High pressure oxidation of $\text{C}_2\text{H}_4/\text{NO}$ mixtures

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Abstract

An experimental and kinetic modeling study of the interaction between C$_2$H$_4$ and NO has been performed under flow reactor conditions in the intermediate temperature range (600-900 K), high pressure (60 bar), and for stoichiometries ranging from reducing to oxidizing conditions. The main reaction pathways of the C$_2$H$_4$/O$_2$/NO$_x$ conversion, the capacity of C$_2$H$_4$ to remove NO, and the influence of the presence of NO$_x$ on the C$_2$H$_4$ oxidation are analyzed. Compared to the C$_2$H$_4$/O$_2$ system, the presence of NO$_x$ shifts the onset of reaction 75-150 K to lower temperatures. The mechanism of sensitization involves the reaction HOCH$_2$CO + NO → CH$_2$OH + CH$_2$O + NO$_2$, which pushes a complex system of partial equilibria towards products. This is a confirmation of the findings of Doughty et al. [Proc. Combust. Inst. 26 (1996) 589-596] for a similar system at atmospheric pressure. Under reducing conditions and temperatures above 700 K, a significant fraction of the NO$_x$ is removed. This removal is partly explained by the reaction C$_2$H$_3$ + NO → HCN + CH$_2$O. However, a second removal mechanism is active in the 700-850 K range, which is not captured by the chemical kinetic model. With the present thermochemistry and kinetics, neither formation of nitro-hydrocarbons (CH$_3$NO$_2$, C$_2$H$_5$NO$_2$, C$_2$H$_5$NO, CHOCH$_2$NO$_2$) nor nitroso-compounds (CH$_3$NO, C$_2$H$_3$NO, C$_2$H$_5$NO, ONCH$_2$CHO, CH$_3$C(O)NO, ONCH$_2$CH$_2$OH) contribute to remove NO$_x$. 
Introduction

Ethylene is an important intermediate in the combustion of most hydrocarbon fuels. Even though the oxidation chemistry of ethylene has been studied extensively in the past, reports on the behavior at high pressure are sparse [1]. In particular, there is little knowledge about the interaction of ethylene with nitrogen oxides at elevated pressure. The presence of nitrogen oxides, even in small amounts, may have a significant impact on fuel oxidation characteristics [2]. Studies at atmospheric pressure [3-5] have revealed a mutual sensitization of the oxidation of NO\textsubscript{x} and C\textsubscript{2}H\textsubscript{4}; a result of interactions of NO\textsubscript{x} with the radical pool and with stable species. Under reducing conditions, C\textsubscript{2}H\textsubscript{4} has the capacity to reduce NO to cyanide and amine species, mainly through the HCCO+NO reaction. This chemistry has been studied at atmospheric pressure, both experimentally and by chemical kinetic modeling [6-10].

To our knowledge, interactions of C\textsubscript{2}H\textsubscript{4} and NO have not previously been studied at increased pressure, despite its relevance for, e.g., engines and gas turbines. The objective of the present work is to determine the effect of pressure on the mutual oxidation of C\textsubscript{2}H\textsubscript{4} and NO, as well as evaluate the capability of ethylene to reduce NO under high pressure conditions and temperatures below 1000 K. The work involves an experimental and kinetic modeling study, analyzing the influence of the temperature and the oxygen content as the most relevant parameters for the C\textsubscript{2}H\textsubscript{4}/NO interaction. The results of the present work are compared to data from an earlier study on oxidation of C\textsubscript{2}H\textsubscript{4} under similar high pressure conditions but in the absence of NO\textsubscript{x} [1].
Experimental

The experiments of the $\text{C}_2\text{H}_4$-$\text{NO}$ interaction have been carried out in a setup which consists of a laboratory-scale high pressure laminar flow reactor designed to approximate plug-flow. The installation is described in detail elsewhere [1, 11] and only a brief description is provided here.

The reactions take place in a tubular quartz reactor (i.d. 8 mm, o.d. 10 mm, lg. 1545 mm) enclosed in a stainless steel tube that acts as a pressure shell. A pressure control system consisting of two thermal mass flow pressure controllers automatically delivers $\text{N}_2$ to the shell-side of the reactor to obtain a pressure similar to that inside the reactor, thus avoiding devastating pressure gradients across the fragile quartz glass. The steel tube is placed horizontally in a tube oven with three individually controlled electrical heating elements that ensure an isothermal reaction zone ($\pm 5$ K) of approximately 43 cm, with steep temperature gradients toward both the inlet and outlet of the reactor tube (Fig. 1). The reactor temperature is monitored by type K thermo-couples ($\pm 2.2$ K or 0.75%) positioned in the void between the quartz reactor and the steel shell. Measured temperature profiles for the reactor have been reported elsewhere [11].

The reactant gases are premixed before entering the reactor. All gases used in the experiments are high purity gases or mixtures with certified concentrations ($\pm 2\%$ uncertainty). The system is pressurized from the feed gas cylinders. The reactor pressure
is monitored upstream of the reactor by a differential pressure transducer and controlled by a pneumatic pressure valve positioned after the reactor, which is designed for steady state operation up to 60 bars. The reactant gas mixture contains 1000 ppm of C$_2$H$_4$ and 500 ppm of NO. The amount of O$_2$ is varied to obtain the desired stoichiometry for each experiment and the balance is made up with N$_2$. A total gas flow rate of 3000 mL (STP)/min is kept constant during the experiments, leading to a gas residence time as a function solely of the reaction temperature, $t_r(s) = 8892/T$ [K].

Downstream of the reactor, the system pressure is reduced to atmospheric level through the pressure reduction valve prior to product analysis, which is conducted by a gas chromatograph, equipped with TCD and FID detectors, and a NO$_x$ chemiluminescence gas analyzer. The GC allows detection of O$_2$, CO, CO$_2$, C$_2$H$_6$, C$_2$H$_4$, C$_2$H$_2$, and CH$_4$ with an overall relative measuring uncertainty in the range ±5%. A similar accuracy is obtained for measurements of NO and NO$_2$ using the NO$_x$ chemiluminescence gas analyzer. The principle of the NO$_2$ measurement is by means of a catalytic converter that reduces NO$_2$ to NO by the use of a metal catalyst with a large surface area. However, HONO and HONO$_2$ are presumably converted to NO by the catalyst as well and thus we assume that the NO$_2$ measurement is in fact the sum of NO$_2$+HONO+HONO$_2$ concentrations. The entire downstream section is maintained at 395 K to avoid condensation of potential condensable components before product analysis. The diluted conditions ensure a low heat release during the reaction.
Chemical kinetic model

The experimental results have been analyzed in terms of a detailed chemical kinetic model for the oxidation of ethylene in the absence and presence of NO. The mechanism used for the modeling study, as well as the corresponding thermodynamic properties, was drawn from previous high-pressure work on conversion of CO/H₂/O₂/NOₓ [11], CH₄/C₂H₆/O₂ [12], and CH₄/O₂/NOₓ [13]. Recently, it was updated to describe C₂H₄ oxidation at high pressure, with particular emphasis on a number of oxygenated C₂-species important under low-temperature conditions [1]. In the present work, the subset describing the hydrocarbon/NOₓ interactions was examined. Table 1 lists thermodynamic properties for selected components, while Table 2 lists key reactions in the C₂H₄-NO oxidation scheme. The full mechanism is available as Supplemental Material. Surface reactions were not included in the model. Our previous work on CH₄ oxidation [12] indicated loss of peroxides, but the similar work on C₂H₄ [1] showed no evidence of surface reactions. Either way, surface loss of peroxides would be minimized under the present conditions since they are rapidly removed by reaction with NO.

As the high pressure and intermediate temperature C₂H₄ oxidation has already been discussed in a previous study [1], the present focus is on the C₂H₄-NOₓ interactions at similar conditions. The presence of NOₓ introduces additional initiation steps for ethylene, with a smaller barrier than the C₂H₄+O₂ reaction. A direct reaction between C₂H₄ and NO₂ forms C₂H₃ and either HONO (R2b) or HNO₂ (R3b). Also addition is
possible (R1) [15], but the formed adduct dissociates rapidly back to reactants. In the absence of direct measurements of $k_{2b}$ and $k_{3b}$, we have applied estimates for the reverse steps by analogy to the corresponding reactions of CH$_3$ [22]. After initiation, the major oxidation path for C$_2$H$_4$ involves the reaction sequence \( C_2H_4 + OH \rightarrow CH_2CH_2OH \), \( CH_2CH_2OH + O_2 \rightarrow HOCH_2CH_2OO \) [1]. Whereas the HOCH$_2$CH$_2$OO peroxide was reported mainly to undergo thermal dissociation to CH$_2$O + CH$_3$O + OH during pure C$_2$H$_4$ oxidation [1], the presence of NO opens up an oxidation path through the fast HOCH$_2$CH$_2$OO+NO reaction (R12). Due to the lack of measured values for $k_{12}$, the rate constant is estimated by analogy to the reaction between C$_2$H$_5$OO and NO.

There are a number of reactions taking place that recycle NO and NO$_2$ directly or through intermediate formation and subsequent decomposition of HNO$_2$, HONO, and HONO$_2$ [11]. Apart from formation of HONO and HONO$_2$, radicals such as CH$_3$, C$_2$H$_3$, C$_2$H$_5$, CH$_2$CHO, CH$_3$CO, and CH$_2$CH$_2$OH may conceivably take out NO$_x$. The CH$_3$+NO$_x$ and C$_2$H$_5$+NO$_x$ reactions, except for C$_2$H$_5$+NO [23], were drawn from Rasmussen et al. [13]. In the present work, we have added a number of reactions between hydrocarbon radicals and nitric oxide to the reaction mechanism, i.e. C$_2$H$_3$ + NO (R4), CH$_2$CHO + NO (R7), CH$_3$CO + NO (R9), and CH$_2$CH$_2$OH + NO (R10). Rate constants for most of these steps have been measured experimentally, though only in a limited pressure and temperature range, and extrapolation to the present conditions is uncertain. For the similar reactions involving NO$_2$ (R5, R6, R8, R11), rate constants are mostly estimates.
Thermodynamic properties for the formed adducts were estimated in the present work (Table 1). Optimized structures and vibrational frequencies (scaled by a factor of 0.99) for hydrocarbon radicals, NO, NO$_2$ and the adducts were obtained with B3LYP/6-311G(d,p) calculations. Energies were obtained via the CBS-QB3 approach of Petersson and coworkers [24], which approximates coupled cluster theory extrapolated to the complete basis set limit. These data yield the bond dissociation enthalpies of the adducts, which were combined with the thermochemistry of NO, NO$_2$ and the radicals [14] to obtain the enthalpies of formation of the adducts. The temperature-dependent entropies and heat capacities were derived from the moments of inertia and the frequencies via the rigid-rotor harmonic-oscillator approximation. For most of these components, data on the thermodynamic properties in literature are scarce. However, our calculated heat of formation for C$_2$H$_3$NO agree with the recent value by Klippenstein and coworkers ([25], personal communication) within 0.5 kcal/mol.

The subset involving reactions between the vinyl radical and nitrogen oxides warrants particular attention in the present work. There are a number of studies on the C$_2$H$_3$ + NO reaction [17, 25-29]; several of them focusing on the inhibiting role of NO in the pyrolysis of acetylene [26-28]. Recent experimental and theoretical results [17, 25] indicate that HCN + CH$_2$O (R4) is the only significant product channel near room temperature and at low pressure. Under the present conditions, we expect the reaction to proceed close to the high-pressure limit. Under these conditions, stabilization of nitrosoethylene (C$_2$H$_3$NO) might be expected, and presumably the fate of this component is important for forming reduced nitrogen species under the current conditions. We have
included a full reaction subset for C$_2$H$_3$NO, with rate constants estimated by analogy to the corresponding reactions of CH$_3$NO [22]. However, with the current thermochemistry for C$_2$H$_3$NO (Table 1), the thermal stability of this component is too low to facilitate reaction with other species. Instead C$_2$H$_3$NO dissociates rapidly, either back to reactants (C$_2$H$_3$ + NO) or to HCN + CH$_2$O. The barrier to form HCN + CH$_2$O is about 37 kcal/mol [25], 15 kcal/mol less than the barrier to C$_2$H$_3$ + NO. In the present work we have assumed that HCN + CH$_2$O is the sole product of the C$_2$H$_3$ + NO reaction, adopting the estimated high pressure limit at 700 K from Striebel et al. [17].

Studies of the C$_2$H$_3$+NO$_2$ reaction are scarce in literature. Geppert et al. [18] identified NO as the only reaction product observed for the vinyl radical reaction with NO$_2$ (R5). An attack of the vinyl radical on the N-atom site of NO$_2$ was suggested to be dominant; the nitroethylene formed could undergo isomerization to vinyl nitrite and subsequently eliminate NO and form the vinyloxy radical (CH$_2$CHO). Some stabilization of nitroethylene would be expected under the present conditions. The thermal dissociation of C$_2$H$_3$NO$_2$ has been studied theoretically [30, 31], but no rate constants have been reported. We have assumed that the C$_2$H$_3$+NO$_2$ recombination reaction (R6) proceeds with an estimated rate constant of $10^{13}$ cm$^3$ mole$^{-1}$ s$^{-1}$.

A calculation at 60 bar and 800 K for the nitrogen adducts with the current thermodynamic properties and dissociation/association kinetics indicates that the nitro species CH$_3$NO$_2$, C$_2$H$_3$NO$_2$, and C$_2$H$_5$NO$_2$, as well as the nitroso compounds CH$_3$NO, C$_2$H$_5$NO, and CH$_3$C(O)NO, have a much higher thermal stability than species such as
C₂H₃NO, ONCH₂CH₂OH, and ONCH₂CHO. It appears that reactions of NO with C₂ radicals such as C₂H₃, CH₂CHO, and CH₂CH₂OH, that may attain considerable concentrations under the present conditions, form adducts with a short lifetime, limiting their importance for removing NO.

Results and discussion

The interaction between C₂H₄ and NO, at concentrations of 1000 and 500 ppm, respectively, has been studied at 60 bar in the 600-900 K temperature range. In addition to temperature, the influence of the excess air ratio ranging from very fuel-rich (λ=0.2) to very fuel-lean conditions (λ=20) has been analyzed. The numerical predictions were obtained using the Plug Flow Reactor model of the CHEMKIN–PRO software [32].

Figure 2 compares experimental and modeling results at reducing conditions, whereas data sets obtained at stoichiometric and oxidizing conditions are presented in Figs. 3 and 4, respectively. In each case, the top graph represents the major carbon species concentration profiles (C₂H₄, CO, and CO₂), whereas the bottom graph shows the behaviour of the nitrogen oxides. Formation of HONO and HONO₂ is favoured by the high pressure of the present work, but presumably these species cannot be distinguished from NO₂ by the chemiluminescence analyzer used in the present study. In the figures, predicted NO₂ is shown as dashed lines, while HONO + HONO₂ + NO₂ are shown as solid lines.
It should be noted that a significant fraction of the fed NO is oxidized to NO$_2$ at low temperatures (600 K) prior to the C$_2$H$_4$ oxidation onset, even at reducing conditions. The conversion of NO to NO$_2$ is facilitated by the high pressure, low temperature, and the presence of O$_2$; conditions that favour the reaction NO + NO + O$_2$ $\rightleftharpoons$ NO$_2$ + NO$_2$. This reaction may occur both in the inlet and outlet sections of the reactor. Consequently, all sections where the mixture is found at high pressure need to be included for an accurate modeling prediction of NO$_x$. The simulations range from the mixing point for NO and O$_2$ prior to the reactor to the pressure reduction valve after the reactor where the pressure is reduced to atmospheric level. The entire temperature profile used as model input, based on measurements from [11], is shown in Fig. 1. It is observed in the graphs that the model predicts accurately the NO and NO$_2$ concentration values at the lowest temperature of study for all stoichiometries except for oxidizing conditions, where the NO-to-NO$_2$ conversion is overpredicted.

Under reducing conditions (Fig. 2), C$_2$H$_4$ is converted mainly to CO and CO$_2$, with minor amounts (< 25 ppm) of C$_2$H$_6$ and CH$_4$ detected at the highest temperatures. Once oxidation of C$_2$H$_4$ is initiated, around 675 K, the NO$_2$ formed in the inlet section is reduced to NO. At 700 K and above, NO is further consumed and the observed total NO$_x$ concentration is reduced about 20-25% compared to the inlet level.

The modeling predictions are generally in good agreement with the experimental results. The conversion of C$_2$H$_4$ to CO and CO$_2$, as well as the reduction of NO$_2$ to NO, is described well. However, while the model predicts well the reduction of NO at the high
temperature end, it is not able to capture the removal of NO\textsubscript{x} observed at temperatures of about 700-850 K.

Under stoichiometric and oxidizing conditions (Figs. 3 and 4), the onset of oxidation is shifted to lower temperatures, 625-650 K. The CO concentration peaks about 75 K above the onset temperature. Again, the fuel oxidation behaviour is well predicted by the model. However, for both conditions the observed CO maximum is somewhat larger and appears at higher temperatures than the model predictions.

Under stoichiometric conditions (Fig. 3), the inlet NO\textsubscript{2} is gradually reduced to NO with increasing temperature, while the higher availability of O\textsubscript{2} under oxidizing conditions (Fig. 4) leads to NO\textsubscript{2} as the main NO\textsubscript{x} compound. The NO/NO\textsubscript{2} partitioning is well predicted under stoichiometric conditions, even though total NO\textsubscript{x} is slightly underpredicted at higher temperatures. Under oxidizing conditions, the model predicts correctly that NO above 700 K is largely oxidized to NO\textsubscript{2}. The discrepancy observed at 600-700 K is attributed to an overprediction of the NO-to-NO\textsubscript{2} conversion in the reactor inlet and heating section. However, it is noteworthy that the model predicts that a considerable fraction of the NO\textsubscript{x} in this temperature range is present as HONO and HONO\textsubscript{2}, rather than NO\textsubscript{2}. Since the conversion efficiency of the analyzer catalyst for reducing HONO and HONO\textsubscript{2} to NO is presently unknown, there is some experimental uncertainty.
Except for the observed NO\textsubscript{x} reduction above 700 K under reducing and stoichiometric conditions, the modeling predictions are in good agreement with the experimental results. This indicates that the important features of the chemistry are captured by the model. Figure 5 provides an overview of the most important oxidation pathways for C\textsubscript{2}H\textsubscript{4} in the presence of NO, according to the model. For all the stoichiometries studied, the main consumption of C\textsubscript{2}H\textsubscript{4} occurs through its reaction with OH to form CH\textsubscript{2}CH\textsubscript{2}OH. Hydroxyethyl mainly recombines with O\textsubscript{2} to form hydroxyethyl peroxide and minor amounts of ethanol, even though under stoichiometric and reducing conditions also the reaction with NO\textsubscript{2} (R11) is important. The HOCH\textsubscript{2}CH\textsubscript{2}OO radical reacts with NO producing CH\textsubscript{3}OH, CH\textsubscript{2}O and NO\textsubscript{2} (R9) and to lesser extent it undergoes thermal dissociation. Under oxidizing conditions, reaction with HO\textsubscript{2} can also contribute to the HOCH\textsubscript{2}CH\textsubscript{2}OO consumption. The intermediates formed by these reactions lead to the formation of CO and CO\textsubscript{2} as the main final products of the C\textsubscript{2}H\textsubscript{4} combustion, through a reaction pathway involving CH\textsubscript{2}O and HCO.

A smaller oxidation pathway for C\textsubscript{2}H\textsubscript{4} involves C\textsubscript{2}H\textsubscript{3}, which is oxidized further by reaction with O\textsubscript{2} and NO\textsubscript{x}. This oxidation pathway allows formation of HCN, along with small amounts of CH\textsubscript{3}NO\textsubscript{2}. Under reducing conditions, the oxygen availability is decreased, and atomic hydrogen becomes more important as a chain carrier. These conditions favour a smaller oxidation pathway through C\textsubscript{2}H\textsubscript{5}. The ethyl radical reacts with NO\textsubscript{2} to form nitro-ethane. In the higher end of the temperature range, C\textsubscript{2}H\textsubscript{5} also reacts with formaldehyde to produce C\textsubscript{2}H\textsubscript{6}, which explains the small amount of C\textsubscript{2}H\textsubscript{6} detected experimentally. A minor fraction of the ethyl radicals feed into the C\textsubscript{1}
hydrocarbon pool to yield CH₄, as was observed under reducing conditions. Some of the methyl radicals formed through this pathway contribute to the formation of nitromethane.

The major oxidation pathways of N-species derived from the model under the present conditions are shown in Figure 6. As the C₂H₄ oxidation takes place, NO and NO₂ react with the radical pool to form a number of N-containing intermediates, mainly HONO and HONO₂, and, to a lesser extent, HCN, C₂H₅NO₂ and CH₃NO₂. HONO is formed mainly by the CH₂O+NO₂ reaction, and under oxidizing conditions, also by reaction of NO₂ with HO₂. Subsequently it is consumed, mainly by its self reaction. HONO₂ is formed entirely by the NO₂+OH addition. Since HONO₂ consumption reactions are generally slow according to the model, this compound tends to accumulate until it dissociates thermally at higher temperatures.

The C₂H₃ + NO reaction (R4) can explain the removal of NO under reducing conditions above 850 K, where the vinyl radical is formed in larger quantities. However, the model does not capture the observed NOₓ reduction in the 700-850 K range. Due to limitations in the measurement equipment, we were unable to detect any N-intermediates and thus it is not possible to conclude on the NOₓ reduction trend. However, Rasmussen et al. [13] recently reported a similar reduction in NOₓ for the CH₄/O₂/NOₓ system, increasing with pressure from 20 to 100 bar. The observed pressure dependence could indicate that the NO removal is initiated by formation of a thermally stable adduct. However, formation of nitro-hydrocarbons (C₂H₅NO₂, CH₃NO₂, C₂H₅NO₂) is limited by the low NO₂
concentration under the reducing conditions of Fig. 2 and, according to the model, the nitroso compounds (C₂H₃NO, CH₃NO, C₂H₅NO, CH₃C(O)NO, ONCH₂CH₂OH, ONCH₂CHO) are either not sufficiently stable above 700 K or formed in too small quantities to take out significant amounts of NOₓ. The uncertainty in the thermodynamic properties of the nitro and nitroso compounds is limited and cannot explain the shortcoming in the modelling predictions. Further work is required to resolve this issue.

Figure 7 compares the experimental results of our previous study [1] with the present work, to show the influence of the presence of NOₓ on C₂H₄ oxidation at high pressure. The high pressure facility and the experimental conditions are the same as in the current work, except for the absence of NOₓ in the reactant mixture. In the absence of NOₓ, the initiation of reaction occurs at about 750 K, independent of stoichiometry. The presence of NOₓ shifts the onset of reaction 75-150 K to lower temperatures, the shift increasing with an increase in the availability of oxygen. For stoichiometric and oxidizing conditions, a complete conversion of C₂H₄ is attained, while under reducing conditions, independently of the presence of NOₓ, almost 60% of the initial C₂H₄ is still unreacted at the highest temperature studied.

The present study confirms the mechanism of sensitization proposed by Doughty et al. [3]. They identified the major reaction pathway for oxidation of ethylene at atmospheric conditions and temperatures below 850 K and/or high [O₂] to involve OH addition to ethylene and subsequent reaction of the hydroxyethyl radical (CH₂CH₂OH), which involves a complex set of reactions in partial equilibria. If NO is present, it reacts fast
with the peroxide adduct (R12), pushing the system of equilibria towards products. However, in the absence of NO, the addition of OH to ethylene is close to equilibrium and products are formed only slowly through reactions of the hydroxyethyl radical. The higher pressures and longer reaction times of the present work push the chemistry towards lower temperatures, but the mechanism is the same as identified by Doughty et al.

Conclusions

An experimental and chemical kinetic study of the interaction between C$_2$H$_4$ and NO has been carried out under flow reactor conditions in the intermediate temperature range (600-900 K) and high pressure (60 bar), varying the stoichiometry from very fuel-rich ($\lambda=0.2$) to fuel-lean ($\lambda=20$). The mutual sensitization of C$_2$H$_4$ and NO$_x$, as well as the ability of C$_2$H$_4$ to remove NO under reducing conditions, has been investigated. A comparison with our earlier high pressure work on the C$_2$H$_4$/O$_2$ system [1] shows that the presence of NO$_x$ shifts the onset of reaction 75-150 K to lower temperatures, the shift increasing with an increase in the availability of oxygen. Under reducing conditions and temperatures above 700 K, a significant fraction of the NO$_x$ is removed, up to 28% compared to the inlet level.

Modeling predictions with a detailed chemical kinetic model are generally in good agreement with the experimental results, except under reducing conditions where the observed removal of NO$_x$ is not explained by the model. The mechanism of sensitization
for the mutual oxidation of C$_2$H$_4$ and NO is attributed to the ability of NO to react rapidly with peroxides. The major oxidation path for C$_2$H$_4$ involves the reaction sequence C$_2$H$_4$ +OH $\rightleftharpoons$ CH$_2$CH$_2$OH, CH$_2$CH$_2$OH + O$_2$ $\rightleftharpoons$ HOCH$_2$CH$_2$OO. The presence of NO facilitates conversion of the peroxide through the reaction HOCH$_2$CH$_2$OO + NO → CH$_2$OH + CH$_2$O + NO$_2$, pushing the system of partial equilibria towards products. This is a confirmation of the findings of Doughty et al. [3] for a similar system at atmospheric pressure.

A number of possibilities for removal of NO under reducing conditions has been investigated. The reaction C$_2$H$_3$ + NO $\rightarrow$ HCN + CH$_2$O is active in removing NO above 850 K. However, a second removal mechanism is active in the 700-850 K range, which is currently not identified. With the present thermochemistry and kinetics, neither formation of nitro-hydrocarbons (CH$_3$NO$_2$, C$_2$H$_3$NO$_2$, C$_2$H$_5$NO$_2$, CHOCH$_2$NO$_2$) nor nitroso-compounds (CH$_3$NO, C$_2$H$_3$NO, C$_2$H$_5$NO, ONCH$_2$CHO, CH$_3$C(O)NO, ONCH$_2$CH$_2$OH) contributes to remove NO$_x$.

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References


Table 1. Thermodynamic properties of selected species in the reaction mechanism. Units are kcal mol$^{-1}$ for $H$, and cal mol$^{-1}$ K$^{-1}$ for $S$ and $C_p$. Temperature ($T$) range is in K.

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Table 2. Selected reactions from the C$_2$H$_4$-NO high pressure subset. Parameters for use in the modified Arrhenius expression $k = AT^b \exp(-E/(RT))$. Units are mol, cm, s, cal.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A$</th>
<th>$n$</th>
<th>$E$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. C$_2$H$_4$ + NO = CH$_3$CH$_2$NO</td>
<td>9.4E11</td>
<td>0.000</td>
<td>14000</td>
<td>[15] est</td>
</tr>
<tr>
<td>2. C$_2$H$_4$ + HONO = C$_2$H$_4$ + NO$_2$</td>
<td>8.1E05</td>
<td>1.870</td>
<td>5504</td>
<td>$k_{CH3+HONO}$ [16]</td>
</tr>
<tr>
<td>3. C$_2$H$_4$ + HNO$_2$ = C$_2$H$_4$ + NO$_2$</td>
<td>8.1E05</td>
<td>1.870</td>
<td>4838</td>
<td>$k_{CH3+HNO2}$ [16]</td>
</tr>
<tr>
<td>Reaction</td>
<td>Equation</td>
<td>Rate Constant</td>
<td>Activation Energy</td>
<td>Notes</td>
</tr>
<tr>
<td>----------</td>
<td>----------</td>
<td>---------------</td>
<td>-------------------</td>
<td>-------</td>
</tr>
<tr>
<td>4.</td>
<td>C₂H₃+NO = HCN+CH₂O</td>
<td>1.1E13 0.000</td>
<td>0</td>
<td>[17], b, see text</td>
</tr>
<tr>
<td>5.</td>
<td>C₂H₃+NO₂ = CH₃CHO+NO</td>
<td>7.7E14 -0.600</td>
<td>0</td>
<td>[18]</td>
</tr>
<tr>
<td>6.</td>
<td>C₂H₃+NO₂ = C₂H₄NO₂</td>
<td>1.0E13 0.000</td>
<td>0</td>
<td>est</td>
</tr>
<tr>
<td>7.</td>
<td>CH₂CHO+NO = ONCH₂CHO</td>
<td>1.5E13 0.000</td>
<td>0</td>
<td>[19]</td>
</tr>
<tr>
<td>8.</td>
<td>CH₂CHO+NO₂ = CH₂CO+HONO</td>
<td>2.0E15 -0.680</td>
<td>1430</td>
<td>[3]</td>
</tr>
<tr>
<td>9.</td>
<td>CH₃CO+NO = CH₃C(O)NO</td>
<td>1.5E14 0.000</td>
<td>0</td>
<td>[20]</td>
</tr>
<tr>
<td>10.</td>
<td>CH₂CH₂OH+NO = ONCH₂CH₂OH</td>
<td>1.6E13 0.000</td>
<td>0</td>
<td>[21]</td>
</tr>
<tr>
<td>11.</td>
<td>CH₂CH₂OH+NO₂ = CH₂O+CH₂OH+NO</td>
<td>7.0E12 0.000</td>
<td>0</td>
<td>[3]</td>
</tr>
<tr>
<td>12.</td>
<td>HOCH₂CH₂OO+NO = CH₂OH+CH₂O+NO₂</td>
<td>1.6E12 0.000</td>
<td>-755</td>
<td>k_C₂H5OO+NO</td>
</tr>
</tbody>
</table>

a: 60 bar, 600-900 K; b: Estimate of k, 700 K
Figure 1. Temperature profiles provided for simulation in the CHEMKIN-PRO software [33]. The model input is divided in three regions. 1st region: From the mixing point of reactants to the entrance of the reactor, 1500 mm at 298 K. 2nd region: Reactor, 1050 mm at the measured temperature profiles in [11]. 3rd region: From the reactor outlet to the pressure reduction valve (1 atm), 1500 mm with a constant decrease of temperature down to 395 K.
Figure 2: Comparison of experimental (symbols) and predicted concentration profiles (lines) as a function of the reactor temperature for the reducing experiment with C$_2$H$_4$/O$_2$/NO ($\lambda = 0.2$). The inlet composition: 1000 ppm C$_2$H$_4$, 600 ppm O$_2$, 500 ppm NO; balance N$_2$. In the bottom graph, solid lines represent NO as well as the sum of NO$_2$+HONO+HONO$_2$, whereas dashed lines refer only to NO$_2$. 
Figure 3: Comparison of experimental (symbols) and predicted concentration profiles (lines) as a function of the reactor temperature for the stoichiometric experiment with C$_2$H$_4$/O$_2$/NO ($\lambda = 1$). The inlet composition: 1000 ppm C$_2$H$_4$, 3000 ppm O$_2$, 500 ppm NO; balance N$_2$. In the bottom graph, solid lines represent NO as well as the sum of NO$_2$+HONO+HONO$_2$, whereas dashed lines refer only to NO$_2$. 
**Figure 4:** Comparison of experimental (symbols) and predicted concentration profiles (lines) as a function of the reactor temperature for the oxidizing experiment with C$_2$H$_4$/O$_2$/NO ($\lambda = 20$). The inlet composition: 1000 ppm C$_2$H$_4$, 60000 ppm O$_2$, 500 ppm NO; balance N$_2$. In the bottom graph, solid lines represent NO as well as the sum of NO$_2$+HONO+HONO$_2$, whereas dashed lines refer only to NO$_2$. 
Figure 5: Main reaction pathways for C species in the C$_2$H$_4$/NO/O$_2$ interaction at the investigated conditions. The solid lines denote pathways important over the range of stoichiometries investigated, while dashed, dot and dash-dotted lines denote pathways important only under reducing-stoichiometric, reducing and oxidizing conditions respectively. The bold solid lines represent the main important pathway.
Figure 6: Main reaction pathways for N species in the C₂H₄/NO/O₂ interaction at the investigated conditions. The solid lines denote pathways important over the range of stoichiometries investigated, while dashed and dash-dotted lines denote pathways important only under reducing-stoichiometric and oxidizing conditions respectively. The bold solid lines represent the main important pathway.
Figure 7: Experimental results of the \( \text{C}_2\text{H}_4 \) concentration as a function of the presence of NO and the stoichiometry: reducing (\( \lambda=0.2 \)), stoichiometric (\( \lambda=1 \)) and oxidizing conditions (\( \lambda=20 \)). Solid symbols represent combustion without NO [1] and open symbols with the presence of a constant amount of 500 ppm of NO. Apart from the presence of NO, inlet composition, pressure, and residence time are the same for each stoichiometry.