

# Kinetic Modeling of Benzene, Toluene and Methyl-Naphthalene Oxidation

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To reliably develop predictive reaction models for complex chemical systems requires integration of large amounts of theoretical, computational, and experimental data collected by numerous researchers. The integration entails assessment of data consistency, model validation, and quantification of uncertainties for model predictions. Approach to the development of mechanistic reaction models consists of conjecturing the reaction mechanism and comparing the predictions of the constructed model to available experimental observations. Typically, such comparisons result in mixed outcomes; some show a reasonably close agreement and some do not. In the latter case, the apparent inconsistency obtained between the model and the experiment is argued to imply either that the model is inadequate or that the experiment (or rather its interpretation) is incorrect. A key requirement for such analysis is the formulation of a dataset, which should consist of the measured observations, a common kinetic model and uncertainty bounds of the measurements and thermokinetic data. Practical fuels such as kerosene, gasoline and diesel are rather complex mixtures of various paraffin and aromatic hydrocarbons. Severe critical problems of a combustion engine are the timing of ignition, and the control of pollutant formation such as poly-aromatic hydrocarbons (PAH) and soot. The present investigation focuses on the uncertainty problems, which appear in the development of the kinetic reaction model of benzene, A1 ( $C_6H_6$ ), toluene ( $C_7H_8$ ) and methyl-naphthalene, A2CH<sub>3</sub> ( $C_{11}H_{10}$ ), to be included in reference fuel models, which describe the main reaction pathways of PAH and soot formation in practical fuels.

**Table 1. Experimental Ignition Delay Data: uncertainty factors**

Factors	Operating conditions	Correlation
Weak and strong ignition (fuel)	T, p, $\phi$ , CG,	Low T, p, $\phi > 0.3 \sim 10$ times
Nonideal gas dynamics behind the reflected shock wave (T, p nonuniformities)	T, p, $t_{meas}$ , CG,	27%-17% Small Dilution ↓
Post-shock compression	T, p, $t_{meas}$ , CG,	$dP/dT \approx 2\text{-}6\%$ /ms $dT/dt \approx 1.2\%$ /ms
Radical impurities	T, p, CG, Person	dilution↑, T,p ↓ ; ?
Temperature measurements	Measurment location	5%
Pressure measurements	T, Measurment location	10%
Concentration measurements (the steepest rate of change)	T, Measurment location	5%

The ultimate aim is to develop a reaction mechanism of a useful size for analysis with an evaluated uncertainty level for kinetic parameters and experimental data, which were used for the model validation. The problem of the experimental data uncertainty evaluation is not trivial. The system of indicators must be developed for objective evaluation of uncertainty intervals of experimental targets.

The present work reports mainly on mechanism validation to predict ignition delay time. Both facility-dependent effects and energy-release phenomena in the reflected shock environment are important and must be included in uncertainty evaluation of experimental data by any tuning of the kinetic parameters to match ignition targets. The strongest factors, which increased the non-ideal conditions in shock tubes and measurement uncertainties are gas dynamics effects - boundary layer formation after the shock wave (tube diameter), long measured ignition time ( $t_{meas} > 500 \mu s$ ), post-shock compression, measurement location, mixture dilution and nature of Carrier Gas (CG), and high pressure. In Table 1, the factors which influence the shock tube measurement error are summarized in the first column. In the second column operating conditions which increase the influence of these factors are determined. The possible errors are evaluated in the third column.

It was assumed that in the best case (strong ignition, diluted mixture,  $t_{meas} = 50ms - 500ms$ , shock tube diameter  $> 10 cm$ ) the uncertainty was  $\sim 15\%$ .

This reaction mechanism has been developed on the basis of the DLR C<sub>0</sub>-C<sub>4</sub> kinetic model with the PAH formation sub-model [1]. During the mechanism's development, the following was determined:

1. the generic reactions for aromatic molecules oxidation
2. the actual uncertainty levels of main reaction rate coefficients and empirical methods for evaluation of rate coefficients of several reaction types
3. the experimental data base for the mechanism validation and optimisation
4. a systematic uncertainty analysis of related experimental data

Finally the predictive models with evaluated uncertainty levels were developed, Fig.1

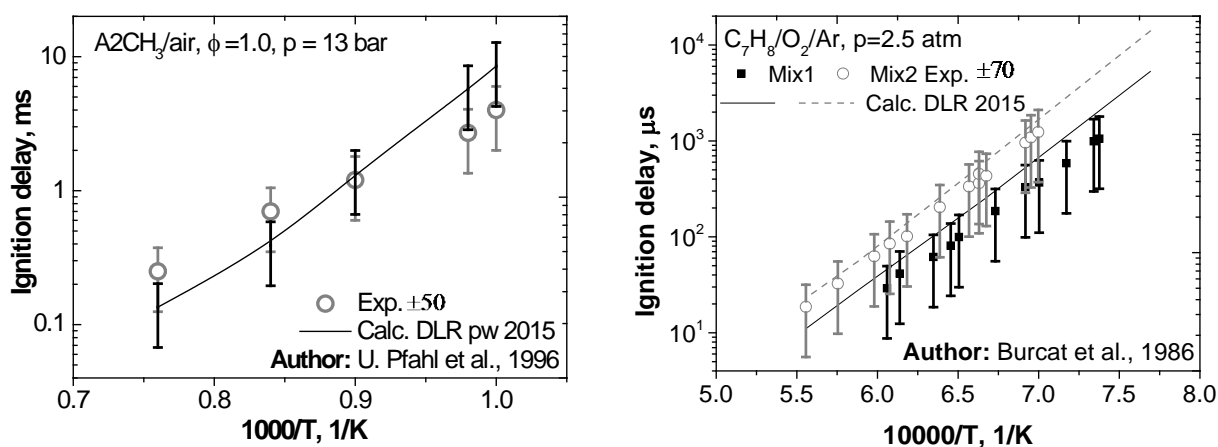


Fig.1 Ignition delay times, measured [2,3] and simulated with developed models:  
a)  $A_2CH_3$ ; b)  $C_7H_8$

## References

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