exhibit high sensitivity, indicating abundant peroxide radicals under this condition. With the increased abundance and importance of peroxide radicals, the reaction cycle involving NO/NO$_2$ is affected greatly; thus, the NO$_2$ additive has a stronger effect on the ignition delay time at low temperatures (1200 K; Figure 3).

Similarly, the CH$_3$ radicals can be consumed at high temperatures via the following four reaction pathways (Figure 14a): (i) most of the CH$_3$ radicals react with HO$_2$ (2.4%) and NO$_2$ (57.5%) via reactions R144 and R1773 to generate CH$_3$O radicals, which can quickly decompose into formaldehyde and H atoms; (ii) reaction R75 ($\text{CH}_2\text{O} + \text{CH}_3 \leftrightarrow \text{HCO} + \text{CH}_4$) consumes the CH$_3$ radicals (7.9%) to form stable molecules HCO and CH$_4$; (iii) the CH$_3$ radicals (2.8%) react with O$_2$ via reaction R148 to form formaldehyde and OH radicals, which actually promote reactivity; and (iv) the CH$_3$ radicals undergo a self-recombination termination reaction to form stable alkane C$_2$H$_6$. However, more CH$_3$ radicals react with NO$_2$ (70.1%) via reaction R1773 at low temperatures to generate CH$_3$O radicals, which promote reactivity, and certain CH$_4$ radicals (9.8%) undergo the self-recombination termination reaction.

The sensitivity analysis for the natural gas with and without a NO$_2$ addition is shown in Figure 11. The 10 most sensitive reactions at specific pressure (10 atm) and temperature conditions (1200 and 1600 K) are presented. For the high-temperature cases (e.g., 1600 K; panels b and d of Figure 11), the results are similar for sensitive reactions with and without NO$_2$. Reaction R1 is sensitive in the two mixtures, and the corresponding sensitivity coefficients are similar. The different reaction is reaction R1773 ($\text{CH}_3 + \text{NO}_2 \leftrightarrow \text{CH}_3\text{O} + \text{NO}$), which promotes the reactivity with an overall small sensitivity coefficient. Hence, the influence of the addition of NO$_2$ to natural gas is weak at high temperatures.

At low temperatures (e.g., 1200 K; panels a and c of Figure 11), the addition of NO$_2$ has a significant effect on the ignition delay time. Only half of the reactions remain the same between the two mixtures (with and without NO$_2$). Reaction R1 is still the most sensitivity reaction; however, its sensitivity coefficient is higher in the mixture with NO$_2$ addition (Figure 11c) than that in the mixture without NO$_2$ addition (Figure 11a). Reaction R1773 becomes the second most important promoting reaction, which has a high sensitivity coefficient. Reaction R1717 is among the most inhibiting reaction as a result of its competition for H atom with reaction R1. Hence, the promoting effect of NO$_2$ addition is more pronounced at low temperatures.
For ethane with and without NO2 added, the 10 most-sensitive reactions at specific pressure (10 atm) and temperature conditions (1100 and 1450 K) are shown in Figure 12. At high temperatures (1450 K; panels b and d of Figure 12), the differences in sensitivity coefficients between these two tested mixtures are relatively small. Reactions R1 (H + O2 ⇄ O+ + OH) and R201 [C2H4 + H (+M) ⇄ C2H5] have the highest sensitivity coefficients for both mixtures, which produce reactive H atoms and OH radicals. Reactions R1, R201, R302 (C2H4 + OH ⇄ C2H3 + H2O), and R330 (C2H3 + O2 ⇄ CH2CHO + O) are the four most sensitive reactions for both neat and NO2-added ethane mixtures. The difference between these two tested mixtures is reaction R1773, which can consume CH3 radicals to form CH3O radicals. However, the sensitivity coefficient of reaction R1773 is small in the mixture with NO2 added. Hence, the effect of NO2 addition on the ignition delay time is mild at a high temperature, similar to the methane case.

At lower temperatures (1100 K; panels a and c of Figure 12), sensitivity coefficients differ considerably for neat and NO2-added mixtures. For neat ethane, the most important reaction at 1100 K is H atom abstraction reaction R196 (C2H6 + HO2 ⇄ C2H5 + H2O2), and H2O2 can decompose into OH radicals via reaction R19 [H2O2 (+M) ⇄ OH + OH (+M)] (Figure 12a). However, reaction R196 becomes insignificant (it does not appear in Figure 12b) at high temperatures. When NO2 is added (Figure 12c), reactions R1785 and R1773 show a considerable promoting effect on ethane ignition, leading to a reduced importance of reaction R196. Mathieu et al. also observed that H atom abstraction from fuel by NO2 plays an important role in low-temperature reactions (fuel oxidation). Therefore, NO2 addition has a modest effect on the reduction of the ignition delay time for ethane; however, this effect is relatively more pronounced at low temperatures than at high temperatures (Figure 5).

At high temperatures, C2H6 is mainly consumed via H atom abstraction by OH (60.2%), H (25.4%), O (6.2%), CH3 (2.4%), and NO2 (1.2%), yielding C2H5 radicals (Figure 14b). Another initial reaction channel is the thermal dissociation of ethane (4.5%), generating CH3 radicals, and...
these can further react with NO₂ (66.6%) via reaction R1773 to yield CH₃O radicals, which can be oxidized to form CH₂O radicals. Subsequently, the CH₃ radicals can be consumed via the following three reaction pathways: (i) the CH₃ radicals decompose into C₂H₄ (81.1%) radicals or react with O₂ (2.6%) to form C₂H₄ radicals; (ii) the CH₃ radicals undergo a termination reaction to form stable alkane C₃H₈ (0.8%); and (iii) the CH₃ radicals react with NO₂ (12.2%) via reaction R1784 to yield C₂H₅O, which can decompose into CH₃ and CH₂O, promoting reactivity. However, at low temperatures, more ethane reacts with NO₂ (3.1%) to form C₂H₅ radicals and more C₂H₅ radicals react with NO₂ (55.7%) to yield C₂H₅O radicals. Hence, the effect of NO₂ addition on the ignition delay time is more pronounced at low temperatures than at high temperatures.

The most sensitive reactions of neat natural gas and CH₄/C₂H₆/NO₂ mixtures at 10 atm and 1500 K are presented in Figure 13. The most important reaction for neat natural gas is the chain-branching reaction R1, which can generate reactive O atoms and OH radicals (Figure 13a), seconded by reactions R148, R195 (C₂H₄ + CH₃ ↔ C₂H₅ + CH₄), R144, and R317 (C₂H₄ + CH₃ ↔ C₂H₅ + CH₄). CH₃ radicals play an essential role for the neat natural gas mixture, indicating that the production and consumption of CH₃ radicals are critical in natural gas ignition. Reaction R128 shows the most inhibiting effect as a result of the consumption of H atoms to form relatively unreactive CH₃ radicals, competing with reaction R1.

For the mixtures with added NO₂ (Figure 13b), several NO₂-related reactions become the most important reactions. Reaction R1 is still the most sensitive reaction when NO₂ is seeded, and the sensitivity coefficient of this reaction is at a maximum for N₂5 but then decreases with an increasing NO₂ concentration (from N₂5 to N₇₅). The reason is that added NO₂ is consumed rapidly via reactions R1773 and R1717 at low NO₂ concentrations, and the production of H atoms and OH radicals can enhance reaction R1. However, for high NO₂ concentrations, added NO₂ persists for a long time before ignition, and reaction R1717 competes with reaction R1 for H atoms; therefore, the sensitivity coefficient of reaction R1 decreases. A similar observation was made in a previous study.

Reaction R1773 becomes the second most promoting reaction for the mixtures, and the sensitivity coefficient increases with an increasing NO₂ concentration. Essentially, when NO₂ is added, the CH₃ radicals react with NO₂ via reaction R1773, downgrading the importance of reactions R148, R195, R144, R317, and R189. Hence, the CH₃ radicals can form CH₂O radicals via reaction R1773, assisting faster formation of H atoms through reaction R91. In addition, reaction R1717 is among the most inhibiting reaction as a result of its competition for H atoms with reaction R1.

To further understand the kinetic features relevant to NO₂-perturbed mixtures, reaction flux analysis for the case of 20% fuel consumption is conducted with the current model at 1500 K and 10 atm, and the results are different for different gas components (Figure 15).

Figure 15a presents the reaction pathways of methane-based mixtures. For neat methane (N₀), the fuel is mainly consumed via the H atom reaction by small radicals, such as OH (60.5%), H (21.4%), O (14.8%), and HO₂ (3.0%), yielding CH₃ radicals. Subsequently, the CH₃ radicals can consume via four reaction pathways. First, most of the CH₃ radicals (47.5%) undergo a self-recombination termination reaction to form stable alkane C₂H₆. Second, the CH₃ radicals (11.3%) via reaction R75 (CH₂O + CH₃ ↔ HCO + CH₄) form stable molecules HCO and CH₄. Third, the CH₃ radicals (19.1%) react with O₂ via reaction R148 (CH₃ + O₂ ↔ CH₂O + OH) to form formaldehyde and OH radicals, which actually promote reactivity. The fourth is that CH₃ radicals (7.2%) combine with HO₂ to generate CH₃O radicals, which can quickly decompose to formaldehyde and H atoms. In the presence of NO₂ unlike the neat methane mixture, more CH₃ radicals (57.5, 75.9, and 80.7% for N₂5, N₅₀, and N₇₅ mixtures, respectively) are consumed via reaction R1773 to form CH₂O radicals, which can decompose thermally to create abundant H atoms, promoting reactivity. With an increasing NO₂ concentration, the consumption of CH₃ radicals via the
termination reactions (products of CH₄ and C₂H₆) decreases to 25.3, 9.7, and 5.1% for N₂₅, N₅₀, and N₇₅ respectively. Therefore, more reactive radicals can be generated instead of stable intermediates, increasing the reactivity of fuel mixtures. Moreover, other oxidation pathways of CH₃ radicals also become less important because of the great contribution of reaction R1773. Reaction pathway analyses of ethane-based mixtures are shown in Figure 15b. For neat ethane (N₀), ethane is mainly consumed via H atom abstraction by small radicals, such as OH (24.8%), H (56.6%), O (11.9%), and CH₃ (2.9%), yielding C₂H₄ radicals, which can further decompose to C₂H₆ (93.2%). The C₂H₄ radicals can also react with CH₃ radicals to form propane (C₃H₈), inhibiting ethane ignition. Another initial channel is the thermal dissociation of ethane (3.7%), generating CH₃ radicals, and these can be further oxidized to yield CH₂O radicals or CH₃O. For the NO₂-added mixtures, only a very few CH₃ radicals, or CH₂O. For the NO₂-added mixtures, only a very few CH₃ radicals are measured in a shock tube due to very low reactivity. However, the concentration of CH₃ radicals, which can decompose thermally to create abundant H atoms, decreases to 81.1, 71.2, and 62.5% for N₂₅, N₅₀, and N₇₅ mixtures, respectively. Therefore, reaction R1784 may restrain the promoting effect of reaction R201, inhibiting the formation of H atoms and C₂H₅. Furthermore, the CH₃ radicals (66.6, 75.3, and 79.7% for N₂₅, N₅₀, and N₇₅ mixtures, respectively) are consumed via the reaction R1773 to form CH₂O radicals, which can decompose thermally to create abundant H atoms, promoting reactivity. However, the concentration of CH₃ radicals is modicum. This may be the reason why the NO₂ additive only results in a modest promoting effect on ethane ignition (Figure 5), in contrast to its effect on methane ignition.

4. CONCLUSION

Ignition delay times of stoichiometric methane, ethane, and natural gas (CH₄/C₂H₆ = 9:1) mixed with NO₂ at 0, 25, 50, and 75% of the fuel concentrations are measured in a shock tube at 1016–1984 K and 5–16 atm. The addition of NO₂ to CH₄/O₂/Ar and CH₄/C₂H₆/O₂/Ar leads to a significant reduction in ignition delay times, and the reduction increases with an increasing NO₂ concentration. However, such a reduction is minor for C₂H₆/O₂/Ar mixtures. The NO₂ promoting effect also shows a strong temperature dependence, and the effect of the pressure on ignition delay time reduction as a result of NO₂ addition is weak. An updated mechanism is proposed and accurately reproduces the ignition delay times measured in this study.

On the basis of the updated mechanism, kinetic analyses are conducted. For CH₄ reactions R1773 (NO₂ + CH₃ ⇌ CH₂O + NO), R1717 (NO₂ + H ⇌ NO + OH), and R1758 (NO + CH₂O ⇌ NO₂ + CH₂O) exhibit higher sensitivity and the role of peroxide radicals is more important at low temperatures than high temperatures. For C₂H₆ reactions R1773 and R1785 (C₂H₅ + HONO ⇌ C₂H₃ + NO) show higher sensitivity at low temperatures than high temperatures.

The significant difference in NO₂ sensitization between methane and ethane is explained by means of the reaction pathway analysis. For CH₄, the vast majority of CH₃ radicals are combined with NO₂ to form CH₂O radicals and the self-recombination reaction of CH₃ radicals (forming C₂H₆) is restrained. Those two factors enhance the ignition of CH₄. However, for C₂H₆ only few CH₃ radicals react with NO₂ to form CH₂O radicals, which can decompose to create C₂H₄ and CH₃ radicals. Hence, the addition of NO₂ has only a modest promoting effect on ethane ignition.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.7b01632.

Data obtained in the present study, effect of the pressure on the ignition delay time, and kinetic model evaluation (PDF)

Mechanism (ZIP)

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Notes

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