The impact of NO_x addition on the ignition behavior of n-pentane Supplemental Material - Comparison of Final and Intermediate Mechanisms

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Additional notes on supplemental materials:

- The preprint of this manuscript, including supplemental materials, is available at `https://doi.org/10.26434/chemrxiv.13720105`
- The v.0 mechanism has been deposited into an open database at `https://github.com/jiweiqi/CollectionOfMechan` `tree/master/Nitrogen/Fuller-2021`
- The experimental data files have been deposited into an open database at `https://github.com/pr-omethe-us/ChemKED-database`

References

1 M. P. Rissanen, S. L. Arppe, A. J. Eskola, M. M. Tammi and R. S. Timonen, *The Journal of Physical Chemistry A*, 2010, **114**, 4811–4817.

2 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 and I. Subcommittee, *Atmospheric Chemistry and Physics*, 2006, **6**, 3625–4055.

3 L. Marrodán, Y. Song, M. L. Lavadera, O. Herbinet, M. de Joannon, Y. Ju, M. U. Alzueta and F. Battin-Leclerc, *Energy & Fuels*, 2019, **33**, 5655–5663.

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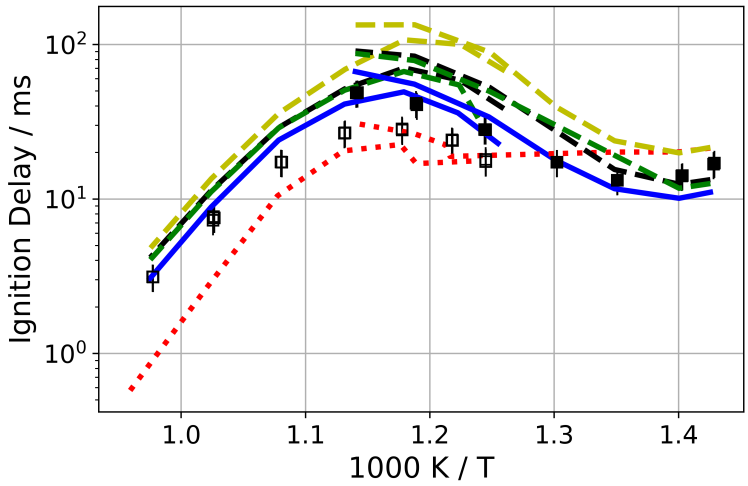
Class	Source	v.0	v.8	v.11	v.12
R + NO_x ⇌ Alkene + {HNO/HONO/HNO_2}	RMG	0.01	0.01	1.00	0.10
R + NO_2 ⇌ RONO	RMG	0.10	1.00	1.00	1.00
RO + NO_x ⇌ $ROONO_x$	RMG	1e-3	1.00	1.00	1.00
R + NO_2 ⇌ RO + NO	Ref. 1	0.10	1.00	1.00	1.00
RO_2 + NO2 ⇌ RO + NO_2	Ref. 2	0.01	1.00	1.00	1.00
RNO2 ⇌ R + NO2	Ref. 3	2.00	1.00	1.00	1.00
$O_2C_5H_{10}OOH$ + NO ⇌ OH + $2CH_2O$ + C_3H_6 + NO_2	Ref. 3	0.00	1.00	1.00	1.00

Table S2-1 Adjustment factors for reaction classes by model iteration ID

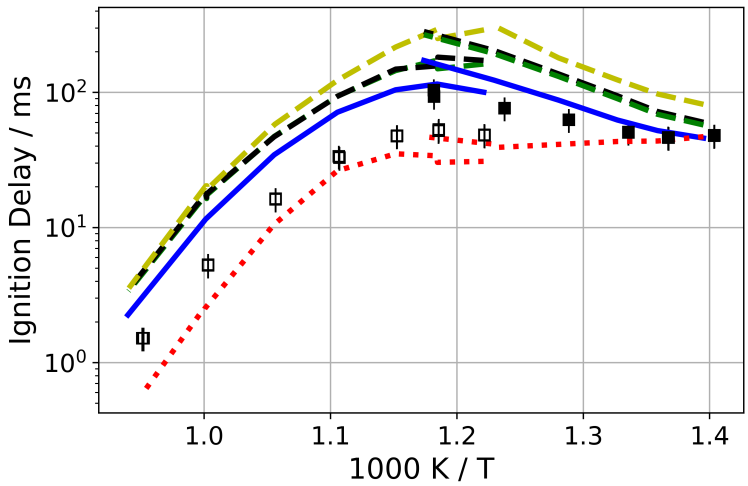
Step-wise evaluation of the mechanism from initial construction through the result presented herein is detailed in table S2-1 and figure S2-1.

In order to reassess the mechanism development in light of the absence of reliable NO-doped experiments, numerous iterations have been performed in which the factors by which rates were adjusted have been "rolled-back" to unity in order to observe the effect on the model predictions. The class of rates obtained from RMG for which values were reduced by a factor of 100 (R + NO_x ⇌ Alkene + {HNO/HONO/HNO_2}, referred) is confirmed to be a particularly sensitive class of reactions. Reanalysis, however, suggests that while decreasing the rates by a factor of ten makes a significant improvement in model predictions, reduction by a factor of one-hundred offers essentially no further gains for the IDT predictions of NO_2 experiments, ceteris parabis.

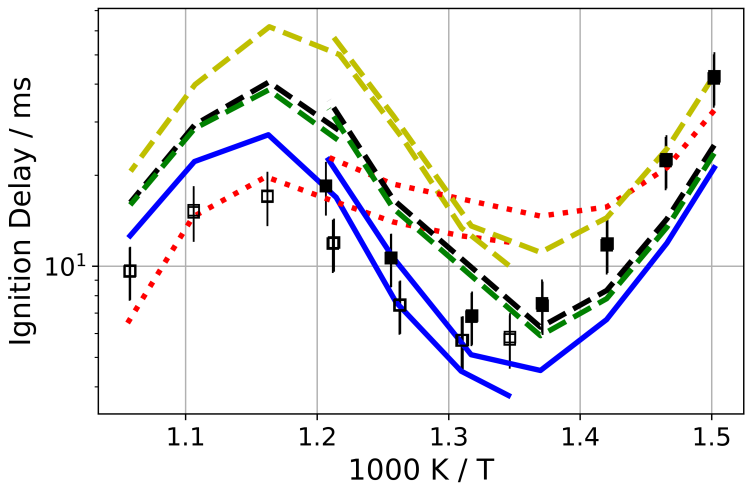
However, if one then proceeds to view the predictions for the available JSR data, where we are confident about NO, figures S2-2 and S2-3 with same color scheme as figure S2-1, the totality of chenges incorporated in the v.0 (final, submitted) model offer a superior fit to the data as compared with the “rolled-back” mechanisms and one which is competitive on fit with the mechanism published in Marrodán *et al.*.



(a) ϕ = 1.0; 333 ppm NO_2



(b) ϕ = 0.5; 333 ppm NO_2



(c) ϕ = 2.0; 333 ppm NO_2

Fig. S2-1 333ppm NO_2-doped experiments with models: present work (solid blue, v.0), Marrodán *et al.* (solid red); present work with all rates reset (dashed yellow, v.11), effect of only reducing R + NO_x ⇌ Alkene + {HNO/HONO/HNO_2} by 10x (dashed black, v.12), effect of only reducing R + NO_x ⇌ Alkene + {HNO/HONO/HNO_2} by 100x (dashed green, v.8).

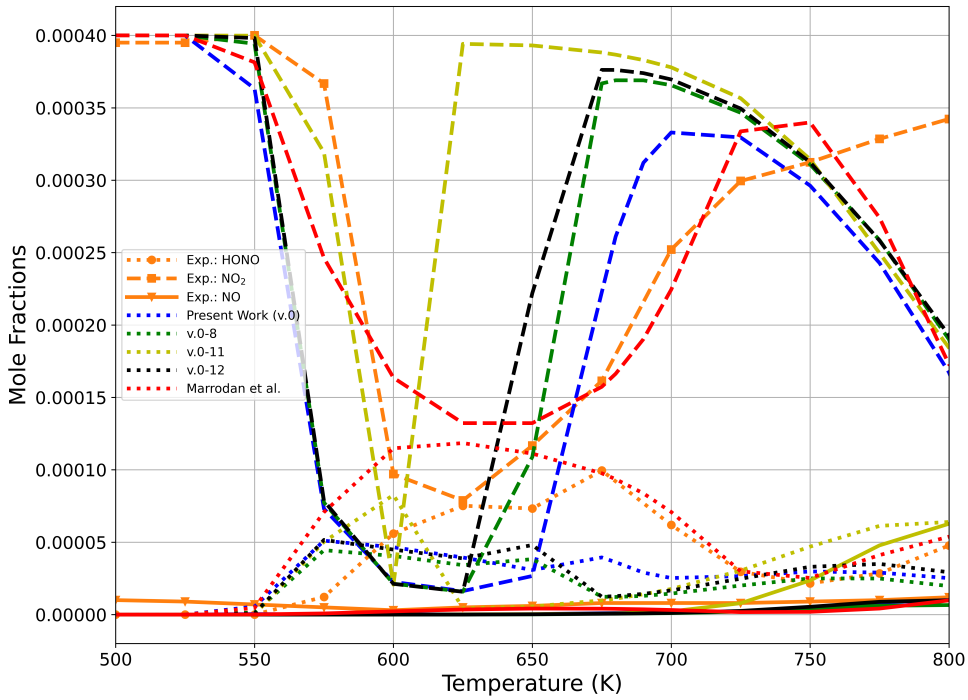


Fig. S2-2 Comparison of mechanisms for pentane oxidation with 400 ppm NO_2 in JSR: experimental measurements (orange) of HONO + HNO_2 (——●), NO_2 (– – –■), HNO_2 (·····▼); present work (solid blue, v.0), Marrodán {*et al.*} *(solid red); present work with all rates reset (dashed yellow, v.11), effect of only reducing R + NO_x ⇌ Alkene + {HNO/HONO/HNO_2} by 10x (dashed black, v.12), effect of only reducing R + NO_x ⇌ Alkene + {HNO/HONO/HNO_2} by 100x (dashed green, v.8).*

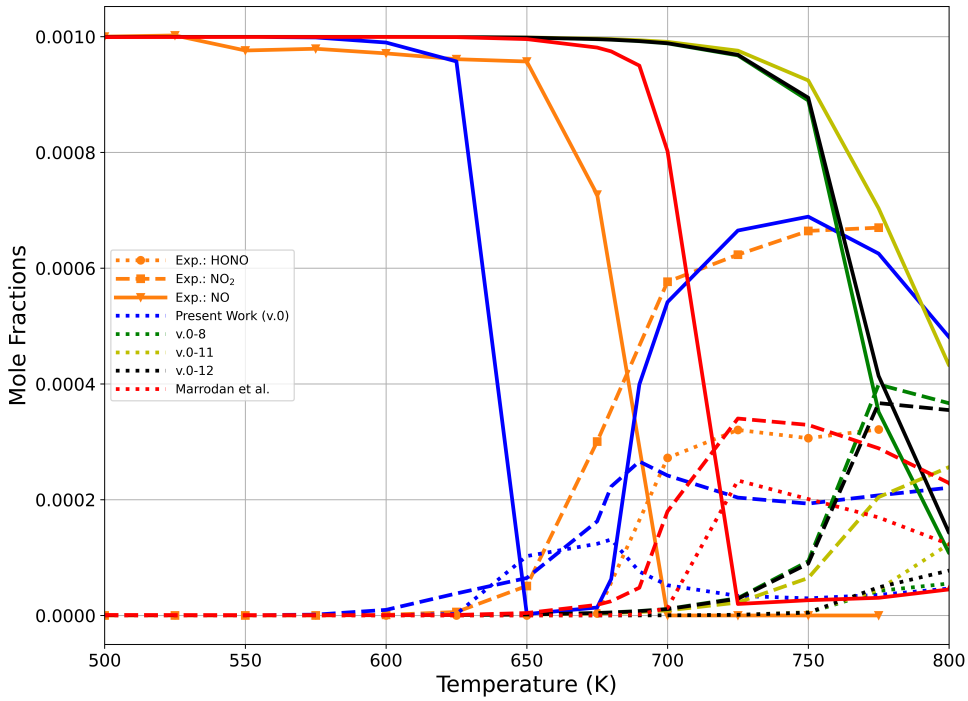


Fig. S2-3 Comparison of mechanisms for pentane oxidation with 1000 ppm NO in JSR: experimental measurements (orange) of HONO + HNO_2 (——●), NO_2 (– – –■), HNO_2 (·····▼); present work (solid blue, v.0), Marrodán {*et al.*} *(solid red); present work with all rates reset (dashed yellow, v.11), effect of only reducing R + NO_x ⇌ Alkene + {HNO/HONO/HNO_2} by 10x (dashed black, v.12), effect of only reducing R + NO_x ⇌ Alkene + {HNO/HONO/HNO_2} by 100x (dashed green, v.8).*