

High pressure study of H_2 oxidation and its interaction with NO

J.M. Colom-Díaz, Á. Millera, R. Bilbao, M.U. Alzueta*

Aragón Institute of Engineering Research (I3A). Department of Chemical and Environmental Engineering, University of Zaragoza, C/Mariano Esquillor s/n, 50018 Zaragoza, Spain

Abstract

The present study deals with the oxidation of H_2 at high pressure and its interaction with NO . The high pressure behavior of the $H_2/NO_x/O_2$ system has been tested over a wide range of temperatures (500-1100 K) and different air excess ratios ($\lambda = 0.5 - 6.4$). The experiments have been carried out in a tubular flow reactor at 10, 20 and 40 bar. NO has been found to promote H_2 oxidation under oxidizing conditions, reacting with HO_2 radicals to form the more active OH radical, which enhances the conversion of hydrogen. The onset temperature for hydrogen oxidation, when doped with NO , was approximately the same at all stoichiometries at high pressures (40 bar), and shifted to higher temperatures as the pressure decreases. The experimental results have been analyzed with an updated kinetic model. The reaction $NO+NO+O_2 \rightleftharpoons NO_2+NO_2$ has been found to be important at all conditions studied and its kinetic parameters have been modified, according to its activation energy uncertainty. Furthermore, the kinetic parameters of reaction $HNO+H_2 \rightleftharpoons NH+H_2O$ have been estimated, in order to obtain a good prediction of the oxidation behavior of H_2 and NO conversion under reducing conditions. The kinetic model shows a good agreement between experimental results and model predictions over a wide range of conditions.

Keywords: Hydrogen oxidation; NO_x interaction; Flow reactor; High pressure

*Corresponding author.
E-mail address: uxue@unizar.es (M. U. Alzueta)

1. Introduction

Hydrogen has been taking attention in the last decades because of its potential as fuel. Due to its high energetic value per mass unit and its almost inexistent contribution to pollution, H_2 is seen as an attractive option [1], although the problem with its high transportation cost makes difficult hydrogen storage. Solutions like ammonia as a hydrogen carrier [2, 3] or on-board reforming of hydrocarbon fuels [4] have emerged to deal with the hydrogen storage issue. Efforts are being undertaken on the development of high pressure combustion systems [5], what has created the need of kinetic models validated in these high pressure conditions and the target of increasing their efficiency. The H_2/O_2 sub-mechanism is the basis in the kinetic models of hydrocarbons oxidation and NO_x formation, being studied in the past years in some works [6, 7, 8, 9], but despite being a reliable subset of reaction, uncertainty towards the determination of precise rate constants still exists. Miller et al. [10] mentioned that repeated direct measurements of the rate parameters of important reactions, even performed independently by several groups, did not decrease the uncertainty of the rate coefficients below a certain limit, as happens for reaction $H + O_2 \rightleftharpoons OH + O$ and reaction $H + O_2 + M \rightleftharpoons HO_2 + M$, where a 30% and 50% uncertainty in their kinetic parameters was estimated, respectively. Hence, new experimental data to validate kinetic models are valuable.

On the other hand, NO_x might be present in combustion processes, and they come from the conversion of the nitrogen in air atmospheres. Thermal NO is the most important source of NO_x in gas combustion and its formation is described by the Zeldovich mechanism [11, 12]. While most of gas fuels (e.g. natural gas) don't have much nitrogen in their composition, in the case of the use of NH_3 as a new fuel, NO_x formation is feasible [13, 14]. The advantages in transportation and storage versus H_2 , together with the existing infrastructure to supply NH_3 , and the fact that potentially can be fully turned into N_2 and H_2O , make ammonia a desirable option among other fuels for combustion purposes. However, apart from NO_x emissions, there are still issues related to this fuel that need a further research in terms of combustion characteristics, being its high ignition energy and its low flammability some of the drawbacks to tackle [15]. In this sense, some studies have proposed the use of other fuels like H_2 blended with NH_3 (till 50:50 ratios), to improve its oxidation behavior [14, 16]. Besides, NH_3 combustion

is not completely understood and some experimental issues are still barriers or unresolved. According to some sources [13, 17], NH_3 has been reported to adsorb on stainless steel surfaces, as to decompose on given materials [18, 19]. Thus, providing new experimental data for NH_3 conversion under different combustion conditions, and assuring a reliable kinetic model for the H_2/NO_x system seems important for addressing NH_3 oxidation.

Less conventional sources of NO_x in combustion processes might be the addition of alkyl-nitrates as cetane enhancers in diesel fuels [20] or the use of exhaust gas recirculation (EGR) [21], which recirculates NO_x back into the combustion chamber among other gases. EGR has been proved to reduce NO_x emissions in diesel engines due to a lower flame temperature but increasing CO and hydrocarbons (HC) emissions. On the other hand, the idea about the addition of H_2 into the intake mixture of a diesel engine with EGR has shown great potential in improving diesel engine performance and reducing NO_x and soot emissions [22, 23]. However, determining the optimum amount of H_2 to add seems to be important to avoid concerns of pre-ignition, backfire, and other combustion problems such as the onset of knock.

Some studies have considered in the past the oxidation of H_2 doped with NO_x . Bromly et al. [24] studied it in a flow reactor at atmospheric pressure, finding that the presence of NO (0-400 ppm) promotes the oxidation of H_2 except for high concentrations of O_2 (22%). This work was extended by Mueller et al. [25], who perturbed the $H_2/O_2/N_2$ system with small amounts of NO at pressures and temperatures ranging from 10 to 14 atm and from 800 to 900 K, respectively, finding that the modeling results were highly sensitive to the $H + O_2 + M \rightleftharpoons HO_2 + M$ pressure-dependent reaction and recommending a kinetic expression for it. This reaction was also studied by Ashman and Haynes [26], who compared theoretical predictions and experimental concentration values of NO_2 in the H_2/O_2 system, allowing them to determine a rate constant and different third body efficiencies (N_2 , H_2O , CO_2 and Ar). This reaction is considered to be important, due to the high number of reactions that become important at high pressures consuming HO_2 radicals.

Autoignition of $H_2/air/NO_x$ mixtures has also been studied in some works. Slack and Grillo [27] tested the addition of both NO and NO_2 (0-4.5%) in a shock tube, in the pressure range of 0.27 to 2 atm, and tempera-

ture range of 800 to 1500 K, finding that the induction times were reduced up to more than an order of magnitude, compared to H_2 conversion in the absence of nitrogen oxides. Laster and Sojka [28] also studied this system, reaching the same conclusion as Slack and Grillo, i.e. the NO addition decreases ignition delay times until a concentration of about 0.5%, and above this concentration induction times are lengthened due to the scavenging of H atoms from NO . They concluded that the NO promoting effect is lessened as temperature rises and pressure decreases. More recently, Mathieu et al. [29] published ignition delay time measurements of $H_2/O_2/NO_2$ mixtures diluted in Ar using shock tube behind reflected shock waves, finding a strong dependency on pressure and NO_2 concentration, which needs thus to be carefully evaluated.

At high pressures, the NO/NO_2 interconversion becomes important, specially at low temperatures and high O_2 concentrations, where NO_2 presence is favored. The presence of NO_x under engine-relevant conditions might influence notably the reactivity of the fuel, through a sequence of reactions in which NO and NO_2 convert less reactive peroxy radicals into more reactive OH and alkyloxy radicals [30]. Knowing accurately the amount of NO/NO_2 that interacts with the fuel seems to be an important task to approach. An important reaction determining the conversion of NO into NO_2 is $NO + NO + O_2 \rightleftharpoons NO_2 + NO_2$. In particular, in the case of premixed reactants feeding, this reaction may occur in the inlet section of the reactor, varying the initial concentration of NO_x chosen for the experiment, which needs thus to be carefully determined.

The present work addresses the oxidation of H_2 and its interaction with NO under high pressure conditions. For this purpose, different experiments of H_2 oxidation in the absence and presence of NO have been performed in a quartz tubular flow reactor at high pressure, studying the influence of temperature (500-1100 K) and manometric pressure (10, 20 and 40 bar), using different stoichiometries related to H_2 ($\lambda = 0.5 - 6.4$). The experimental conditions chosen are useful to validate a kinetic model for describing hydrogen oxidation, over a wide range of conditions that might occur in any high-pressure system where H_2 is oxidized and interacts with NO_x species.

2. Experimental

The experiments have been carried out in a high-pressure flow reactor set-up, which is described in detail elsewhere [31]. Testing different manometric pressures (10, 20 and 40 bar) and different stoichiometries in the temperature range of 500-1100 K, the oxidation of H_2 and its interaction with NO have been studied. Briefly, the set-up includes gas cylinders that supply the gases to the system, while mass flow controllers assure a total flow rate of 1 L (STP)/min. Gases used in this work (H_2 , O_2 and NO) have been highly diluted in nitrogen and different concentrations of oxygen have been tested. The experimental conditions are detailed in Table 1. The $H_2/NO/O_2$ system has been tested at different stoichiometries (oxidizing, stoichiometric and reducing atmospheres with respect to H_2 , λ_{H_2} in Table 1), while the comparison with the NO/O_2 and H_2/O_2 systems has been done only under oxidizing conditions. The reaction system included a quartz tubular reactor (inner diameter of 6 mm and 1500 mm in length) enclosed in a stainless-steel tube that acts as a pressure shell. The steel tube is placed horizontally in a tubular oven, with three individually controlled electrical heating elements that ensure an isothermal reaction zone of approximately 56 cm, with a uniform temperature profile (± 10 K). The reactor temperature is monitored by type K thermocouples positioned between the quartz reactor and the steel shell. An example of the temperature profiles at 40 bar can be seen in Figure 1. Gas residence time depends on pressure and temperature and it can be expressed as: $t_r[s] = 261.1 P[\text{bar}]/T[\text{K}]$ in the isothermal zone of the reactor. The total gas residence time is calculated taking into account the temperature profiles in the experimental entire set-up. An example of the total gas residence time in the entire set-up is shown in Table 1, corresponding to a temperature of 875 K in the isothermal part of the reactor. Previously to the gas analysis systems, gases pass through a filter and a condenser to ensure gas cleaning and water-free content. Products are analyzed by a gas chromatograph equipped with thermal conductivity detector (TCD) to detect H_2 and a continuous chemiluminescence analyzer to detect NO and NO_2 . The uncertainty of the measurements is estimated within 5%.

Table 1: Experimental conditions. The total flow rate is balanced with N_2 . Parameter λ_{H_2} is calculated according to the reaction $H_2 + 1/2O_2 \rightleftharpoons H_2O$ and parameter λ_{NO} according to the reaction $NO + 1/2O_2 \rightleftharpoons NO_2$. The residence time is referred, as an example, to the entire set-up at one particular temperature in the isothermal zone of the reactor (875 K).

Set	P (bar)	H_2 (ppm)	NO (ppm)	λ_{H_2}	λ_{NO}	t_r (s)	O_2 (ppm)
1	40	937	530	6.4	11.3	107	3000
2	20	935	517	6.4	11.6	56	3000
3	10	920	524	6.5	11.5	29	3000
4	40	1029	-	5.8	-	107	3000
5	20	930	-	6.4	-	56	3000
6	10	910	-	6.6	-	29	3000
7	40	-	521	-	11.5	107	3000
8	20	-	508	-	11.8	56	3000
9	10	-	514	-	11.7	29	3000
10	40	1022	485	0.98	2.1	107	500
11	20	1050	525	1.3	2.6	56	675
12	40	1024	535	0.5	0.9	107	250
13	20	1000	520	0.5	1	56	250

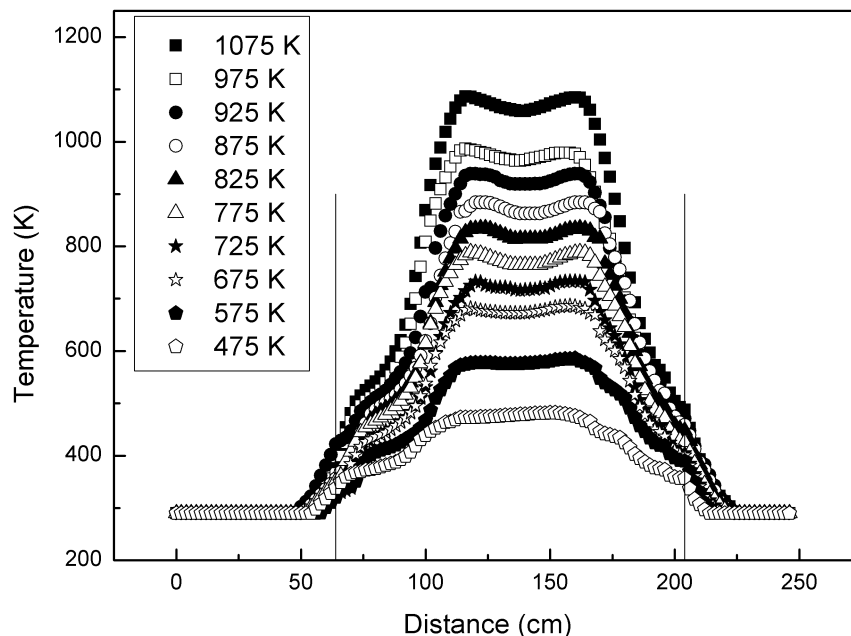


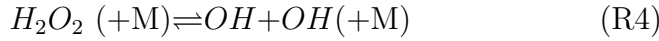
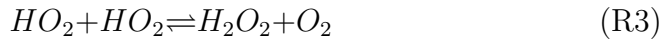
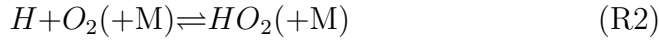
Figure 1: Temperature profiles in the entire experimental set-up at 40 bar, as a function of the set-up length. 0 cm corresponds to the point where the gases are premixed, while the reactor zone starts at 64 cm and ends at 204 cm.

3. Kinetic Model

The experimental results have been interpreted in terms of kinetic modeling using Chemkin-PRO. The kinetic model used in this work is a revised and updated version of the work of Giménez-López et al. [32], who performed experiments of C_2H_4/NO mixtures at high pressure (60 bar) and different stoichiometries in a flow reactor. The subset for H_2/O_2 has been taken from the work of Hashemi et al. [8] on H_2 oxidation at high pressures in a flow reactor, which was based on the kinetic model developed by Burke et al. [33]. Thermodynamic data were taken from the same sources as the submechanisms.

Consumption of hydrogen can be described as a chain of reactions, being R1 the main step in the H_2 oxidation. Radicals HO_2 are formed due to the

reaction of atomic H with oxygen through R2, then, are recombined to form H_2O_2 in R3. In the last step, R4, through H_2O_2 decomposition provides OH radicals for the consumption step R1 [8, 25]. R5 is considered to be important for H_2 conversion initiation at all stoichiometries and found to be one of the most sensitive [8]. Kinetic parameters for this reaction were taken from Giménez-López et al. [32], because they are more updated values compared to the ones used in the H_2/O_2 sub-mechanism by Hashemi et al. [8] and provide a better modeling behavior in this work.



The competition between reactions R2 and R6 determines the generation of chain carriers in combustion of hydrogen, as well as of most hydrocarbons [34, 35].



In the present work, operating at high pressures, the H_2 oxidation behavior has been explained to happen under conditions dominated by reactions involving HO_2 and H_2O_2 (e.g. [8]). When NO is added to the system, the role of HO_2 as a chain terminator is changed, and HO_2 is consumed by NO in R7, forming NO_2 and OH . Then, NO_2 reacts with H radicals to give back NO and OH radicals (R8), forming a well known NO/NO_2 catalytic cycle, represented by R7 and R8 [24, 25, 27], with $HO_2 + H \rightleftharpoons OH + OH$ as net reaction.

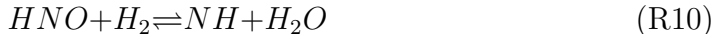


In the work of Mathieu et al. [29] on ignition delay time measurements of $H_2/O_2/NO_2$ mixtures diluted with Ar , using shock tube behind reflected shock waves, a strong sensitivity of reaction R9 was found in their analysis. R9 is followed by the rapid decomposition of $HONO$ to NO and OH , promoting the overall oxidation of H_2 . They used the kinetic parameters from Park et al. [36] for reaction R9.



Chai and Goldsmith [30] studied rate coefficients for fuel+ NO_2 , predicting the formation of HONO, and they distinguished 3 different isomers (cis- $HONO$, trans- $HONO$ and HNO_2). As said by Zhang et al. [37], the total rate of the 3 isomers formation calculated by Chai and Goldsmith [30] is in excellent agreement with that reported in both the Park et al. [36] experimental measurement and Rasmussen et al. [9] calculation. In this work, we use the recent kinetic parameters for the three different isomers from Chai and Goldsmith [30]. Although modeling studies rarely distinguish the $HONO$ isomers as the products of R9, a slight improvement in the onset temperature of H_2 conversion at all conditions was found in this work including the different isomers.

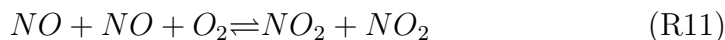
The work from Glarborg et al. [38], where the ability of H_2 to reduce nitric oxide under conditions relevant for the reburning process was studied, remarked the importance of species like HNO to react with H_2 , finding that the only kinetic parameters available for R10, by Röhrig and Wagner [39], gave a H_2 conversion too fast compared to their experimental data and finally not using this reaction in their model.



We also found that the kinetic parameters [39] overpredict the consumption of H_2 , and we estimated the kinetic constant to be 7E8 ($cm^3 \cdot mol^{-1} \cdot s^{-1}$), obtaining good agreement between experimental results and model predictions, as well as for H_2 as for NO_x concentrations at high temperatures, as can be seen in the next section. A comparison in the model predictions without R10 can be found in the supplementary material (Figure S1), where the consumption of H_2 is not well captured if R10 does not occur and is overpredicted with the kinetic parameters from the bibliography [39]. R10

was found to be important only under reducing conditions, while no impact was observed at other stoichiometries. An accurate determination of the rate constant for R10 would be desirable.

The amount of NO and NO_2 that enters the reactor zone can affect the oxidation behavior of hydrogen. NO molecules can be converted to NO_2 through R11 before entering the reactor, since the gases are premixed at room temperature.



Due to high pressures and the presence of oxygen, there will have a mixture of NO/NO_2 at the reactor inlet. This was observed while the oven was still cool (290 K) and has been pointed in previous works experimenting with NO at high pressures [31, 40, 41]. For this reason, in the present work, the model was run with temperature profiles, an example shown in [Figure 1](#), that describe the entire experimental set-up: from the mixing point of the reactants to the entrance of the reactor, the reactor itself, and from the reactor outlet to the pressure reduction valve (1 atm).

In order to simulate the experimental data, the kinetic parameters of R11 were revised in the present work. Some uncertainty exists towards R11 [42], for which most reliable value of activation energy determined up to date is $-4.41 [\pm 3.33]$ kJ/mol [43]. We have taken the pre-exponential factor recommended by Atkinson et al. [43] and varied the activation energy in the uncertainty limits, taking the inferior limit, what makes an apparent activation energy of -7.74 kJ/mol (-1850 cal/mol), and which seems to be adequate in all the experimental conditions of this work to reproduce properly the NO/NO_2 concentrations. As can be seen in [Figure S2](#) from the supplementary material, the kinetic parameters chosen are in reasonable agreement with experimental data reported in the past at low temperatures [44, 45, 46, 47], more than with the latest review of this reaction [43], which is mainly based on the work of Olbregts [48].

4. Results and discussion

Different systems have been tested under oxidizing conditions: $H_2/NO/O_2$, H_2/O_2 and NO/O_2 (sets 1 to 9 in Table 1), and their results have been plotted showing the comparisons between them. In Figure 2, the results corresponding to the conversion of the system H_2/O_2 with and without NO addition are shown, at 10, 20 and 40 bar under oxidizing conditions. Pressure has a little effect on the conversion onset of H_2 when NO is not present, showing approximately 50 K difference in the reaction onset between the three pressures, and shifting the conversion to lower temperatures as the pressure increases. When NO is added to the system, the promotion of H_2 conversion to lower temperatures is increased as pressure rises, and comparatively greater than in the experiment without NO . In the case of 40 bar, there is a difference of 125 K in the reaction onset, and only 25 K in the case of 10 bar. With respect to NO_x , pressure has an important influence on the NO/NO_2 ratio, showing a major concentration of NO_2 as the pressure rises, due to R11, and a slight conversion back to NO as the temperature increases. The experimental trends of H_2 conversion and NO/NO_2 concentrations are well captured by the mechanism, confirming the behavior mentioned in the literature about NO_x promoting H_2 oxidation. This promotion can be explained through the interconversion of NO and NO_2 converting radicals HO_2 into more active radicals OH , as has been mentioned in the kinetic modeling section. The ability to capture this behavior (hydrogen promotion) is, in part, achieved by the proposed kinetic parameters of R11, which is important predicting the amount of NO and NO_2 that enters the reaction zone, influencing hydrogen ignition as well as the oxidation process at high pressures, and might be seen as an improvement in the predictions of the kinetic model.

It is worth to mention that the balance of NO_x closes fairly well (near 100%) in all the cases, except at 40 bar and under oxidizing conditions, where at high temperatures there is a NO_x decrease of approx. 20% (Figure 2). This behavior of NO_x balance not closing at 100% was not seen in the experiment without hydrogen at 40 bar (set 7) (Figure 3). A similar study of the $CO/H_2/O_2/NO_x$ system [9] in a flow reactor at high pressures did not show a loss of NO_x when working at 50 bar and high oxidizing conditions ($\lambda=68$ for H_2). According to the present results, we might conclude that some interaction NO_2/H_2 not captured by the model is occurring in our experimental conditions at 40 bar and high temperatures. Another possible

explanation could be related with the formation of nitric acid. As said by Ajdari et al. [41], if water vapor is present in pressurized flue gas systems, the formation of gaseous nitric acid and nitrous acid and the decomposition of nitrous acid may proceed as shown by reactions: $N_2O_4 + H_2O = HNO_2 + HNO_3$ and $2HNO_2 = NO + NO_2 + H_2O$, what could explain the loss of NO_x as nitric acid, but this has not been possible to prove.

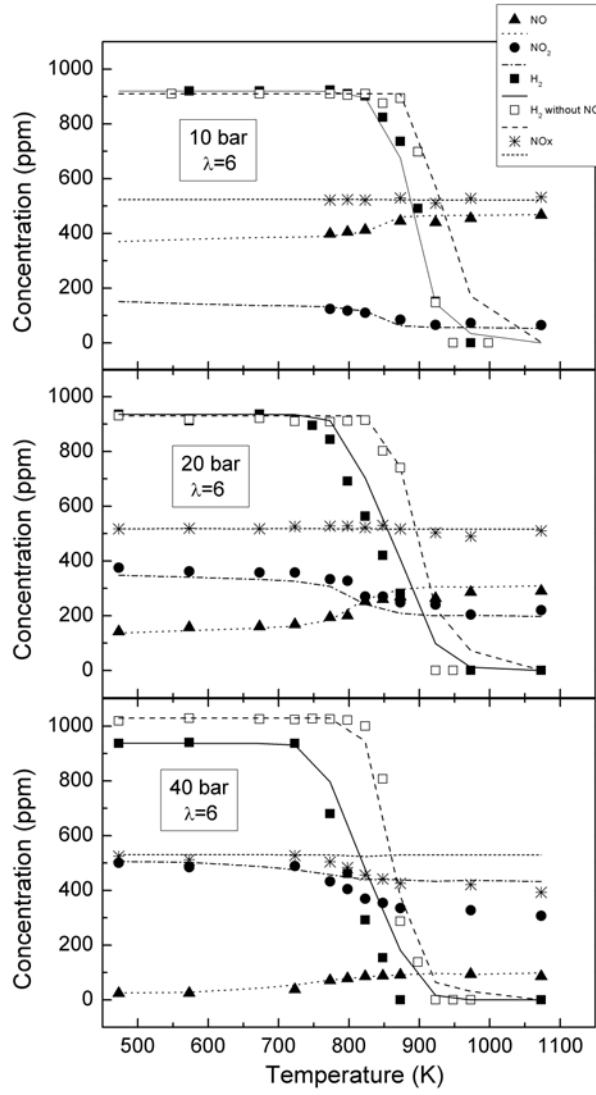
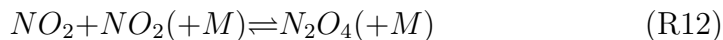


Figure 2: Results obtained under oxidizing conditions (λ referred to H_2) at 10 bar (up), 20 bar (centre) and 40 bar (down). Solid symbols correspond to experimental results in the presence of NO , while open symbols represent concentrations in the experiments without NO . Lines denote simulations of the model. Conditions of sets 1 to 6 in Table 1.

In [Figure 3](#), the comparison of the results in the system NO/NO_2 with and without H_2 , at 40, 20 and 10 bar under oxidizing conditions can be observed. Due to the major amount of radicals when hydrogen is present, NO and NO_2 react through R7 and R8, while in the system without hydrogen, the main reaction is the NO/NO_2 interconversion (R11), being favoured the NO presence at low pressures and high temperatures. In the current simulations, the concentration of NO_2 is the sum of NO_2 and N_2O_4 , the latter only found to be important under 40 bar, with a maximum concentration of around 35 ppm in the reactor outlet section, according to the model. Due to the equilibrium between these two species, represented by R12, the existing N_2O_4 molecules are totally converted to NO_2 as the pressure is decreased to 1 bar in the relief valve of the set-up. The experimental trends are fairly well fitted by the model and the balance of NO_x does not close only at 40 bar.



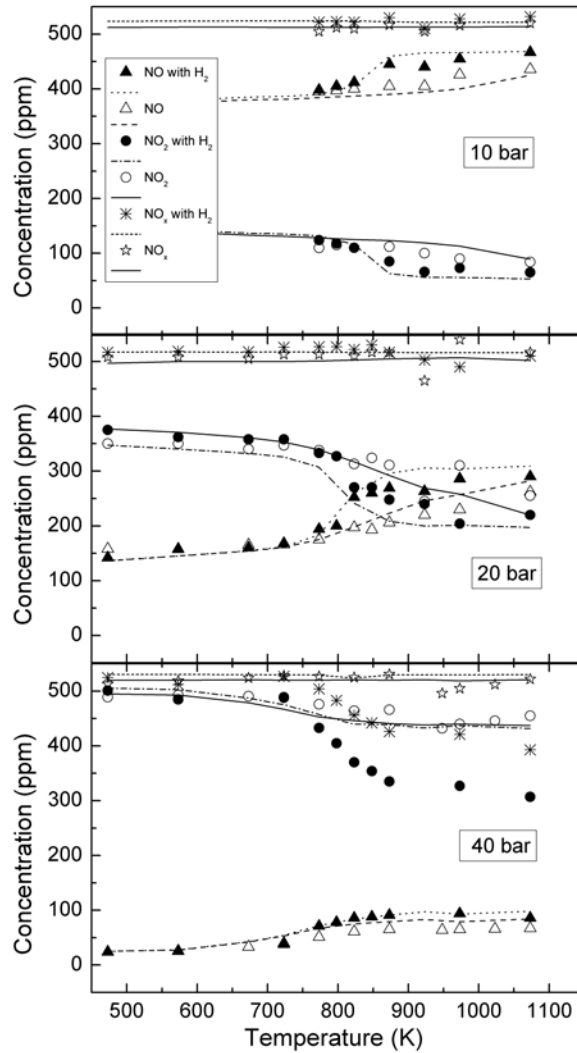


Figure 3: Results obtained under oxidizing conditions (λ_{NO} approximately 12) at 10 bar of pressure (up), 20 bar (centre) and 40 bar (down). Solid symbols correspond to experimental results in the presence of H_2 , while open symbols represent concentrations in the experiments without H_2 . Lines denote simulations of the model. Conditions of sets 1-3 and sets 7-9 in Table 1.

Figure 4 shows the results of H_2 conversion in the presence of NO for stoichiometric conditions and different pressures. Under these conditions, the NO_2/NO ratio is higher as the pressure increases, as mentioned before, and the onset temperature for H_2 conversion remains the same at 40 bar as for oxidizing conditions (773 K), but finishes at higher temperatures due to the lack of oxygen. At 20 bar, the reaction starts at higher temperatures in comparison to the case of 40 bar, around 823 K. The kinetic model reproduces well the experimental data.

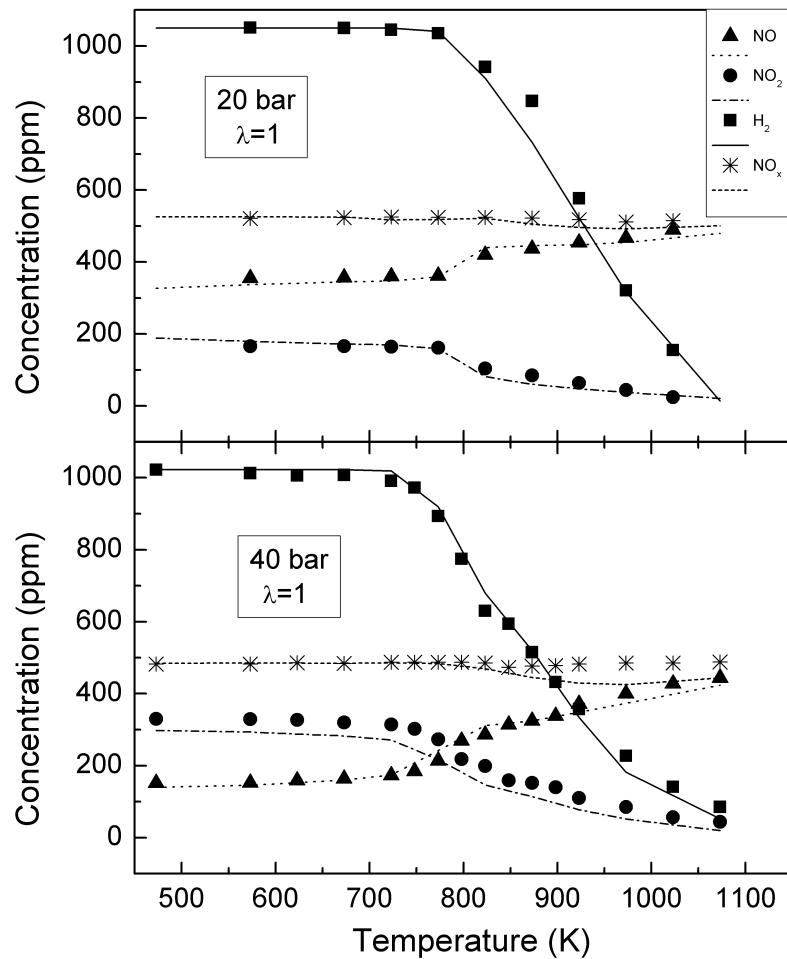
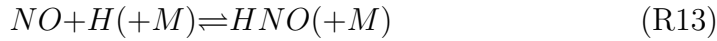


Figure 4: Results obtained under stoichiometric (λ referred to H_2) conditions at 20 bar (up) and 40 bar (down). Symbols represent experimental measurements and lines denote simulations of the model. Conditions of sets 10 and 11 in Table 1.

Similar results are plotted, in [Figure 5](#), for experiments performed under reducing conditions. The onset temperature for the reaction of hydrogen at 40 bar remains the same as for other stoichiometries (773 K), which is dif-

ferent to what was observed in the work of Hashemi et al. [8] of hydrogen oxidation at high pressures (50 bar) in a flow reactor, where they found that the onset of the reaction happened at lower temperatures under reducing conditions, compared to stoichiometric and oxidizing conditions, due to the competition between R2 and R6. In our case, when NO is added, R2 remains the main path in the oxidation of H_2 , involving HO_2 radicals in the oxidation process. This oxidation process is more effective at higher pressures (40 bar) and R2 starts to compete with R6 as the pressure drops, shifting the onset of the reaction to higher temperatures, as seen in the results of Figure 5. At 40 bar, the H_2 conversion onset is well captured by the model as well as its experimental trend. However, in the case of 20 bar, the experimental H_2 concentration suffers a sudden experimental decrease that is predicted smoothlier by the model. The general conversion trends are still well captured by the model, and the modification of the kinetic parameters of R10 clearly improves the prediction of H_2 concentration at 20 and 40 bar under reducing conditions, as well as the drop of NO_x at 40 bar (Figure 5 down). This can be explained because NO reacts with H radicals to form HNO, through R13, then R10 occurs and NH is formed, which will end up reacting with NO to form N_2 and OH through R14.



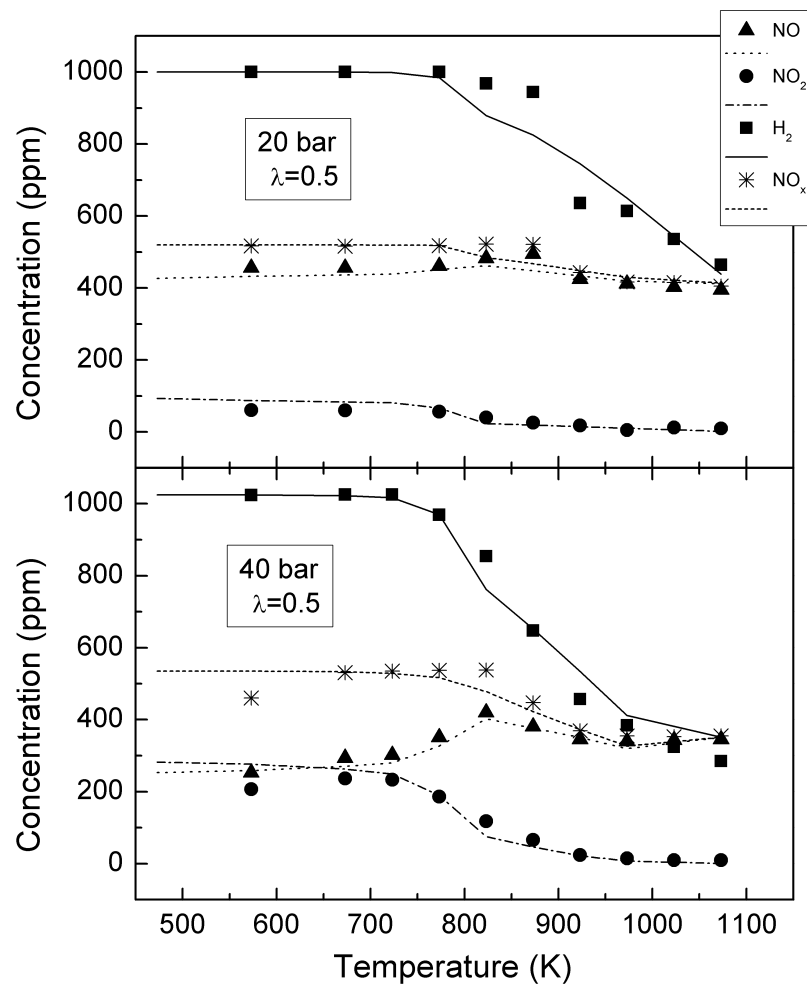


Figure 5: Results obtained under reducing conditions (λ referred to H_2) at 20 bar (up) and 40 bar (down). Symbols represent experimental measurements and lines denote simulations of the model. Conditions of sets 12 and 13 in Table 1.

5. Conclusions

The system $H_2/NO/O_2$ has been studied in a tubular quartz flow reactor. Experiments under different controlled conditions, such as high manometric pressures (10, 20 and 40 bar), in the temperature range of 500-1100 K, testing different excess ratios for H_2 ($\lambda = 0.5 - 6.4$) have been carried out. The results obtained are useful for practical purposes where different technologies can be used. The results have been interpreted in terms of kinetic modeling, using an updated mechanism from recent works and modifying the kinetic parameters of the reactions: $2NO + O_2 \rightleftharpoons NO_2 + NO_2$, according to the uncertainty of its activation energy; and the $HNO + H_2 \rightleftharpoons NH + H_2O$ reaction, proposing a rate constant of $7E8 \text{ (cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}\text{)}$, which reproduces fairly well the oxidation of H_2 under reducing conditions. This kinetic model allows us to predict results about the H_2 oxidation and its interaction with NO under a variety of operating conditions.

NO has been found to promote H_2 oxidation under oxidizing conditions, reacting with the HO_2 radical to form the more active OH radical, which enhances the conversion of hydrogen. The onset for hydrogen oxidation when doped with NO is the same at all stoichiometries at high pressures (40 bar), and is shifted to higher temperatures as the pressure decreases. The kinetic model matches fairly well the experimental data at all conditions, explaining the oxidation of H_2 and NO under oxidizing, stoichiometric and reducing conditions, except for the case of 40 bar under oxidizing conditions, where a 20% drop of the NO_x balance has been found and can not be predicted by the model, presumably by some interaction between NO_2/H_2 or the possible formation of nitric acid, which needs a more detailed study.

6. Acknowledgements

The authors express their gratitude to Aragón Government and European Social Fund (GPT group), and to MINECO and FEDER (Project CTQ2015-65226/PPQ and grant BES-2016-076610) for financial support.

References

- [1] J. K. Unni, P. Govindappa, L. M. Das, Development of hydrogen fuelled transport engine and field tests on vehicles, *International Journal of Hydrogen Energy* 42 (2017) 643–651.

- [2] C. Plana, S. Armenise, A. Monzón, E. García-Bordejé, Ni on alumina-coated cordierite monoliths for in situ generation of CO -free H_2 from ammonia, *Journal of Catalysis* 275 (2010) 228–235.
- [3] W. Wang, J. M. Herreros, A. Tsolakis, A. P. York, Ammonia as hydrogen carrier for transportation; investigation of the ammonia exhaust gas fuel reforming, *International Journal of Hydrogen Energy* 38 (2013) 9907–9917.
- [4] S. Martin, A. Wörner, On-board reforming of biodiesel and bioethanol for high temperature pem fuel cells: Comparison of autothermal reforming and steam reforming, *Journal of Power Sources* 196 (2011) 3163–3171.
- [5] Basic research needs for clean and efficient combustion of 21st century transportation fuels, Tech. rep., Office of Science, U.S. Department of Energy (2006).
- [6] M. P. Burke, M. Chaos, Y. Ju, F. L. Dryer, S. J. Klippenstein, Comprehensive H_2/O_2 kinetic model for high-pressure combustion, *International Journal of Chemical Kinetics* 44 (2012) 444–474.
- [7] Z. Hong, D. F. Davidson, R. K. Hanson, An improved H_2/O_2 mechanism based on recent shock tube/laser absorption measurements, *Combustion and Flame* 158 (2011) 633–644.
- [8] H. Hashemi, J. M. Christensen, S. Gersen, P. Glarborg, Hydrogen oxidation at high pressure and intermediate temperatures: experiments and kinetic modeling, *Proceedings of the Combustion Institute* 35 (2015) 553–560.
- [9] C. L. Rasmussen, J. Hansen, P. Marshall, P. Glarborg, Experimental measurements and kinetic modeling of $CO/H_2/O_2/NO_x$ conversion at high pressure, *International Journal of Chemical Kinetics* 40 (2008) 454–480.
- [10] J. A. Miller, M. J. Pilling, J. Troe, Unravelling combustion mechanisms through a quantitative understanding of elementary reactions, *Proceedings of the Combustion Institute* 30 (2005) 43–88.

- [11] Y. B. Zeldovich, The oxidation of nitrogen in combustion and explosions, *Acta Physicochem* 21 (1946) 577–628.
- [12] M. Abián, M. U. Alzueta, P. Glarborg, Formation of NO from N_2/O_2 mixtures in a flow reactor: Toward an accurate prediction of thermal NO , *International Journal of Chemical Kinetics* 47 (2015) 518–532.
- [13] O. Mathieu, E. L. Petersen, Experimental and modeling study on the high-temperature oxidation of ammonia and related NO_x chemistry, *Combustion and Flame* 162 (2015) 554–570.
- [14] D. Pugh, P. Bowen, A. Valera-Medina, A. Giles, J. Runyon, R. Marsh, Influence of steam addition and elevated ambient conditions on NO_x reduction in a staged premixed swirling NH_3/H_2 flame, *Proceedings of the Combustion Institute* 37, in press. doi:<https://doi.org/10.1016/j.proci.2018.07.091>.
- [15] A. Valera-Medina, D. Pugh, P. Marsh, G. Bulat, P. Bowen, Preliminary study on lean premixed combustion of ammonia-hydrogen for swirling gas turbine combustors, *International Journal of Hydrogen Energy* 42 (2017) 24495–24503.
- [16] H. Nozari, G. Karaca, O. Tuncer, A. Karabeyoglu, Porous medium based burner for efficient and clean combustion of ammonia–hydrogen–air systems, *International Journal of Hydrogen Energy* 42 (2017) 14775–14785.
- [17] S. Salimian, R. Hanson, C. Kruger, Ammonia oxidation in shock-heated $NH_3 - N_2O - Ar$ mixtures, *Combustion and Flame* 56 (1984) 83–95.
- [18] D. A. Cooper, E. B. Ljungstroem, Decomposition of ammonia over quartz sand at 840–960 °C, *Energy & Fuels* 2 (1988) 716–719.
- [19] Y. Song, H. Hashemi, J. M. Christensen, C. Zou, P. Marshall, P. Glarborg, Ammonia oxidation at high pressure and intermediate temperatures, *Fuel* 181 (2016) 358–365.
- [20] M. Hartmann, K. Tian, C. Hofrath, M. Fikri, A. Schubert, R. Schießl, R. Starke, B. Atakan, C. Schulz, U. Maas, F. K. Jäger, K. Kühling, Experiments and modeling of ignition delay times, flame structure and intermediate species of EHN -doped stoichiometric n-heptane/air combustion, *Proceedings of the Combustion Institute* 32 (2009) 197–204.

- [21] D. Agarwal, S. K. Singh, A. K. Agarwal, Effect of exhaust gas recirculation (*EGR*) on performance, emissions, deposits and durability of a constant speed compression ignition engine, *Applied Energy* 88 (2011) 2900–2907.
- [22] L. Wang, D. Liu, Z. Yang, H. Li, L. Wei, Q. Li, Effect of H_2 addition on combustion and exhaust emissions in a heavy-duty diesel engine with *EGR*, *International Journal of Hydrogen Energy* 43 (2018) 22658–22668.
- [23] P. K. Bose, D. Maji, An experimental investigation on engine performance and emissions of a single cylinder diesel engine using hydrogen as inducted fuel and diesel as injected fuel with exhaust gas recirculation, *International Journal of Hydrogen Energy* 34 (2009) 4847–4854.
- [24] J. Bromly, F. Barnes, P. Nelson, B. Haynes, Kinetics and modeling of the $H_2/O_2/NO_x$ system, *International Journal of Chemical Kinetics* 27 (12) (1995) 1165–1178.
- [25] M. A. Mueller, R. A. Yetter, F. L. Dryer, Measurement of the rate constant for $H + O_2 + M = HO_2 + M$ ($M = N_2, Ar$) using kinetic modeling of the high-pressure $H_2/O_2/NO_x$ reaction, *Symposium (International) on Combustion* 27 (1998) 177–184.
- [26] P. J. Ashman, B. S. Haynes, Rate coefficient of $H + O_2 + M = HO_2 + M$ ($M = H_2O, N_2, Ar, CO_2$), *Symposium (International) on Combustion* 27 (1998) 185–191.
- [27] M. Slack, A. Grillo, Investigation of hydrogen-air ignition sensitised by nitric oxide and by nitrogen dioxide, Tech. rep., NASA Report CR-2896 (1977).
- [28] W. R. Laster, P. E. Sojka, Autoignition of H_2 /air/ NO_x mixtures - the effect of temperature and pressure, *Journal of Propulsion and Power* 5:4 (1989) 510–512.
- [29] O. Mathieu, A. Levacque, E. Petersen, Effects of NO_2 addition on hydrogen ignition behind reflected shock waves, *Proceedings of the Combustion Institute* 34 (2013) 633–640.

- [30] J. Chai, C. F. Goldsmith, Rate coefficients for fuel+ NO_2 : Predictive kinetics for $HONO$ and HNO_2 formation, Proceedings of the Combustion Institute 36 (2017) 617–626.
- [31] L. Marrodan, Á. Millera, R. Bilbao, M. U. Alzueta, High-pressure study of methyl formate oxidation and its interaction with NO , Energy & Fuels 28 (2014) 6107–6115.
- [32] J. Giménez-López, M. Alzueta, C. Rasmussen, P. Marshall, P. Glarborg, High pressure oxidation of C_2H_4/NO mixtures, Proceedings of the Combustion Institute 33 (2011) 449–457.
- [33] M. P. Burke, M. Chaos, Y. Ju, F. L. Dryer, S. J. Klippenstein, Comprehensive H_2/O_2 kinetic model for high-pressure combustion, International Journal of Chemical Kinetics 44 (2012) 444–474.
- [34] Y. Zhang, Z. Huang, L. Wei, J. Zhang, C. K. Law, Experimental and modeling study on ignition delays of lean mixtures of methane, hydrogen, oxygen, and argon at elevated pressures, Combustion and Flame 159 (2012) 918–931.
- [35] C. Fotache, T. Kreutz, C. Law, Ignition of counterflowing methane versus heated air under reduced and elevated pressures, Combustion and Flame 108 (1997) 442–470.
- [36] J. Park, N. D. Giles, J. Moore, M. C. Lin, A comprehensive kinetic study of thermal reduction of NO_2 by H_2 , The Journal of Physical Chemistry A 102 (1998) 10099–10105.
- [37] Y. Zhang, O. Mathieu, E. L. Petersen, G. Bourque, H. J. Curran, Assessing the predictions of a NO_x kinetic mechanism on recent hydrogen and syngas experimental data, Combustion and Flame 182 (2017) 122–141.
- [38] P. Glarborg, P. G. Kristensen, K. Dam-Johansen, M. U. Alzueta, A. Millera, R. Bilbao, Nitric oxide reduction by non-hydrocarbon fuels. implications for reburning with gasification gases, Energy & Fuels 14 (2000) 828–838.
- [39] M. Röhrig, H. G. Wagner, An investigation about the NH ($X^3\Sigma^-$) formation in the thermal decomposition of HN_3 , Berichte der Bunsengesellschaft für Physikalische Chemie 98 (1994) 1073–1076.

- [40] C. L. Rasmussen, A. E. Rasmussen, P. Glarborg, Sensitizing effects of NO_x on CH_4 oxidation at high pressure, *Combustion and Flame* 154 (2008) 529–545.
- [41] S. Ajdari, F. Normann, K. Andersson, F. Johnsson, Modeling the nitrogen and sulfur chemistry in pressurized flue gas systems, *Industrial & Engineering Chemistry Research* 54 (2015) 1216–1227.
- [42] O. B. Gadzhiev, S. K. Ignatov, S. Gangopadhyay, A. E. Masunov, A. I. Petrov, Mechanism of nitric oxide oxidation reaction ($2NO + O_2 = 2NO_2$) revisited, *Journal of Chemical Theory and Computation* 7 (2011) 2021–2024.
- [43] R. Atkinson, D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, R. G. Hynes, M. E. Jenkin, M. J. Rossi, J. Troe, Evaluated kinetic and photochemical data for atmospheric chemistry: Volume *I* - gas phase reactions of O_x , HO_x , NO_x and SO_x species, *Atmospheric Chemistry and Physics* 4 (2004) 1461–1738.
- [44] C. England, W. H. Corcoran, The rate and mechanism of the air oxidation of parts-per-million concentrations of nitric oxide in the presence of water vapor, *Industrial & Engineering Chemistry Fundamentals* 14 (1975) 55–63.
- [45] I. C. Hisatsune, L. Zafonte, Kinetic study of some third-order reactions of nitric oxide, *The Journal of Physical Chemistry* 73 (1969) 2980–2989.
- [46] J. D. Greig, P. G. Hall, Thermal oxidation of nitric oxide at low concentrations, *Transactions of the Faraday Society* 63 (1967) 655–661.
- [47] P. G. Ashmore, M. G. Burnett, B. J. Tyler, Reaction of nitric oxide and oxygen, *Transactions of the Faraday Society* 58 (1962) 685–691.
- [48] J. Olbregts, Termolecular reaction of nitrogen monoxide and oxygen: A still unsolved problem, *International Journal of Chemical Kinetics* 17 (1985) 835–848.

Supplementary Material

”High pressure study of H_2 oxidation and its interaction with NO ”

J.M. Colom-Díaz, Á. Millera, R. Bilbao, M.U. Alzueta

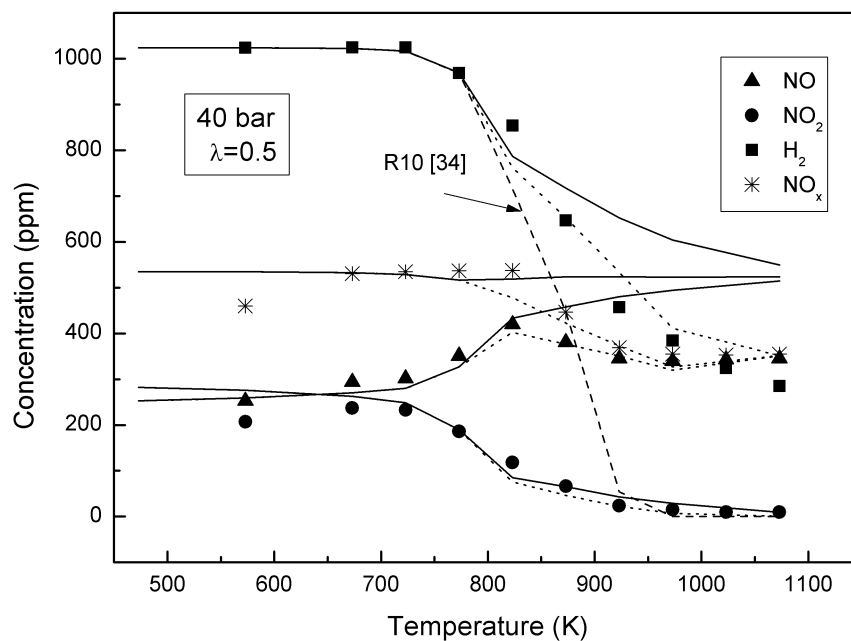


Figure S1: Set 12 from Table 1. Results under reducing conditions at 40 bar of pressure. Symbols represent experimental measurements and lines denote simulations of the model. Solid lines indicate the simulation without R10 in the model, dotted lines the simulation with our estimation for rate constant of R10: $7E8 \text{ (cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}\text{)}$, and dashed line shows the simulation of H_2 concentration using the kinetic parameters of R10 from Röhrig and Wagner [39].

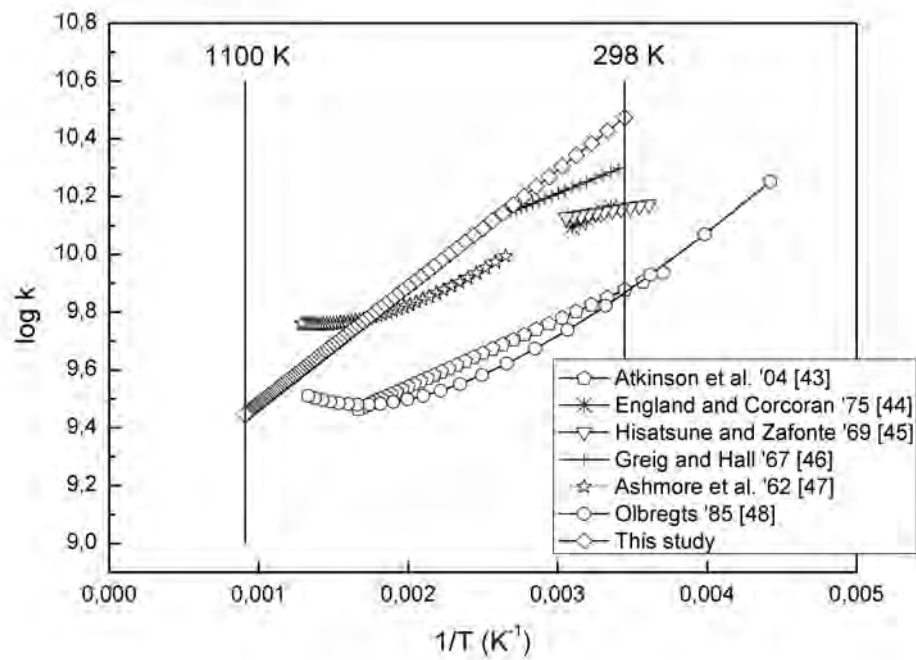


Figure S2: Comparison of different values for the kinetic constant logarithm of R11 ($2NO+O_2\rightleftharpoons NO_2+NO_2$) vs. $1/T(K)$, from the literature [43, 44, 45, 46, 47, 48] and the estimation of this study.