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Interaction between 2,5-Dimethylfuran and Nitric Oxide: Experimental and Modeling Study

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S Supporting Information

ABSTRACT: In the present work, the interaction between 2,5-dimethylfuran (2,5-DMF) and NO has been investigated. The study includes experimental and modeling data on the evaluation of the influence of the temperature, stoichiometry, and 2,5-DMF concentration on the NO conversion as well as on the 2,5-DMF conversion in the presence of NO. The experiments were performed in an isothermal quartz flow reactor at atmospheric pressure in the temperature range of 800–1400 K. Some of the results of the present work were compared to the experimental and modeling data from an earlier study on 2,5-DMF conversion under similar conditions but in the absence of NO. The results reveal that the temperature, stoichiometry, and 2,5-DMF concentration play an important role on the conversion of NO. Likewise, these variables also influence the 2,5-DMF conversion regime in the presence of NO.

1. INTRODUCTION

Nitrogen oxides (NO and NO₂, referred together as NO_x) and particulate matter (PM), mainly soot, are the most critical pollutants produced by diesel engines. Because of the trade-off between the NO_x and PM emissions (mainly because NO_x formation is favored under fuel-lean conditions, while soot is formed when oxygen is lacking), it is difficult to reduce simultaneously both emissions. However, several techniques to reduce together and individually these emissions have been proposed, and fuel reformulation is one of them.¹ In this regard, different studies demonstrate that adding oxygenates to diesel combustibles can substantially reduce PM emissions without significant effects on NO_x emissions.^{2–5}

A candidate to be used as an additive is 2,5-dimethylfuran (C₆H₈O; 2,5-DMF), and in addition to the experiments conducted on diesel engines,^{6,7} several experimental and computational studies have explored its pyrolysis and oxidation.^{8–15} However, the interaction between 2,5-DMF and pollutants, such as NO, to our knowledge, has not yet been studied. Thus, to understand which is the principle that governs the reduction of NO in the presence of 2,5-DMF as well as the pyrolysis and oxidation processes of 2,5-DMF in the presence of NO, both experimental and modeling efforts are required in this field.

In this context, the aim of the present work was to perform an experimental and kinetic study on the interaction between 2,5-DMF and NO in various reaction environments. Experiments were performed under well-controlled flow reactor conditions over the temperature range of 800–1400 K and at atmospheric pressure. Under these conditions, the oxygen concentration was varied from pyrolytic to very fuel-lean conditions. The impact of the inlet C/N ratio value was analyzed, varying the initial 2,5-DMF concentration, i.e., varying the initial atomic C amount. On the other hand, a modeling study was performed using a detailed gas-phase chemical kinetic mechanism compiled from the literature and which describes

the pyrolysis and oxidation of 2,5-DMF and the interaction of NO with some hydrocarbons. Additionally, experimental data obtained in a previous work, where the experimental conditions were similar to the present work but in the absence of NO¹, have been considered to analyze the influence of the NO presence on the 2,5-DMF conversion.

2. EXPERIMENTAL SECTION

Experiments have been carried out in an atmospheric pressure gas-phase installation. It basically consists of a gas feeding system, a reaction system, and a conditioning and gas analysis system. The setup for this installation has been presented in detail elsewhere^{16,17} and is described here only briefly.

The interaction between 2,5-DMF and NO at atmospheric pressure takes place in a quartz flow reactor, designed for obtaining plug flow conditions,¹⁸ with a reaction zone of 8.7 mm inside diameter and 200 mm in length. The reactor tube is placed in a three-zone electrically heated furnace, ensuring a uniform temperature profile within ± 10 K throughout the reaction zone. 2,5-DMF, O₂, and NO, stored in gas cylinders, are fed to the reactor through mass flow controllers and together with water vapor and N₂ are injected at the top of the reactor in up to four separate streams. Water vapor, approximately 6000 ppm, is introduced in the reactor by saturating a N₂ stream through a water bubbler, and N₂ is used to achieve a total flow rate of 1000 mL standard temperature and pressure (STP)/min. The gas residence time (t_r) is a function of the temperature in the reaction zone and, for a given total flow rate of 1000 mL (STP)/min, is given by t_r (s) = 195/ T (K). The product gas is quenched at the outlet of the reaction zone by an air flow, and before analysis, it passes through a condenser and filter to ensure gas cleaning. The outlet gas composition is measured using a microchromatograph (Agilent 3000A), which detects and quantifies 2,5-DMF, CO, CO₂, and H₂, and continuous Uras 14 IR and Uras 26 IR analyzers from ABB for CO/CO₂ and NO, respectively. Also, a Fourier transform infrared (FTIR) spectrometer (Genesis II, Ati Mattson) is used to check the formation of some nitrogen species,

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such as NO₂, N₂O, HCN, and NH₃. The uncertainty of the concentration measurements is estimated as $\pm 5\%$, except for the FTIR spectrometer, which is estimated as $\pm 10\%$.

3. MODELING SECTION

The experimental results have been analyzed in terms of a detailed gas-phase chemical kinetic mechanism compiled for this investigation, to identify the reactions that mainly have influence on the NO conversion in the presence of 2,5-DMF as well as the 2,5-DMF conversion in the presence of NO under the experimental conditions of the present work. The mechanism used for the simulations is the same used in our previous work focused on pyrolysis and oxidation of 2,5-DMF without NO,¹ which is largely based on a work by Sirjean et al.¹⁴ The subsets of the interactions between NO_x with some radicals, C₁/C₂ hydrocarbons, oxygenated hydrocarbons, and other compounds of interest, taken from Alzueta et al.¹⁹ and updated in a number of works,^{20,21} were added to the base mechanism. The thermodynamic data were taken from the same source as the subsets of the mechanism. Calculations were performed using the Chemkin²² software, with the SENKIN plug flow reactor code, assuming temperature and pressure constants in the reaction zone. The full mechanism and thermodynamic data can be found in the Supporting Information.

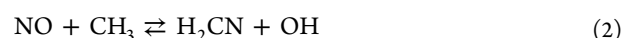
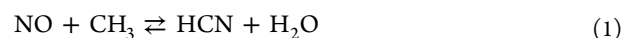
4. DISCUSSION OF RESULTS

In this work, we have investigated the interaction between 2,5-DMF, a proposed fuel additive,¹⁴ and NO. In such a way, the NO conversion in the presence of 2,5-DMF and the 2,5-DMF conversion in the presence of NO were studied. The experiments have been carried out at atmospheric pressure, from pyrolytic to very fuel-lean conditions (specifically, $\lambda = 0, 0.3, 0.7, 1, 5$, and 30), using different inlet C/N ratio values (0.67 and 2) and in the temperature range of 800 – 1400 K. The impact of the C/N ratio value has been analyzed by keeping constant the inlet NO concentration (900 ppm) and varying the initial atomic C amount (600 and 1800 ppm). In this way, the effect of the inlet concentration of 2,5-DMF on the NO conversion has been studied as well as on its own conversion in the presence of NO. Table 1 summarizes the conditions for each set of experiments, which were all performed under highly

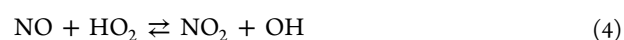
diluted conditions to ensure an isothermal reaction zone. Additional experimental data were taken from previous work,¹ where the 2,5-DMF conversion was investigated under the same conditions of the present work but in the absence of NO.

4.1. NO Conversion in the Presence of 2,5-DMF. The NO conversion, at atmospheric pressure using 2,5-DMF, has been studied for different λ values and varying the inlet C/N ratio value, i.e., varying the initial concentration of 2,5-DMF (100 and 300 ppm). Figure 1 shows the experimental data and the model predictions of the NO concentration profile as a function of the temperature for the inlet C/N ratio values of 0.67 and 2 and for all λ values studied. The top panels show the concentration profile of NO for fuel-rich and stoichiometric conditions, and the bottom panels show the concentration profile of NO for fuel-lean conditions. The modeling predictions match the experimental measurements reasonably well, although better predictions are seen for fuel-rich and stoichiometric conditions.

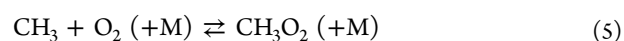
For $\lambda \leq 1$, the concentration of NO decreases as both the temperature and oxygen concentration increase. The model results indicate that, under pyrolytic ($\lambda = 0$), fuel-rich ($\lambda = 0.3$ and 0.7), and stoichiometric ($\lambda = 1$) conditions, the reactions between NO and the CH₃ radicals to give nitrogen species, such as HCN and H₂CN (reactions 1 and 2), are an important step for the consumption of NO.



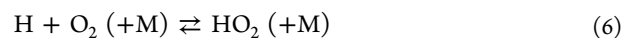
For $T \geq 1275$ K, the NO conversion is more pronounced because there is an increase in the formation of the CH₃ radicals by the decomposition of 2,5-DMF. Also, with increasing the concentration of oxygen, eventually $\lambda = 0.7$ and 1 , the greatest reduction of NO is because, in these conditions, besides reactions 1 and 2, reactions between NO and the CH₃O₂/HO₂ radicals to give NO₂ (reactions 3 and 4) become important as well.



Reactions 3 and 4 become more important under fuel-lean conditions ($\lambda = 5$ and 30). For these leaner conditions, the CH₃ radicals are not consumed by reactions 1 and 2. Nevertheless, they react with molecular oxygen to give the CH₃O₂ radicals (reaction 5), which react with NO according to reaction 3.



On the other hand, the HO₂ radicals are formed significantly by the reaction between the H radicals, produced by the decomposition of 2,5-DMF and molecular oxygen, as shown in reaction 6, a reaction that is considerably favored under very fuel-lean conditions.



Under fuel-lean conditions ($\lambda = 30$) and for the lowest temperatures considered in the present work, the calculations show that the NO concentration diminished as a result of the NO \rightarrow NO₂ conversion (reactions 3 and 4). However, as the temperature is increased, NO₂ reacts with the radical pool, basically by the reaction 7 or 8, and NO begins to become dominant again. The present results suggest that the NO/NO₂ interconversion does not contribute to a net NO removal. In

Table 1. Experimental Conditions: $T = 800$ – 1400 K, Flow Rate = 1000 mL (STP)/min, and t_r (s) = $195/T$ (K)^a

set	C ₆ H ₈ O (ppm)	O ₂ (ppm)	λ	NO (ppm)	C/N molar ratio	reference ^b
1	100	0	0	900	0.67	pw
2	100	0	0	0		Alexandrino et al. ¹
3	100	225	0.3	900	0.67	pw
4	100	525	0.7	900	0.67	pw
5	100	525	0.7	0		Alexandrino et al. ¹
6	100	750	1	900	0.67	pw
7	100	3750	5	900	0.67	pw
8	100	22500	30	900	0.67	pw
9	100	22500	30	0		Alexandrino et al. ¹
10	300	675	0.3	900	2	pw
11	300	22500	1	900	2	pw
12	300	67500	30	900	2	pw
13	300	67500	30	0		Alexandrino et al. ¹

^aN₂ is used to close the balance. ^bpw denotes the present work.

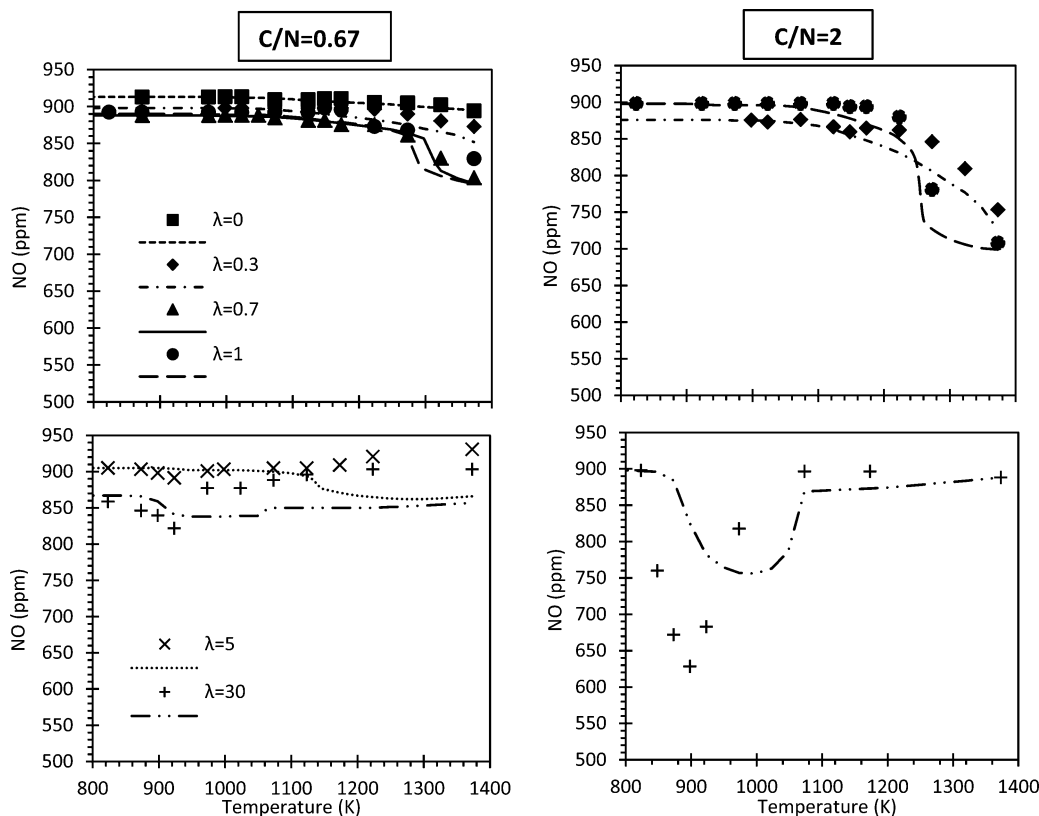
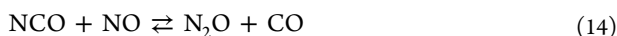
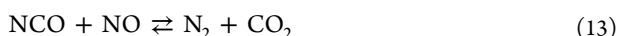
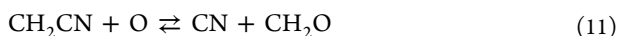
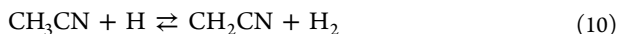
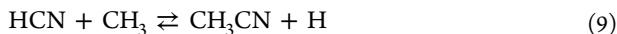


Figure 1. Concentration profile of NO as a function of the temperature for C/N = 0.67 and 2, at atmospheric pressure. In the top panels, fuel-rich and stoichiometric conditions (sets 1, 3, 4, 6, 10, and 11 in Table 1), and in the bottom panels, fuel-lean conditions (sets 7, 8, and 12 in Table 1). Symbols denote experimental data, and lines denote model predictions.

this way, under the conditions of this work, 2,5-DMF is not seen to exert a negative influence on the NO emissions. However, a beneficial effect of adding 2,5-DMF is not observed either.



The no detection of HCN in any of the experiments under fuel-rich and stoichiometric conditions suggests that, under the conditions of the present work, HCN readily forms N_2 or N_2O by consecutive reactions, which can be found through model calculations, as shown below.

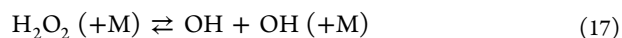


4.2. 2,5-DMF Conversion in the Presence of NO. The inlet C/N ratio, i.e., C amount, has been found to influence the NO conversion. Thus, it may be interesting to evaluate if this ratio value also has an influence on the 2,5-DMF conversion. In this context, Figure 2 shows the $[\text{2,5-DMF}]_{\text{out}}/[\text{2,5-DMF}]_{\text{in}}$ ratio values as a function of the temperature for the C/N ratio values of 0.67 and 2 and for the different λ values studied. Figure 2 shows that the inlet C/N ratio is seen to have a slight

influence on 2,5-DMF only to fuel-lean conditions, i.e., $\lambda = 30$ (Figure 2c), although model calculations show no appreciable influence. However, in our previous study,¹ we detected that, in the absence of NO and $\lambda = 30$, the concentration of 2,5-DMF is seen to have a considerable influence on its conversion, and for the higher concentration (300 ppm), the onset of the consumption of 2,5-DMF is shifted at lower temperatures (Figure 3). Calculations indicate that, for $\lambda = 30$ and in both the absence and presence of NO, 2,5-DMF is consumed mainly by OH addition to form acetylene, the acetyl radical, and acetaldehyde, according to reaction 15.



This fact suggests that the onset of the 2,5-DMF conversion, in the absence and presence of NO under very fuel-lean conditions, is determined by the concentration of the OH radicals in the reaction environment. While in the presence of NO, the OH radicals are formed by the reaction between the NO and HO_2 radicals (reaction 4), in the absence of NO, the principal step to the formation of the OH radicals depends upon the concentration of 2,5-DMF, the reaction between the H radicals and O_2 (reaction 16) and the decomposition of the H_2O_2 radicals (reaction 17) for 100 and 300 ppm, respectively. Both the H and H_2O_2 radicals are formed from 2,5-DMF.



For $\lambda = 30$, 100 ppm of 2,5-DMF, and in the absence of NO, the H radicals are consumed by their reactions with oxygen to yield HO_2 or O and OH through reactions 6 and 16,

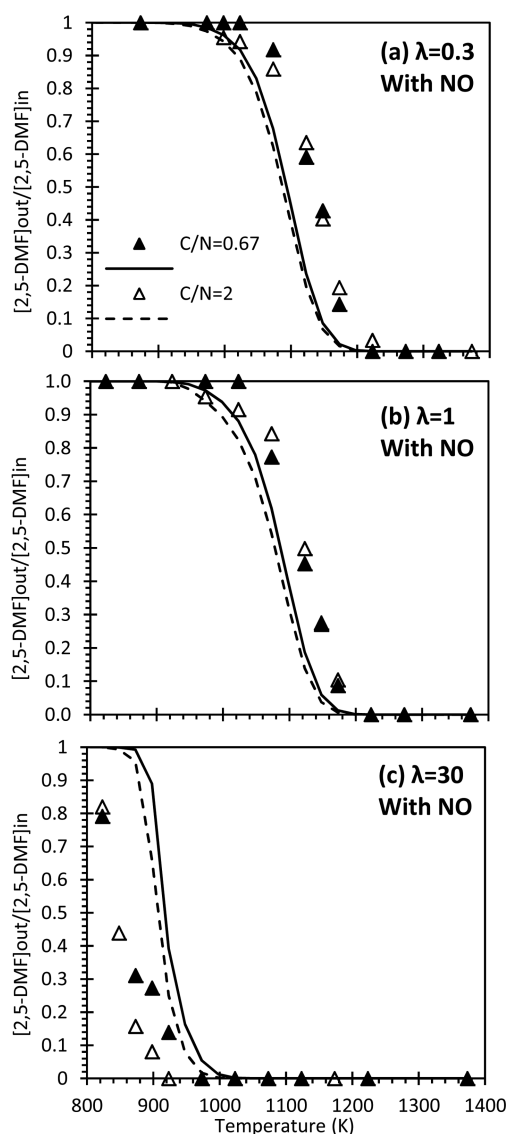


Figure 2. $[2,5\text{-DMF}]_{\text{out}}/[2,5\text{-DMF}]_{\text{in}}$ ratio values as a function of the temperature for $C/N = 0.67$ and 2 and $\lambda = 0.3, 1$, and 30 at atmospheric pressure (a, sets 3 and 10 in Table 1; b, sets 6 and 11 in Table 1; and c, sets 8 and 12 in Table 1). Symbols denote experimental data, and lines denote model predictions.

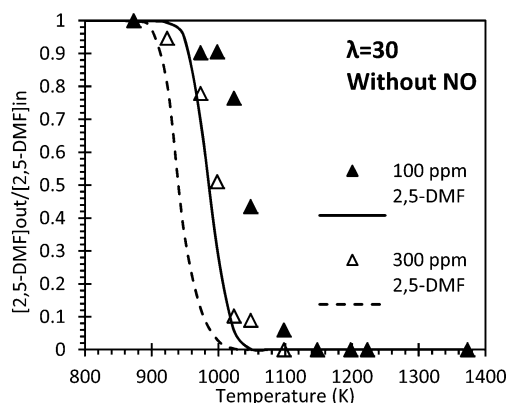
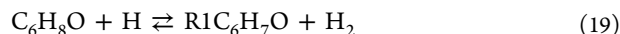


Figure 3. $[2,5\text{-DMF}]_{\text{out}}/[2,5\text{-DMF}]_{\text{in}}$ ratio values as a function of the temperature for $\lambda = 30$ at atmospheric pressure and in the absence of NO (sets 9 and 13 in Table 1). Symbols denote experimental data, and lines denote model predictions.

respectively. The competition between both reactions diminishes the production of the OH radicals and, consequently, diminishes the rate of reaction 15. However, H_2O_2 is only consumed by reaction 17 (the reaction belongs to the case of 300 ppm of 2,5-DMF); consequently, the OH radicals are largely formed and increment the rate of reaction 15, shifting the onset of consumption of 2,5-DMF at lower temperatures.

With the aim of understanding the influence of the presence of NO on the 2,5-DMF conversion for a given inlet 2,5-DMF concentration and different λ values, Figure 4 shows an example of the comparison between the concentration profiles of 2,5-DMF as well as the main products (CO , CO_2 , and H_2) in the absence and presence of NO for 100 ppm of 2,5-DMF, $\lambda = 0, 0.7$, and 30 , and atmospheric pressure. Similar trends are found for 300 ppm of 2,5-DMF (not shown). The model agrees well with the experimental data obtained, although certain discrepancies are seen for $\lambda = 30$.

Under pyrolytic conditions ($\lambda = 0$), the concentration profile of 2,5-DMF and the concentration profile of the pyrolytic products (CO , H_2 , and CO_2 in a minor amount) are not modified by the presence of NO. This suggests a similar governing chemistry in these experiments. Under these conditions, in both the absence and presence of NO, CO and H_2 are formed by decomposition of CH_3CO radicals (reaction 18) and hydrogen abstraction from the methyl group of 2,5-DMF to yield the resonance-stabilized 5-methyl-2-furanylmethyl radical ($\text{R1C}_6\text{H}_7\text{O}$) (reaction 19), respectively.



Under fuel-rich and stoichiometric conditions ($\lambda = 0.3, 0.7$, and 1), the presence of NO does not influence the concentration profile of 2,5-DMF. As an example, Figure 4 shows the results obtained for $\lambda = 0.7$. However, under these environments and at intermediate and high temperatures, the presence of NO acts to diminish the formation rate of the oxidation products (CO , CO_2 , and H_2). Calculations show that, at a low temperature (about 1125 K), the formation of CO and H_2 is initiated by reactions 18 and 19, respectively. This occurs for both the absence and presence of NO. Nonetheless, with an increasing temperature, reactions involving other radicals, such as CHCO and CHO as well as some product intermediates, begin to be more important to the formation of CO and H_2 . The presence of NO leads to the occurrence of competing reactions, which act to diminish the concentration of the radicals that produce CO and H_2 . The formation of CO_2 is originated by the reaction of CO with the radical pool, basically with the OH radicals.

Under fuel-lean conditions ($\lambda = 5$ and 30 , shown as an example for $\lambda = 30$ in Figure 4), the presence of NO shifts the onset of 2,5-DMF consumption to lower temperatures, consequently advancing the beginning of the formation of the combustion products (CO and CO_2). This behavior is caused by the higher concentration of the radicals in the reaction environment, which react with 2,5-DMF. In the absence of NO, competing reactions occur, which reduce the formation of the radicals, as explained above in the absence of NO (Figure 3).

In summary, from fuel-rich to stoichiometric conditions and for the intermediate and high temperatures considered in this work, the presence of NO causes the occurrence of competing reactions, which act to diminish the formation rate of the products. On the other hand, under fuel-lean conditions and for the low temperatures of this work, the presence of NO

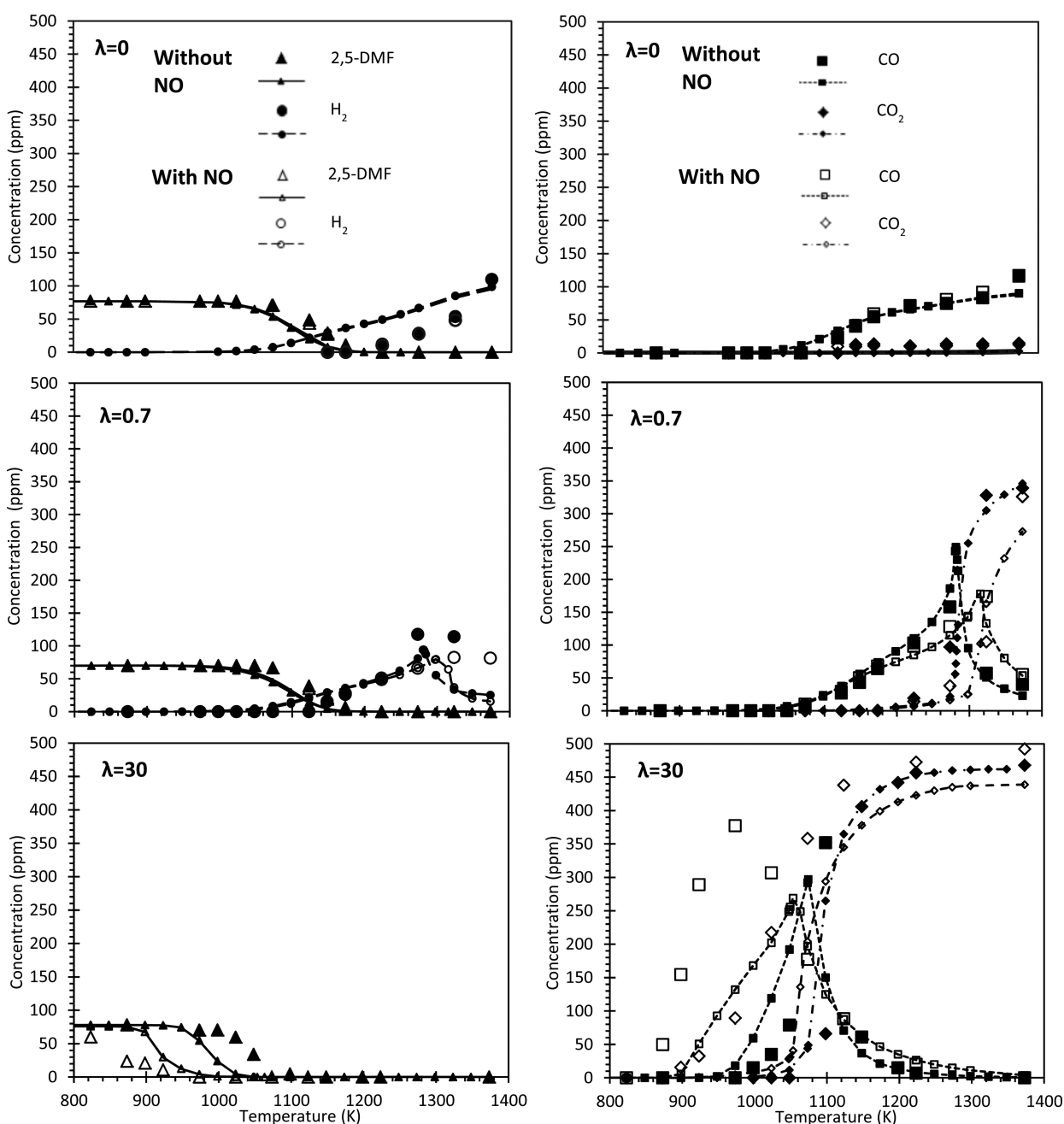


Figure 4. Interaction with NO of 100 ppm of 2,5-DMF for $\lambda = 0, 0.7$, and 30 and at atmospheric pressure. Full symbols, experimental data without NO; empty symbols, experimental data with NO; lines with full symbols, model predictions without NO; and lines with empty symbols, model predictions with NO. Data in the absence of NO correspond to sets of a previous work,¹ and data in the presence of NO correspond to sets 1, 4, and 8 in Table 1 of the present work.

increases the formation of the radicals, which react with 2,5-DMF, thus shifting the profile concentration of 2,5-DMF at lower temperatures.

Sensitivity analyses for the conversion of CO were carried out to identify the reactions affecting the results more. Sensitivity plots can be found in the Supporting Information.

5. CONCLUSION

The NO conversion in the presence of 2,5-DMF and the 2,5-DMF conversion in the presence of NO have been investigated in a quartz flow reactor at atmospheric pressure by varying the temperature, the stoichiometry, and the 2,5-DMF concentration. The experimental results have been interpreted in terms

of a detailed chemical kinetic mechanism, through which the main reactions involved in the interaction between NO and 2,5-DMF, under the experimental conditions studied here, have been identified.

Experimental and theoretical results are, in general, in good agreement and show that, for fuel-rich conditions, with increasing temperature and oxygen and 2,5-DMF concentrations, the NO conversion increases. However, under fuel-lean conditions and in the intermediate- and high-temperature intervals, NO after reaching a minimum starts to be formed again by the reactions between NO_2 and the radical pool. In this way, the interconversion of NO/ NO_2 does not contribute to a net NO removal, and according to the conditions tested, a

high λ value ($\lambda = 30$), a high 2,5-DMF concentration (300 ppm), and a low temperature (about 900 K) result in the greatest conversion of NO to NO₂. Under the conditions of the work, 2,5-DMF is not seen to exert a negative influence on the NO emissions. However, a beneficial effect of adding 2,5-DMF is not observed either. On the other hand, the concentration of 2,5-DMF in both the absence and presence of NO does not have an appreciable influence on the 2,5-DMF conversion under fuel-rich and stoichiometric conditions ($\lambda = 0.3$ and 1). For fuel-lean conditions ($\lambda = 30$), the influence of the 2,5-DMF concentration on its conversion is appreciable and more noticeable in the absence of NO. Also, under pyrolytic conditions and for a given inlet 2,5-DMF concentration, the presence of NO does not modify the 2,5-DMF conversion regime. However, from fuel-lean to fuel-rich conditions, the presence of NO modifies the 2,5-DMF oxidation regime by varying the concentration of the radical pool.

■ ASSOCIATED CONTENT

■ Supporting Information

Detailed kinetic mechanism and thermodynamic data in Chemkin format and sensitivity plots. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Alexandrino, K.; Millera, A.; Bilbao, R.; Alzueta, M. U. *Proc. Combust. Inst.* **2014**, manuscript submitted.
- (2) Yao, C.; Cheung, C. S.; Cheng, C.; Wang, Y.; Chan, T. L.; Lee, S. C. *Energy Convers. Manage.* **2008**, 49, 1696–1704.
- (3) Wang, J.; Wu, F.; Xiao, J.; Shuai, S. *Fuel* **2009**, 88, 2037–2045.
- (4) Cheung, C. S.; Zhu, R.; Huang, Z. *Sci. Total Environ.* **2011**, 409, 523–529.
- (5) Gill, S. S.; Tsolakis, A.; Herreros, J. M.; York, A. P. E. *Fuel* **2012**, 95, 578–586.
- (6) Chen, G.; Shen, Y.; Zhang, Q.; Yao, M.; Zheng, Z. *Energy* **2013**, 54, 333–342.
- (7) Zhang, Q.; Chen, G.; Zheng, Z.; Liu, H.; Xu, J.; Yao, M. *Fuel* **2013**, 103, 730–735.
- (8) Djokic, M.; Carstensen, H.; Van Geem, K. M. *Proc. Combust. Inst.* **2013**, 34, 251–258.
- (9) Friese, P.; Bentz, T.; Olzmann, M.; Simmie, J. *Proceedings of the 5th European Combustion Meeting*; Cardiff, Wales, June 28–July 1, 2011.
- (10) Wu, X.; Huang, Z.; Yuan, T.; Zhang, K.; Wei, L. *Combust. Flame* **2009**, 156, 1365–1376.
- (11) Somers, K. P.; Simmie, J. M.; Gillespie, F.; Conroy, C.; Black, G.; Metcalfe, W. K.; Battin-Leclerc, F.; Dirrenberger, P.; Herbinet, O.;

- Glaude, P.; Dagaut, P.; Togbé, C.; Yasunaga, K.; Fernandes, R. X.; Lee, C.; Tripathi, R.; Curran, H. J. *Combust. Flame* **2013**, 160, 2291–2318.
- (12) Grela, M. A.; Amorebieta, V. T.; Colussi, A. J. *J. Phys. Chem.* **1985**, 89, 38–41.
 - (13) Lifshitz, A.; Tamburu, C.; Shashua, R. *J. Phys. Chem.* **1998**, 102, 10655–10670.
 - (14) Sirjean, B.; Fournet, R.; Glaude, P.; Battin-Leclerc, F.; Wang, W.; Oehlschlaeger, M. A. *J. Phys. Chem. A* **2013**, 117, 1371–1392.
 - (15) Simmie, J. M.; Metcalfe, W. K. *J. Phys. Chem. A* **2011**, 115, 8877–8888.
 - (16) Alzueta, M. U.; Bilbao, R.; Finestra, M. *Energy Fuels* **2001**, 15, 724–729.
 - (17) Alzueta, M. U.; Serinyel, Z.; Simmie, J. M.; Curran, H. J. *Energy Fuels* **2010**, 24, 1511–1520.
 - (18) Kristensen, P. G.; Glarborg, P.; Dam-Johansen, K. *Combust. Flame* **1996**, 107, 211–222.
 - (19) Alzueta, M. U.; Bilbao, R.; Millera, A.; Glarborg, P.; Ostberg, M.; Dam-Johansen, K. *Energy Fuels* **1998**, 12, 329–338.
 - (20) Abián, M.; Silva, S.; Millera, A.; Bilbao, R.; Alzueta, M. U. *Fuel Process. Technol.* **2010**, 91, 1204–1211.
 - (21) Alzueta, M. U.; Aranda, V.; Monge, F.; Millera, A.; Bilbao, R. *Combust. Flame* **2013**, 160, 853–860.
 - (22) Kee, R. J.; Rupley, F. M.; Miller, J. A. *Chemkin-II: A Fortran Chemical Kinetics Package for the Analysis of Gas-Phase Chemical Kinetics*; Sandia National Laboratories: Albuquerque, NM, 1991; Report SAND87-8215.