Experimental and modeling study of fuel interactions with an alkyl nitrate cetane enhancer, 2-ethyl-hexyl nitrate

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Colloquium:

Reaction Kinetics
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Abstract

This study investigates the autoignition behavior of two gasoline surrogates doped with an alkyl nitrate cetane enhancer, 2-ethy-hexyl nitrate (2EHN) to better understand dopant interactions with the fuels, including influences of accelerating kinetic pathways and enhanced exothermicity. A primary reference fuel (PRF) blend of n-heptane/iso-octane, and a toluene reference fuel (TRF) blend of n-heptane/iso-octane/toluene are used where the aromatic fraction of the latter is set to 20% (liquid volume), while the content of n-heptane is adjusted so that the overall reactivity of the undoped fuels is similar, e.g., Anti-Knock Index (AKI) of ~91, Cetane Number (CN) ~25. Doping levels of 0.1, 1.0 and 3.0% (liquid volume basis) are used where tests are conducted within a rapid compression machine (RCM) at a compressed pressure of 21 bar, covering temperatures from 675 to 1025 K with stoichiometric fuel-oxygen ratios at $O_2 = 11.4\%$.

At the experimental conditions, it is found that the doping effectiveness of 2EHN is fairly similar between the two fuels, though 2EHN is more effective in the aromatic blend at the lowest temperatures, while it is slightly more effective in the non-aromatic blend at intermediate temperatures. Kinetic modeling of the experiments indicates that although some of the reactivity trends can be captured using a detailed model, the extents of predicted Cetane Number enhancement by 2EHN are too large, while differences in fuel interactions for the two fuels results in excessive stimulation of the non-aromatic blend. Sensitivity analysis using the kinetic model indicates that the CH_2O and CH_3O_2 chemistry are very sensitive to the dopant at all conditions. The rate of 2EHN decomposition is only important at low temperatures where its decomposition rate is slow due to the high activation energy of the reaction. At higher temperatures, dopant-derived 3-heptyl radicals are predicted to play an important role stimulating ignition. Finally, nitrogen chemistry becomes important only at the highest doping levels, primarily through the formation of methyl and ethyl nitrite, and nitric acid.

Key Words:

rapid compression machine, cetane enhancer, alkyl nitrates, fuel interactions

1.0 Introduction

Alkyl nitrates are identified as effective fuel additives which can be used in very small quantities (e.g., 1 to 1000 ppm) to improve the ignition quality of 'low grade' fuels. Ignition quality is often designated using Cetane Number (CN) where high values, e.g., $CN > 60$, indicate very reactive fuels, such as those with significant amounts of linear paraffins, while low values, e.g., $CN < 30$, indicate less reactive fuels, such as ones with high iso-paraffinic or aromatic content. Low fuel reactivity can lead to problems in diesel combustion concerning power output, engine deposits, high emissions, rough operation, and cold starting. Fuel reactivity has also been identified as an important parameter influencing the performance and controllability of advanced combustion schemes, such as homogeneous charge compression ignition (HCCI) [1] and reactivity controlled compression ignition (RCCI) [2]. It has been suggested that fuel additives could be one way to dynamically control fuel reactivity during engine operation in order to cover a wide range of combustion modes.

Alkyl nitrates, and other cetane enhancers such as peroxides, e.g., di-tert-butyl peroxide (DTBP), are highly reactive compounds containing weak intramolecular bonds which lead to rapid decomposition at modest temperatures. This means that in practical combustors they break down early in the combustion process. Decomposition yields active chemical species; in the case of alkyl nitrates, alkyl radicals, aldehydes and nitrogen dioxide are formed. These products interact with the fuel and other gases, e.g., O_2 , to accelerate the ignition process. The early reactions often have some exothermicity and thus can provide a thermal stimulant to supplement the accelerating kinetic pathways. Alkyl nitrates are advantageous due to their low cost and chemical stability outside of the combustion chamber. Peroxides, for instance, can react with the fuel during storage resulting in increased rates of gum, varnish and sediment formation during engine operation.

Alkyl nitrates and peroxides have been investigated in fundamental experiments, as well as combustion engines, while a number of detailed theoretical and modeling studies have also been undertaken [3-17]. Single-shot spray chambers have been used [3], as have RCMs [4-6], shock tubes [7-8] and flow reactors [9]. Engine studies have utilized conventional and low temperature combustion (LTC) direct injection schemes [10-12], as

well as HCCI [13] and RCCI [14-15]. Chemical kinetic models have been developed to predict the decomposition behavior of 2EHN and DTBP [5, 16-17], and the sensitizing effects they have on some fuels of interest, e.g., n-heptane [8].

Currently however, there is still a lack of fundamental understanding regarding a number of issues related to fuel additives, including:

1. How do additives interact with fuel components (e.g., paraffins, branched alkanes, aromatics, olefins, etc.) across a range of engine operating conditions?
2. What are the influences of exothermicity and accelerating kinetic pathways?
3. Can interactions and influences be reliably predicted, along with impacts to pollutant formation?
4. Are there optimal additives that can be used across a range of operating modes, including LTC?

The objective of this study is to provide insight into these questions. Experiments and modeling are conducted where tests are performed using an RCM. Two different gasoline surrogates are used in order to discern the influence of aromatic content on the effectiveness of 2EHN, while the overall level of reactivity is similar. Gasoline surrogates are employed here as opposed to diesel ones due to the relevance of gasoline to some LTC modes [12] as well as single-fuel RCCI [14-15] where cetane enhancers are of interest, while a relevant range of doping levels is explored. Chemical kinetic models are developed and simulations conducted of the RCM experiments. Sensitivity and rate-of-production (ROP) analyses are also performed to facilitate an understanding of the mechanistic interactions.

The rest of this paper is organized as follows. First, the experimental facilities and techniques are described, after which the kinetic model and simulation framework are discussed. The results are then presented, followed by a summary and conclusions of the current work.

2.0 Experimental

Argonne's twin, opposed-piston RCM is used for this study. Its capabilities are detailed elsewhere [18], however a brief description is provided here. The reaction chamber (RC) has a 50.8 mm bore with a clearance

height at maximum compression of 26.5 mm. Creviced pistons are employed to minimize fluid dynamic effects during compression and improve post-compression charge homogeneity. The crevice volume fraction is ~14% of the RC volume. Hydraulic pistons are used to actuate compression and lock the pistons at TDC. Compression times are typically less than 20 ms. For this work, the geometric compression ratio (CR) is maintained at 14.3:1, while the effective compression ratio, which accounts for heat loss, is ~10.2:1.

Pressure histories are measured using a Kistler 601A transducer mounted flush in the RC side wall. The transducer output is conditioned by a Kistler SCP-Slim amplifier (Model 2852A12) with the data captured at 20 kHz. To minimize thermal shock effects, the diaphragm is coated with a 0.75 mm thick layer of Momentive TSE399 RTV silicon. Minimal loss in sensitivity and thus determination of the compressed conditions and ignition delay times (τ) are verified by comparing pressure rise rates during compression with data acquired using the uncoated transducer.

Liquid blends of PRF91 and TRF91 surrogates + 2EHN are prepared gravimetrically, with a relative error in doping level of $\pm 1\%$. To prepare the test mixtures, the liquid fuels are injected directly into an external 5.6 L, stainless steel mixing vessel, while the gases are manometrically delivered. An Omega PX419-100A5V transducer is used to measure the partial pressures, with relative errors in the resulting equivalence ratio (ϕ) and $\%O_2$ of $\pm 3\%$. The mixing vessel is heated to 35 C (± 5 C) to promote fuel vaporization and the complete mixture is allowed a 120 minute period to diffusively homogenize before use. For the highest doping levels the tank is heated to 50 C to ensure complete vaporization of the additive. Test gases are metered through a heated supply line into the evacuated RC until the prescribed initial pressure (P_0) is reached, where an Omega PX01C1-050AI transducer (± 0.17 kPa) is used. The RC temperature is varied using a resistive heating element wrapped around the exterior of the chamber and cylinders, and controlled by a Yokogawa UP350E PID controller. A 30 minute period is used with each temperature change to ensure thermal equilibration. After introduction into the RC, the test gas is allowed to heat and homogenize for at least 7 minutes to minimize pre-test thermal stratification and decrease variability in the experiments. This is found to be especially important for the highly doped mixtures where spurious preignition heat release is observed during tests using shorter wait times. To

improve data fidelity, the RC is frequently disassembled and cleaned. The interior walls are washed with acetone, and the reassembled RCM is placed under low vacuum, and heated to 120 C for 1 hour to remove any remaining contaminants. The mixing vessel is purged with inert gas, heated to 65 C and placed under low vacuum for 1 hour to evacuate the volume.

In the current study, high purity (99.99%) nitrogen, argon, and oxygen are used which were supplied by Airgas. The liquid fuels include: iso-octane (99.8%, Sigma-Aldrich), n-heptane (99+%, Acros Organics), toluene (99.8%, Sigma-Aldrich), and 2-ethyl-hexyl nitrate (97%, Sigma-Aldrich). The undoped TRF blend has an aromatic content of 20% (by liquid volume) with the n-paraffinic content adjusted to 12.8% achieve AKI near 91 (CN ~ 25). All mixtures use stoichiometric fuel-oxygen conditions, with the oxygen mole fraction set to 11.4%. The diluent for these tests is either pure nitrogen, or a blend of 0.25/0.75 nitrogen/argon. Significant dilution is used here to account for the substantial cetane enhancement of the doped fuels where very short ignition delay times result. 2EHN doping levels are 0.0, 0.1, 1.0 and 3.0% liquid volume basis. The highest temperatures are not covered in these tests for the 3.0% doping level due to the fuel's excessive reactivity.

The compressed temperatures are achieved by varying the initial temperature (T_0), from 25 to 100 C, as well as the diluent composition. P_0 is adjusted slightly to achieve 21 bar (± 0.3 bar) compressed pressures (P_c). Two tests are conducted at each condition to ensure repeatability, with typical ignition delay time variations near ± 1 -2 ms. The compressed temperatures (T_c) are calculated using the adiabatic core model, along with the measured pressure histories. The specific heat ratios are determined via c_p fits in the CHEMKIN database. Before calculating the temperatures, the pressure records are smoothed using a Savitzky-Golay algorithm that employs a 3rd order polynomial with a window of 20 data points.

For this study, comparisons are made using T_c of the undoped fuel mixtures, since many of the doped mixtures experience heat release during the piston compression process, as discussed in the Results section. Ignition delay times, τ , are defined as the time from the end of compression to the point of rapid pressure rise associated with the main heat release. In the case of two stage ignition, 1st stage ignition is defined as the time from end of compression to the first distinguishable pressure rise, i.e., a peak in dP/dt . The end of compression

is defined by the peak in pressure for a non-reactive, undoped mixture, i.e., with O₂ replaced by N₂, where the reactive tests are time-shifted to in order correspond with the non-reactive pressure trace, such that the reactive and non-reactive pressures are assumed to be equal at a CR of 4:1. This procedure is undertaken to reduce measurement uncertainties for conditions where substantial heat release occurs during compression, and results in some variability, e.g., ± 0.25 ms, in the measured delay times, but ensures consistency between all of the tests. Ignition delay times shorter than 1 ms are discarded. Compiled ignition times are provided in the Supplementary Material.

3.0 Modeling

Two kinetic models are used here which consist of a base fuel mechanism, a sub-mechanism for the additive, and a sub-mechanism for the nitrogen chemistry. The fuel mechanism is the Lawrence Livermore National Laboratory (LLNL) detailed gasoline surrogate model, which includes decomposition and interaction pathways for four fuel components including n-heptane, iso-octane, toluene and pentene [19-21]. The sub-mechanism for the additive, 2EHN, is based on the work of Bornemann et al. [17]. In this 2EHN decomposes in two steps. First, the interior O-N bond is cleaved to release NO₂; after this the ethyl-hexyloxy radical β -scissions into C₇H₁₅-3 and CH₂O.

Two sub-mechanisms for nitrogen chemistry are explored here, one which is a skeletal compilation and includes basic pathways for the formation and consumption of NO, N₂O and NO₂, H-atom abstractions from the surrogate fuel by NO₂, and HONO decomposition [8]. A comprehensive, detailed mechanism is also assembled that includes pathways described in GRIMech 3.0 [22], Dagaut and co-workers [23-26], Glarborg and co-workers [27-28] Faravelli and co-workers [29], Battin-Leclerc and co-workers [30], and Naik and co-workers [31]. In particular, reactions are included to describe interactions with nitrous and nitric acid (HONO, HONO₂), hydrogen cyanide (HCN) and others, along with various fuel-specific interactions. NO_x reactions with fuel-derived molecules (RH) are summarized as follows: $\text{RH} + \text{NO} = \text{R} + \text{HNO}$, $\text{RH} + \text{NO}_2 = \text{R} + \text{HONO}$, $\text{R} + \text{NO} = \text{olefin} + \text{HNO}$, $\text{R} + \text{NO} = \text{RNO}$, $\text{R} + \text{NO}_2 = \text{RNO}_2$, $\text{RO}_2 + \text{NO} = \text{RO} + \text{NO}_2$, $\text{RO}_2 + \text{NO} = \text{RONO}_2$, $\text{RO} + \text{NO} = \text{R}'\text{O} + \text{HNO}$, $\text{RO} + \text{NO}_2 = \text{RONO}_2$,

$\text{RNO} + \text{radical} = \text{olefin} + \text{NO} + \text{radical}$, $\text{RNO}_2 + \text{radical} = \text{olefin} + \text{NO}_2 + \text{radical}$, $\text{RONO}_2 = \text{R}'\text{O} + \text{HONO}$, $\text{RONO}_2 + \text{OH} = \text{RO} + \text{HONO}_2$. Many of these have not been considered in previous combustion models. New rate constants are based on analogous small molecule reactions, while new thermochemistry is computed using the THERM software [32]. Uncertainties associated these additional species are not considered significant since the model exhibits little sensitivity in τ to the detailed fuel-specific interactions at the conditions explored here. More details of the extended NOx mechanism can be found in [18].

Simulations of the RCM experiments are conducted using CHEMKIN II where the adiabatic core hypothesis is employed. As per convention, empirical expressions that account for heat loss in the opposed-piston RCM are utilized where these are derived based on experiments using non-reactive mixtures [33]. An adiabatic, single-zone is utilized with time-varying volume where the calculations are initialized before the piston compression process starts and conducted to just after the point of main heat release, i.e., ignition. Effects of reactivity during compression are thus taken into account, where this is especially important for the doped mixtures, as discussed in the Results section. Small integration errors associated with the empirical piston trajectories are taken into account by slightly modifying the velocity profiles ($\pm 0.3\%$) and P_0 ($\pm 2\%$) to achieve compressed conditions consistent with the experiments (differences less than 1% in T_c and P_c).

While this simulation approach has been successfully used in the past to model single-stage fuels in RCM experiments [33], it does not properly account for physical-chemical couplings that occur in RCMs due to reaction chamber – crevice interactions during multi-stage ignition events [34]. Unfortunately, a more physically realistic expression for the ANL RCM was not available for this study. This is a slight limitation of the current model where some uncertainties are introduced ($\sim 10\text{-}25\%$ in τ). For a detailed discussion of the aspects of this the reader is referred to ref. [34].

A brute force, or local sensitivity analysis is also conducted at two representative temperatures, $T = 684$ K and 836 K, with the other conditions, e.g., P_c , ϕ , consistent with the experiments. Only the “LLNL + detailed NOx” mechanism is considered here. For simplicity, these calculations assume an adiabatic, constant volume

reactor. The forward and reverse A-factors for each of the i^{th} reactions are perturbed individually by a factor of 2 so that sensitivity coefficients can be calculated via

$$S_i = \frac{d(\ln(\tau))}{d(\ln(k))} = \frac{k}{\tau} \frac{d(\tau)}{d(k)} \approx \frac{\ln(\tau_2/\tau_1)}{\ln(k_2/k_1)} \quad (1)$$

where the subscripts “1” and “2” indicate perturbations about the base mechanism. While this approach does not capture interactions between reactions, or uncertainties in individual rate constants as a global sensitivity analysis would [35], it is straightforward to undertake and provides a fair indication of important reactions leading to fuel decomposition and ignition.

4.0 Results

The experimental and modeling results are presented as follows. First, the data and simulations of the experiments are discussed, with this followed by a review of the sensitivity and ROP analyses.

4.1 Experimental conditions

Figure 1 illustrates measured and computed ignition delay times for the two undoped gasoline surrogates, PRF91 and TRF91, covering temperatures from $T_c = 675$ to 1025 K. Also included in this figure for reference are ANL data for iso-octane-‘air’ mixtures (PRF100) conducted at $p = 20$ bar, $\phi=1.0$ and 21% O_2 ; these are the RCM Workshop conditions [36] and are presented here to demonstrate the reliability of the current dataset. The data for the PRF91 and TRF91 mixtures can be seen to have measured ignition times that are much longer than the PRF100 mixture, where this is due to the high level of dilution used in the current experiments. Also visible in this figure is that while the LLNL mechanism reasonably predicts the 1st and 2nd stage ignition times for the PRF100 cases, the predictions are generally too fast for the undoped PRF91 and TRF91 mixtures. However, it should be noted that the differences in negative temperature coefficient (NTC) behavior between the two fuels that are seen in the experiments, e.g., the crossover point near 750 K and the slopes in the NTC region (where the TRF91 mixture is seen to be flatter which corresponds to its octane sensitivity), are

adequately predicted by the detailed mechanism. The predictions for the PRF91 mixture are slightly better than for the TRF91 mixture.

Figure 2 presents representative pressure traces at a low temperature condition, $T = 710$ K, for the two fuels covering all of the doping conditions. It should be noted that some of the reactive data are shifted to match the non-reactive traces at a CR of 4:1 as noted earlier. Simulation results using the two mechanisms are included. Here, it can be seen that at these conditions, the experiments do not indicate that the dopant substantially alters the extents of heat release, or pressure / temperature rise during the 1st stage of ignition, even for the highest doping level, though the timings of the 1st stage are shifted considerably relative to the undoped mixtures. The modeling results indicate somewhat similar trends, but the τ shifts due to the 2EHN are noticeably different. Fairly comparable behavior is observed between the predictions using the detailed and the skeletal NO_x models, but only at the lowest doping condition. As the doping fraction increases however, the influence of the detailed nitrogen chemistry becomes apparent. This is evident for both surrogate mixtures. This feature is consistent across most of the temperature range, as will be discussed. Also noticeable in Fig. 2 is that there appears to be more 1st stage heat release / temperature rise in the simulations than in the measurements. Some of this discrepancy can be attributed to the simulation approach used here [34], but it is unclear how much. Additionally visible upon close inspection, though perhaps not with the resolution provided here, is that there is substantial reactivity during the compression stroke for the simulations, where this is also seen in some of the doped experiments.

Figures 3 and 4 summarize the experimental measurements for the PRF91 and TRF91 blends where an effectiveness ratio, defined as $R_{\text{eff}} = \tau_{\text{doped}} / \tau_{\text{undoped}}$, is plotted as a function of the inverse temperature. Here the plots utilize T_c based on the undoped mixtures. R_{eff} provides an indication of how influential 2EHN is in accelerating the reactivity of the mixture. A number of features are evident in these figures. First, the PRF91 and TRF91 mixtures exhibit very similar behavior, for the experiments and both of the models. There appears to be a peak in R_{eff} near 740 K where the 2EHN has minimal influence. This is near the transition from low temperature to NTC chemistry for these fuels. On the lower temperature side of this peak there is not much

difference in R_{eff} between the three different doping levels. However, at higher temperatures the effectiveness is a very non-linear function of doping level. This non-linear behavior corresponds to observations made in operating engines [10-15]. Further, it can be seen that R_{eff} is much lower around 830 K, where this indicates that 2EHN is very effective. There are noticeable discrepancies between the experimental and modeling results. Not only do the models over-predict the reactivity of the undoped fuels, but the enhancement due to 2EHN is excessive. It should be noted however, that the general curvature of the model trends seems to be similar to the experimental measurements, e.g., the peak in R_{eff} near 740 K with lower values at higher and lower temperatures. Finally, it is seen that the detailed nitrogen chemistry is predicted to be important only at the higher doping levels. This feature is discussed more in Section 4.2

Figure 5 illustrates the influence of fuel-specific interactions by plotting the ratio of R_{eff} for TRF91 to R_{eff} for PRF91 fuel. Here, values greater 1.0 indicate that 2EHN is more effective in the non-aromatic fuel, while values less than 1.0 indicate that 2EHN is more effective in the aromatic fuel. It can be seen that across most of the temperature range, the experiments indicate that the relative effectiveness is close to 1.0, i.e., $\pm 15\%$, though at low temperatures and high doping levels 2EHN is more effective in the TRF91 mixture. At high temperatures, $T > 900$ K, 2EHN is more effective in the TRF91 mixture, but only at the lowest doping level. The two models on the other hand, indicate that 2EHN is markedly more effective in the non-aromatic mixture covering most of the NTC regime.

4.2 Sensitivity analysis

A summary of the sensitivity analysis is reviewed here while the individual S_i 's are provided in the Supplementary Material. The top 20 reactions for all of the conditions investigated are listed there, with these designated at times during the simulation where the temperature is computed to rise by $\Delta T = 25, 100$ and 800 K relative to the initial condition. These give an indication of which reactions are sensitive during the early, intermediate and later stages of the ignition process. Note that at $T = 684$ K, the nominal temperature rise from

the 1st stage ignition for the undoped mixtures is approximately $\Delta T = 150$ K; at $T = 836$ K there is no defined 1st stage ignition for the undoped mixtures.

Simulation results using the unperturbed LLNL mechanism at the nominal conditions are discussed first. Figure 6 illustrates computed mole fractions for CH_2O , QOOH , and OH as functions of instantaneous temperature for the two temperatures considered. For this analysis all of the QOOH species are included, though the largest fractions are hydroperoxy octyl and hydroperoxy heptyl radicals. Only two PRF91 and two TRF91 mixtures are presented, one which is undoped and the other which is doped at 3.0%. Note that the PRF91 results are shifted vertically for better visibility, where the start of the calculation is indicated by a horizontal hatched bar (with the data record truncated below 10^{-3} ppm). Here it is easily seen that the concentrations of these important intermediates are significantly stimulated by the presence of 2EHN, where this particularly occurs during the early stage of the ignition process, i.e., before the temperature rise of $\Delta T = 25$ K is realized. Further during the ignition process, it can be seen that the species trajectories for the undoped and doped mixtures tend to converge. This behavior seems to indicate that it is primarily the lower temperature chemistry that is perturbed by the fuel additive.

The sensitivity analysis for undoped PRF91 at $T = 684$ K indicates typical sensitivities to $\text{RH} + \text{OH} = \text{R} + \text{H}_2\text{O}$ and $\text{RO}_2 = \text{QOOH}$ at the early time, additionally to $\text{O}_2\text{QOOH} = \text{KETO} + \text{OH}$ at the intermediate time, and H_2O_2 , CH_2O , HCO and CH_3O_2 relevant reactions at the later time. At $T = 836$ K, $\text{RH} + \text{HO}_2 = \text{R} + \text{H}_2\text{O}_2$ becomes important at all times, as do reactions involving H_2O_2 . CH_2O and CH_3O_2 chemistry are somewhat less important. As the fuel is doped at $T = 684$ K, 2EHN decomposition becomes important, but only during the early stage. Reactions involving the $\text{C}_7\text{H}_{15-3}$ radical, e.g., $\text{R} + \text{O}_2 = \text{RO}_2$ and $\text{RO}_2 = \text{QOOH}$, etc., also become important, but again only at the early time. On the other hand, reactions involving CH_2O and CH_3O_2 become very important at all times. Only for 3.0% 2EHN, $\text{NO}_2 + \text{OH} = \text{HONO}_2$ becomes significant, but also just at the early time. At $T = 836$ K, the doped mixture indicates increasing sensitivity to again, the $\text{C}_7\text{H}_{15-3}$ related reactions, but at this condition these are important throughout the ignition period. There is little sensitivity to the 2EHN decomposition since it is quite rapid at this temperature. However, CH_2O and CH_3O_2 reactions are again sensitized by the addition of 2EHN. At

$T = 836\text{ K}$, $\text{CH}_3\text{NO}_2 = \text{CH}_3 + \text{NO}_2$ is the only nitrogen-relevant reaction that is sensitive, where this influence seems to be only at early times.

The analysis for undoped TRF91 at $T = 684\text{ K}$ shows nearly identical results to undoped PRF91, except with the addition of toluene-specific reactions. At $T = 836\text{ K}$, the results are very similar to undoped PRF91, however the isomerization of 3-heptyl-peroxy radicals to hydroperoxy 3-heptyl radical (QOOH) is found to be influential at all times. As the fuel is doped at $T = 684\text{ K}$, the sensitive reactions are again very similar to the doped PRF91 blends. This finding corresponds to the trends seen in Fig. 5 where the predicted ratios of R_{eff} 's are close to 1.0. At $T = 836\text{ K}$ some differences between the fuels become apparent in the model. The aromatic fuel is more sensitive to the dopant-derived 3-heptyl radical reactions, and these sensitivities are consistent across all times during the ignition process. CH_2O chemistry is slightly less important for the doped TRF91 at this higher temperature. Finally, $\text{NO} + \text{HO}_2 = \text{NO}_2 + \text{OH}$ is the only NO_x relevant reaction observed to be important, but just at the highest doping level.

4.3 Rate of production analysis

A summary of the ROP analysis is reviewed here while the individual results are provided in the Supplementary Material. This analysis is undertaken in order to understand differences between predictions using the detailed and skeletal NO_x mechanisms, therefore the fate of NO_2 is considered. Simulations are conducted at $T = 684\text{ K}$ for the two fuel blends at a doping level of 3% with results analyzed at $\Delta T = 25\text{ K}$, in a manner similar to the sensitivity analysis.

The ROP results indicate that for the skeletal mechanism, the primary pathways for production and consumption are $\text{NO} + \text{HO}_2 = \text{NO}_2 + \text{OH}$ and $\text{NO}_2 + \text{H} = \text{NO} + \text{OH}$, respectively, where this 'NO – NO_2 loop' can generate substantial amounts of OH. The detailed mechanism however, exhibits more complex interactions where methyl and ethyl nitrite, and nitric acid formation consume NO_2 , while $\text{R} + \text{NO}_2 = \text{RO} + \text{NO}$ and $\text{RO}_2 + \text{NO} = \text{RO} + \text{NO}_2$ are substantial consumers and producers of NO_2 , respectively. These additional reactions significantly compete with

the NO – NO₂ loop so that less OH is generated in the detailed mechanism, and this constrains the reactivity enhancement at the highest doping level.

5.0 Conclusions

Experiments and modeling are conducted to investigate the autoignition behavior of two gasoline surrogates doped with 2EHN to better understand dopant interactions with non-aromatic and aromatic fuels, including accelerating kinetic pathways and enhanced exothermicity. RCM experiments are conducted at $\phi = 1$, $P_c = 21$ bar, $O_2 = 11.4\%$ and $T_c = 650$ - 1025 K with doping levels of 0.0, 0.1, 1.0 and 3.0%. The results indicate that the doping effectiveness of 2EHN is fairly similar between the two simple surrogates studied here, where minor influences are observed at the lowest temperatures, while at higher temperatures, i.e., in the NTC regime, the influence is large and very non-linear with doping level. 2EHN seems to be slightly more effective in the aromatic blend at the lower temperatures, but somewhat more effective in the non-aromatic blend at intermediate temperatures. Very little change is observed in the exothermicity of ignition, e.g., the extents of heat release during the 1st stage of ignition, however more investigation of this is warranted, especially since CH_3O_2 has been identified as influential towards intermediate temperature heat release (ITHR) in HCCI engines. Investigations using other aromatics, including polycyclic structures would be informative.

Kinetic modeling indicates that although some of the reactivity trends can be captured using a detailed model, the extents of predicted cetane enhancement are too large, while the differences in fuel interactions between the two fuels lead to excessive stimulation of the non-aromatic blend. The model indicates that the CH_2O and CH_3O_2 chemistry are very sensitive to the dopant at all conditions, while 2EHN decomposition only seems to be sensitive at low temperatures where its decomposition rate is slower due to the high activation energy of the reaction (~ 40 kcal/mole). At higher temperatures, dopant-derived 3-heptyl radicals are predicted to play an important role stimulating ignition, and nitrogen chemistry becomes important only at the highest doping levels, primarily through the formation of methyl nitrite and nitric acid. The formation of methyl and

ethyl nitrite, as well as nitric acid are predicted to compete with the 'NO – NO₂ loop' where this reduces the production of OH, and thereby constrains the effectiveness of 2EHN.

This study helps to improve the fundamental understanding of alkyl nitrate additives at engine-relevant conditions, where this can lead to more sophisticated models which may give better agreement with experimental measurements and be useful in engine simulations.

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Figures

Figure 1 – Ignition delay times as function of temperature for three undoped fuels.

Image:

53mm tall x 67mm wide

$(53 + 10) \times 2.2 \text{ word/mm} = 139 \text{ words}$

Caption: 13 words

Figure 2 – Representative experimental and simulated pressures as functions of time for $T_c = 710$ K.

Image:

74mm tall x 67mm wide

$(74 + 10) \times 2.2 \text{ word/mm} = 185 \text{ words}$

Caption: 16 words

Figure 3 – Effectiveness ratio as function of temperature for PRF91 mixes.

Image:

53mm tall x 67mm wide

$(53 + 10) \times 2.2 \text{ word/mm} = 139 \text{ words}$

Caption: 11 words

Figure 4 – Effectiveness ratio as function of temperature for TRF91 mixes.

Image:

53mm tall x 67mm wide

$(53 + 10) \times 2.2 \text{ word/mm} = 139 \text{ words}$

Caption: 11 words

Figure 5 – Relative doping effectiveness as function of temperature.

Image:

53mm tall x 67mm wide

(53 + 10) x 2.2word/mm = 139 words

Caption: 9 words

Figure 6 – Mole fractions of CH_2O , QOOH AND OH as functions of temperature for undoped (lines) and 3.0% doped (lines + symbols) mixtures at two constant volume conditions, $T_i = 684 \text{ K}$ (solid) and $T_i = 836 \text{ K}$ (dashed).

Image:

53mm tall x 67mm wide

$(53 + 10) \times 2.2 \text{ word/mm} = 139 \text{ words}$

Caption: 39 words

Figure Captions

Figure 1 – Ignition delay times as function of temperature for three undoped fuels.

Figure 2 – Representative experimental and simulated pressures as functions of time for $T_c = 710$ K.

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