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Theoretical Study of Toluene Oxidation: H-abstraction reactions by OH, HO_2, O, O_2 and benzyl radical addition to O_2. Implications to Kinetic Modelling.

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Highlights

- Relevant rate constants for toluene oxidation obtained at the highest level of theory affordable for 9 heavy atoms system
- H-abstraction reactions and relative branching ratio between benzyl and methylphenyl radical formation strongly impacts overall reactivity
- Benzyl radical addition to O_2 mostly proceeds through a direct bimolecular channel forming benzaldehyde and OH.

1. Introduction

Alkylated aromatics such as toluene represent a significant fraction of the components in commercial transportation fuels. Furthermore, aromatic hydrocarbons precede the formation of poly-aromatic hydrocarbons (PAHs), key precursors in soot and particulate matter formation. These factors clearly justify the academic and industrial interest in better assessing toluene combustion properties at a fundamental level. The recent work of Zhang et al. [1] stemmed from the consideration that different toluene kinetic models available in the literature showed quite controversial behaviors in terms of overall reactivity. Firstly, the toluene portion of the POLIMI kinetic mechanism was updated based on recent literature and on the comprehensive kinetic modelling studies of Zhang et al. [1] and Yuan et al. [2]. Figure 1 shows results from the sensitivity analysis carried out for a stoichiometric toluene/air mixture, at p=20 bar and three different temperatures (T=689, 1044 and 1400 K), thus covering conditions of relevance in internal combustion engines. This work presents a methodical theoretical investigation of some of the relevant reaction pathways highlighted in Figure 1. The impact of this estimates on the performances of the POLIMI toluene kinetic model are discussed, highlighting open challenges still to be addressed.

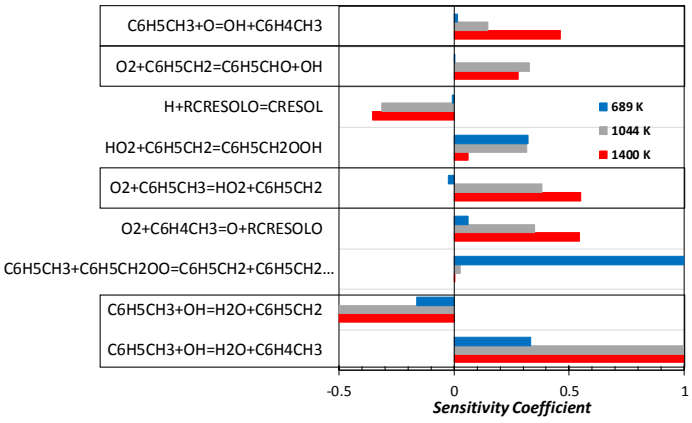

Figure 1. Normalized sensitivity coefficients of temperature increase to rate constants for the POLIMI updated mechanism. Adiabatic constant volume batch reactor simulations, toluene/air, φ=1.0, p=20 bar.

2. Methods

Geometry optimizations and frequency calculations for reactants, wells, transition states and products have been carried out at the M062x/6-311+g(d,p) level. Potentials for internal rotations and coupled internal rotations were obtained from relaxed scans at the same DFT level. High level single point energies have been obtained at CCSD(T)/aug-cc-pVTZ, DF-MP2/aug-cc-pVTZ and aug-cc-pVQZ level, to allow for complete basis set extrapolation. Low-frequency torsional motions were taken into account in the partition function calculation according to the one-dimensional hindered rotor method. Internal reaction coordinate (IRC) calculations were performed with a step size of ~0.016 Å to confirm the existence of the single imaginary frequency saddle point, often allowing the location of reactant-like and product-like van der Waals complexes. The one-dimensional tunneling correction was applied to the canonical TST rate constants according to the Eckart model.

3. Results and discussion

As an example, Figure 2a compares results from theoretical calculations of H-abstractions by OH with experiments and previous estimates. Figure 2b shows the critical branching ratio between benzyl and methylphenyl radicals, dramatically impacting toluene reactivity (Figure 1).

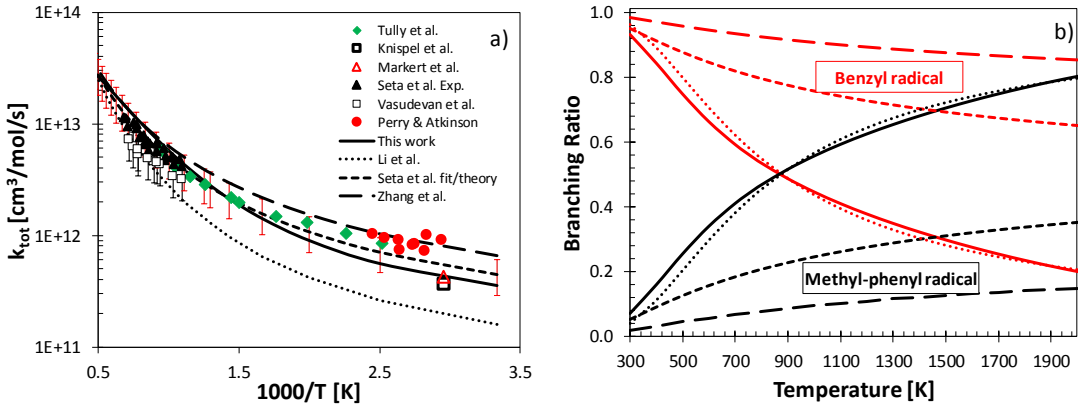

Figure 1. a) comparison of the total rate constant of OH + toluene with previous studies and with experimental measurements (symbols). b) branching ratio between benzyl radical ($C_6H_5CH_2$) and methylphenyl lumped radical ($C_6H_4CH_3$).

4. Conclusions

This study advances the knowledge on toluene combustion kinetics by means of an effective coupling of theoretical rate constants calculations and kinetic modelling analyses. Impact of high accuracy kinetic rate constants on the POLIMI kinetic model helps to highlight further areas of investigation, of relevance for both the kinetics of combustion of transport reference fuels and for pollutants formation.

References

[1] Zhang, Y., Somers, K.P., Mehl, M., Pitz, W.J., Cracknell, R.F., Curran, H.J., Proc. Combust Inst. 36., 2017, pp. 413-421.
[2] Yuan, W., Li, Y., Dagaut, P., Yang, J., & Qi, F. Combust. Flame 162(1), 2015, pp. 3-21.

Keywords
Toluene, Combustion, Theoretical calculations, Kinetic Rate Constants

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CURRENT AND PREVIOUS POSITIONS

Oct 2017-present Assistant Professor (RTDa) at Politecnico di Milano Department of Chemistry, Materials, and Chemical Engineering
Feb 2017- Oct 2017 Post-Doctoral Researcher at Politecnico di Milano Department of Chemistry, Materials, and Chemical Engineering)
2013-2017 PhD Student at Politecnico di Milano (Department of Chemistry, Materials, and Chemical Engineering)

EDUCATION

2007-2010 Bachelor Degree in Chemical Engineering at Politecnico di Milano (September 2010). Final Mark 101/110. Thesis title "*Modelli di surrogati per combustibili areonautici*". Supervisor: Prof. T. Faravelli and Prof. A. Cuoci.
2010-2013 Master Degree in Chemical Engineering at Politecnico di Milano (September 2010). Final mark: 110/110 (*cum laude*). Thesis title "*Experimental and kinetic modelling study of n-butanal and n-pentanal auto-ignition in a Shock Tube*". Supervisor: Prof. T. Faravelli, Prof. E. Ranzi, Prof. H. J. Curran (National University of Ireland, Galway)
2013-2017 Ph. D. (*cum laude*) in Industrial Chemistry and Chemical Engineering. Thesis title: "Development of kinetic mechanisms for the combustion of renewable fuels" Supervisor: Prof. T. Faravelli

VISITING POSITIONS

2012 (March-September), 2013 (October), 2015 (February) Visiting Master and Ph.D Student at National University of Ireland Galway, hosted by the group of Prof. H.J. Curran. Experimental and kinetic modelling study of aldehydes oxidation in shock tubes and rapid compression machines.
2016 (January-August) Visiting Ph.D Student at Chemical Science and Engineering Division, Argonne National Laboratory, IL, USA hosted by the group of Dr. S.J. Klippenstein and co-supervised by Prof. C. Cavallotti. Activity: theoretical methods for the estimation of rate constants, ab initio and kinetic modelling study of toluene oxidation, implementation of automatic tools to integrate theoretical rate constant calculations into kinetic model development.

FELLOWSHIPS AND AWARDS

2013-2017 PhD scholarship, Italian Minister of Education (MIUR), Italy
2017 2nd position, PhD Award, PhD School in Industrial Chemistry and Chemical Engineering

TEACHING ACTIVITIES

2013-2017 Teaching Assistant "Fundamentals of Combustion" ("Principi di Combustione", Prof. E. Ranzi, Prof. A. Frassoldati)
2014-2016 Teaching Assistant "Combustion and Pollutant formation" ("Combustione e formazione di inquinanti") Prof. A. Frassoldati

SUPERVISION OF STUDENTS

Bachelor Thesis internships: Ayoub El Ziani, Matteo Mensi, Nicholas Ferrari, Giorgio Pastore, Nicolò Rossi, Andrea Volontè, Andrea Locaspi, Stefano Bonanomi, Samuel Avvantaggiato

Master Thesis projects:
Loris Vernier "Kinetic Modelling of NOx formation/consumption: from methane to PRFs" 2015
Giorgio Porro "Kinetic modeling of methyl chloride pyrolysis and combustion" 2015
Andrea Zanetti "Curve Matching: a generalized framework for combustion model validation" 2017
Alice Rigamonti "Automatic Modelling System: A database infrastructure to develop, validate and evaluate scientific models. An application to combustion kinetic models" 2017
Cristina Rizzo "Experimental and Kinetic Modelling Study of C_2-C_5 Linear Alcohols" 2017
Veronica Ruvituso "Kinetic Modelling of pyrocarbon deposition" 2017
Fabio De Capitani "Kinetic Modelling of MILD oxy-methane combustion" 2017

SCIENTIFIC INTERESTS

- Kinetic modeling of pyrolysis and combustion of fossil and biofuels, pollutants formation, heterogeneous kinetics.
- Theoretical calculations of rate constants and thermochemical parameters.
- Development and assessment of detailed kinetic mechanisms, simplification of kinetic mechanisms.
- Experimental measurements in rapid compression machines and shock tubes.
- Data formatting, data analysis, big data, data exchange.

PUBLICATIONS (as of October 2017)

Scopus Database: 14 publications, 144 citations, h-index=5
Google Scholar Database: 14 publications, 177 citations, h-index=5

1. Pelucchi, M., Somers, K. P., Yasunaga, K., Burke, U., Frassoldati, A., Ranzi, E., Curran H.J., Faravelli, T. (2015). *An experimental and kinetic modeling study of the pyrolysis and oxidation of n-C3-C5 aldehydes in shock tubes.* Combustion and Flame, 162(2), 265-286.
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3. Ranzi, E., Cavallotti, C., Cuoci, A., Frassoldati, A., Pelucchi, M., & Faravelli, T. (2015). *New reaction classes in the kinetic modeling of low temperature oxidation of n-alkanes.* Combustion and flame, 162(5), 1679-1691.

4. Pelucchi, M., Bissoli, M., Cavallotti, C., Cuoci, A., Faravelli, T., Frassoldati, A., Ranzi, E., Stagni, A. (2014). *Improved kinetic model of the low-temperature oxidation of n-heptane.* Energy & Fuels, 28(11), 7178-7193.
5. Nativel, D., Pelucchi, M., Frassoldati, A., Comandini, A., Cuoci, A., Ranzi, E., Chaumeix, N., Faravelli, T. (2016). *Laminar flame speeds of pentanol isomers: An experimental and modeling study.* Combustion and Flame, 166, 1-18.
6. Pelucchi, M., Ranzi, E., Frassoldati, A., Faravelli, T. (2016). *Alkyl radicals rule the low temperature oxidation of long chain aldehydes.* Proceedings of the Combustion Institute.
7. Pelucchi, M., Cavallotti, C., Ranzi, E., Frassoldati, A., Faravelli, T. (2016*). Relative Reactivity of Oxygenated Fuels: Alcohols, Aldehydes, Ketones, and Methyl Esters.* Energy & Fuels, 30(10), 8665-8679.
8. Bernardi, M. S., Pelucchi, M., Stagni, A., Sangalli, L. M., Cuoci, A., Frassoldati, A., Secchi, P., Faravelli, T. (2016). *Curve matching, a generalized framework for models/experiments comparison: An application to n-heptane combustion kinetic mechanisms*. Combustion and Flame, 168, 186-203.
9. Ranzi, E., Frassoldati, A., Stagni, A., Pelucchi, M., Cuoci, A., Faravelli, T. (2014). Reduced Kinetic Schemes of Complex Reaction Systems: Fossil and Biomass-Derived Transportation Fuels. International Journal of Chemical Kinetics, 46(9), 512-542.
10. Pelucchi, M., Bissoli, M., Rizzo, C., Zhang, Y., Somers, K.P., Frassoldati, A., Curran, H.J., Faravelli, T. (2017). *A kinetic modelling study of alcohols operating regimes in a HCCI engine.* SAE International Journal of Engines 10.2017-24-0077 (2017).
11. Debiagi, P. E. A., Gentile, G., Pelucchi, M., Frassoldati, A., Cuoci, A., Faravelli, T., & Ranzi, E. (2016). *Detailed kinetic mechanism of gas-phase reactions of volatiles released from biomass pyrolysis.* Biomass and Bioenergy, 93, 60-71.
12. Carrera, A., Pelucchi, M., Stagni, A., Beretta, A., & Groppi, G. (2017). *Catalytic partial oxidation of n-octane and iso-octane: Experimental and modeling results.* International Journal of Hydrogen Energy.

INTERNATIONAL CONFERENCES PRESENTATION (as of October 2017)

1. "Kinetic modeling of Biofuels: Pyrolysis and Auto-Ignition of Aldehydes" **International Conference on Biomass** 4th-7th May 2014, Florence, Italy
2. "Curve Matching: a generalized framework for combustion model validation" COST Topical Workshop, **European Combustion Meeting**, Budapest, Hungary 30th March 2015
3. "Detailed kinetic mechanisms for practical applications: new reaction classes and model reduction" **Invited Speaker at young researchers colloquium, Clean Air 2015**, Lisbon, Portugal, 8th July 2015
4. "Toward a fully automated systems to develop, validate and evaluate combustion kinetic mechanisms" Smartcats, **COST CM1404 meeting**, Lisbon, Portugal November 2016
5. "Alkyl Radicals Rule the Low Temperature Oxidation of long chain aldehydes" **36th International Symposium on Combustion**, Seoul, South Korea, 1st-5th August 2016
6. "Ab Initio and Kinetic Modelling Study of Toluene Oxidation" 10th **International Conference on Chemical Kinetics**, Chicago, USA 21st-25th May 2017
7. "Kinetic Modelling Study of Alcohols operating regimes in HCCI Engines" **13th International Conference on Engines and Vehicles**, Capri, IT, 10th-14th September 2017