

Simulated Autoignition Temperature and Oxidation of Cyclohexane using a QSSA Reduced Mechanism

R. Porter¹, M. Fairweather^{*1}, J. F. Griffiths², K. J. Hughes¹, A. S. Tomlin¹

¹School of Process, Environment and Materials Engineering, and

²School of Chemistry, University of Leeds, Leeds LS2 9JT, UK

Abstract

Automated procedures have been applied to reduce a reaction mechanism describing the oxidation of cyclohexane from 499 species to 60 necessary species. The quasi steady state approximation (QSSA) combined with reaction lumping is applied to further eliminate a number of intermediate species. The resulting 35 species mechanism gives predictions of both the pressure - ambient temperature (p - T_a) ignition diagram and ignition delay times which are in good agreement with those of the full scheme at the low temperature ignition boundary, thus facilitating the calculation of autoignition temperature (AIT). The kinetic features of the reduced mechanisms have been analysed using element flux visualization software.

Introduction

There is a continuing need for reduced hydrocarbon kinetic mechanisms, primarily for their inclusion in computational fluid dynamics (CFD) codes which can be used for engine research and development, or to optimize processes carrying out the partial oxidation of hydrocarbons and eliminate explosion hazards on such plants. Current comprehensive oxidation mechanisms are too large to be incorporated into CFD, and without realistic (reduced) chemical kinetics, the accuracy and overall usefulness of such computer tools is severely diminished. A further, yet sometimes overlooked, justification for performing mechanism reduction is that kinetic understanding can be gained from the analysis of reduced mechanisms. Global uncertainty analysis techniques can be used to elucidate poorly known Arrhenius or thermokinetic parameters which can cause discrepancies when model output is compared to experiment. These techniques involve running many simulations with both individual runtime and number of simulations scaling with mechanism size and so mechanism reduction is an established prerequisite [1]. Other kinetic techniques are greatly facilitated by the use of short mechanisms such as rate of production and element flux analyses.

Cycloalkanes are a major constituent in automotive fuels, with up to 3% in petrol and 35% in diesel. However, relatively little attention has been paid to their combustion characteristics [2]. Furthermore, autoignition hazards are often encountered during the partial oxidative processing of cyclohexane due to its low minimum ignition temperature (MIT), measured at 533 K, using the standard test procedures (IEC 60079-4, DIN 51794, ASTM 659-78, BS 4056 and EN 14522) [3]. In fact, the 'textbook' safety case of the explosion at the Flixborough Nypro plant in 1974 was caused by the (induced) ignition of cyclohexane, used to make precursors for nylon manufacture. The accident caused the deaths of 28 people and completely destroyed the plant.

In this paper, we use a comprehensive mechanism to simulate the stoichiometric combustion of cyclohexane in air. Recently developed software is applied to automatically reduce the reaction mechanism to a skeleton mechanism, which reproduces the numerically predicted p - T_a ignition diagram and ignition delay times output from the full model over a wide range of operating conditions. Using a multiple stage reduction method, a further reduction can be achieved to give a shorter mechanism, applicable to a narrower low-temperature range of relevance to the prediction of AIT. The application of the QSSA combined with reaction lumping is then illustrated, yielding a substantially reduced mechanism with commensurate computational time savings obtained. With the aid of KINALC subroutines [4] and element flux visualization software [5], analysis of the fluxes of carbon atoms during isothermal oxidation has been undertaken using one of the reduced mechanisms. This shows the major reaction pathways of fuel to oxygenated cyclic compounds, the breakage of the ring to form aldohydroperoxides and ketohydroperoxides and their subsequent decomposition.

Numerical Models and Methods

The full cyclohexane mechanism to which the techniques were applied originates from DCPR-CNRS Nancy [2, 6] and comprises 499 species in 1025 reversible reactions and 1298 irreversible reactions (2323 mixed reactions in total or equivalent to 3348 irreversible reactions).

The resulting system of ordinary differential equations (ODEs) was solved for a closed vessel reactor with spatial uniformity assumed using the SPRINT integration package [7]. Output predictions from the full mechanism were used to construct a p - T_a ignition diagram using an automated bisection method (Fig. 1). This diagram and individual temperature profiles from the full scheme were used as the benchmark against which reduced models were validated. Using the p - T_a

* Corresponding author: m.fairweather@leeds.ac.uk

Proceedings of the European Combustion Meeting 2007

ignition diagram as a reference, a number of operating conditions were selected to be used as input for the sensitivity analysis/reduction software. The software uses local Jacobian and rate sensitivity-based methods applied to conditional information obtained from several reaction times at the selected operating conditions. Thresholds are applied to the magnitudes of the sensitivity measures for species and reactions, providing an automatic means of reducing the mechanism. Further details of the reduction software, along with a description of the procedure used to automatically generate the p-T_a ignition diagram, can be found elsewhere [8, 9]. These techniques yield skeleton mechanisms which contain only the essential or necessary subset of species and reaction steps required to reproduce important reaction features. At this point the scheme is still a normal chemical kinetic mechanism, compatible with standard integration packages.

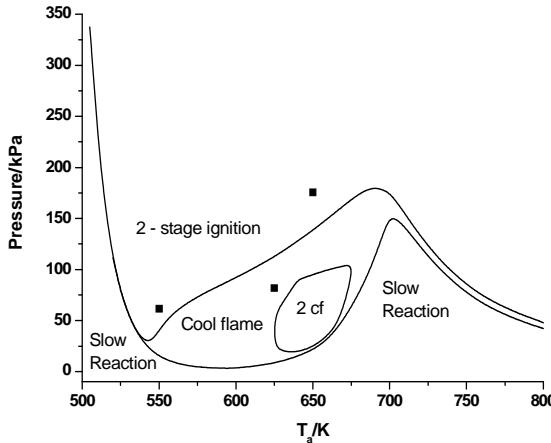


Fig. 1. Full Nancy scheme simulated p-T_a ignition diagram for stoichiometric c-C₆H₁₂ + air in a closed vessel under spatially uniform conditions. Ignition diagrams were computed at 5K intervals using an automatic generation procedure, giving precision of the boundary to ± 0.2 kPa. Black squares; user selected operating conditions of reduction.

Further reduction may be achieved by the exploitation of the range of time scales present in the system via the application of the Quasi Steady State Approximation combined with reaction lumping [10, 11]. The QSSA method is employed in mechanism reduction to identify species which react on a very short time scale and locally equilibrate with respect to species whose concentrations vary on a slower timescale. These fast reacting species are known as quasi-steady state (QSS) species and their removal can reduce the stiffness of the resulting reduced models. The main assumption of the QSSA is that the equilibration of the QSS species is instantaneous. The concentration of the QSSA species can then be determined (to a good approximation) from a local algebraic expression rather than a differential equation. The algebraic expression is

derived by setting the QSS species rate of production (f_i^q) to zero, i.e.

$$f_i^q = 0 . \quad (1)$$

The QSSA must be applied to selected amenable species which will not incur great error to the numerical solution of the reacting system, i.e. those species which react on fast timescales (QSS species). The QSS species must always be intermediates and are usually radicals. Algorithms are available to numerically identify the QSS species. One such method, based on local perturbation analysis, was proposed by Turányi *et al* [10]. Since the method is local, it evaluates the instantaneous error of the quasi steady state approximation, and if large can propagate to cause errors in the concentrations of important species. The instantaneous error (Δc_i^s) for a single species can be expressed as;

$$\Delta c_i^s = \left| \frac{1}{J_{ii}} \frac{dc_i}{dt} \right| \quad (2)$$

where J_{ij} is the system Jacobian equal to $\partial f_i / \partial c_j$.

Previous applications of the QSSA to complex kinetic schemes have tended to employ iterative methods to solve the algebraic expressions for the concentrations of coupled QSS species. Although this results in a reduction in the number of differential equations that need to be solved, additional computational effort is required to solve for the QSS species, which limits the speed-up that can be achieved. Substantial computational savings can be made when the QSS species are removed via reaction lumping [11]. In its simplest form a reaction scheme or subset consists of a set of reactions from reactants going to intermediates, or a coupled set of intermediates, which then form products. Via reaction lumping, this set of reactions is changed to a single reaction involving only reactants going to products. Intermediates are therefore eliminated. The rate constants of the lumped reactions will be algebraic combinations of other rate parameters and intermediate species concentrations and are derived subsequent to the application of QSSA. This is illustrated in the following, where B is a QSS species linking the reactant A to the product C.



By setting $d[B]/dt = 0$, we get the expression

$$k_1[A] = [B](k_{-1} + k_2) , \quad (4)$$

which leads to

$$[B] = [A] \left(\frac{k_1}{k_{-1} + k_2} \right) . \quad (5)$$

By defining the lumped reaction as A going to C in a forward irreversible step;



we can derive an algebraic expression for the rate parameter k' by considering the rate of change of concentration of A

$$k' = k_1 \left(1 - \frac{k_{-1}}{k_{-1} + k_2} \right). \quad (7)$$

The above fundamental principles can be applied to problems of increasing complexity with both the involvement of second order reactions and coupled blocks of QSS species which are required to be eliminated in unison. In such cases, manual analytical solutions can become too intractable and no longer viable. However, solutions can be achieved by the use of algebraic manipulation packages such as MAPLE [12].

One approach to the generation of reaction schematics is through the use of element flux analysis. The idea of element flux analysis was introduced in [13] and uses reaction rates to identify the major sources and sinks of elements at a variety of reaction times. The element fluxes are most usefully calculated for C, H or O. Fluxes were calculated at a number of time points during the reaction simulation [14]. A program called FluxViewer [5] was then used to read the reaction flux information and view, either stepwise or as an animation, the kinetic connections between species as the reaction progresses. Thresholds could be applied to the magnitudes of the fluxes in order to filter out insignificant connections.

Results from Model Reduction and Kinetic Analysis

First, the reduction to a mechanism whose output gives good agreement over a wide low-temperature range (500 – 800 K) will be shown. The strategy of multiple stage species reductions was utilized, that is, the mechanism is partially reduced, then the techniques are reapplied to the partially reduced mechanism. The procedure is repeated successively. The need to perform a second stage reduction arises because, during the iterative Jacobian analysis, redundant species can be incorporated into the reduced mechanism before all necessary species have been included. These incorporated redundant species can be more easily removed by performing a second stage reduction due to the altered couplings. The need for a two-stage reduction strategy is not unique to Jacobian analyses but has also been used by other researchers in the reduction method of direct relation graphs [15]. Three stages of species reduction gave a skeleton scheme comprising 104 species in 541 reactions which enabled a very accurate prediction of the ignition diagram (Fig. 2) with commensurate accuracy in the time dependent response.

The reduction of the cyclohexane mechanism thus far retains excellent agreement with the low temperature ignition boundary generated with the full mechanism over the temperature range of 500 – 550 K. Therefore, further reductions were carried out in order to assess what is the minimum size of mechanism which will retain these characteristics.

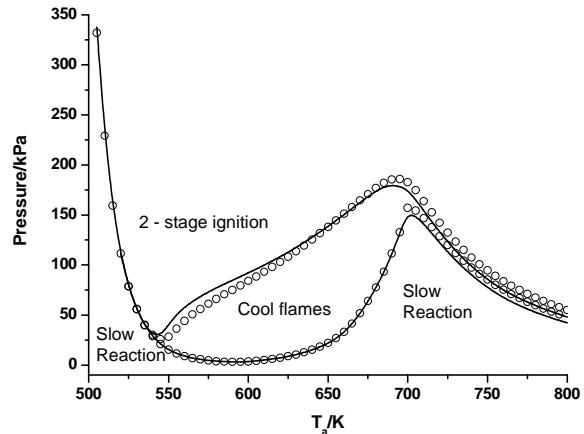


Fig. 2. Comparison of the p-T_a ignition diagrams produced by the full and species reduced mechanisms for stoichiometric cyclohexane in air showing the full mechanism (solid line) and reduced mechanism comprising 104 species and 541 reactions (open circles).

The reduced mechanism comprising 104 necessary species and 541 reactions was used as the starting point for the further reductions. Two alternative operating conditions for sensitivity analysis were selected close to the low temperature ignition boundary at 510K, 306.6kPa and 530K, 74kPa. The objective of the reduction was to produce a further reduced scheme which will retain the characteristics of the low temperature ignition boundary and low temperature time dependent behaviour produced using the full mechanism. The reduction proceeded by performing further multi-stage Jacobian analyses. This resulted in the creation of a reduced mechanism comprising 68 species in 493 irreversible reactions. Next, principal component analysis (PCA) methods were employed to remove reactions. The number of reactions was successfully reduced and this resulted in a mechanism comprising 60 necessary species, plus 8 redundant product only species and 238 irreversible reactions. This mechanism is shown diagrammatically in Fig. 3.

The QSSA combined with reaction lumping was applied to the 60 necessary species mechanism to further eliminate a number of intermediate species whilst incurring little error to output ignition delay predictions. Thresholds were applied to the calculated instantaneous QSSA error for each species over all considered time points, thus providing an automatic way of identifying QSS species. These procedures gave a successful prediction of the ignition diagram (Fig. 5) and ignition delay times (Fig. 6) based on a mechanism

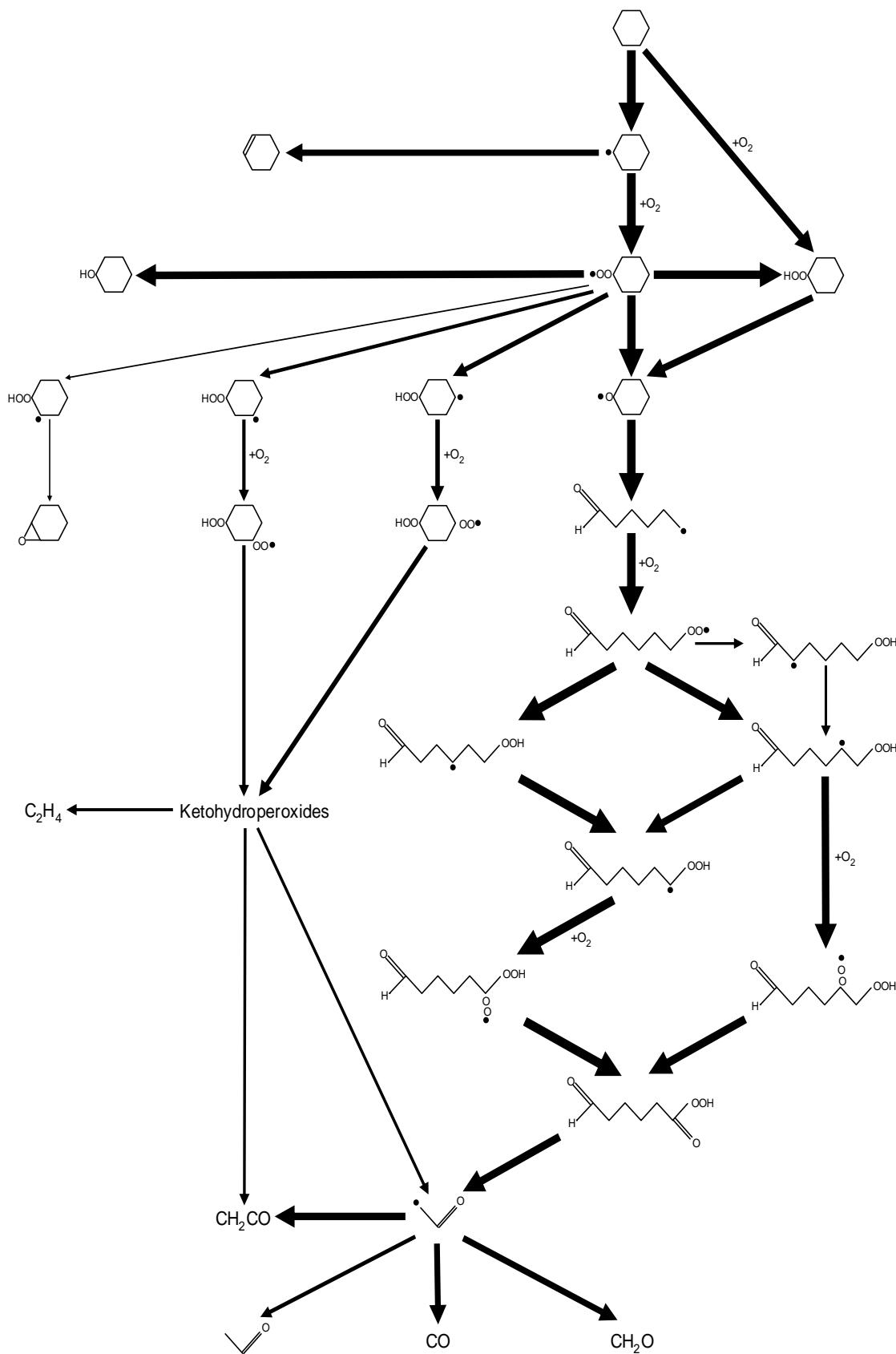


Fig. 3. Major fluxes of carbon atoms during simulated isothermal oxidation of cyclohexane in air using the 60 species 238 reactions mechanism. Conditions relate to the molar proportions 1:2, 470 K and 1 atm. Arrow thickness is scaled to magnitude of element flux.

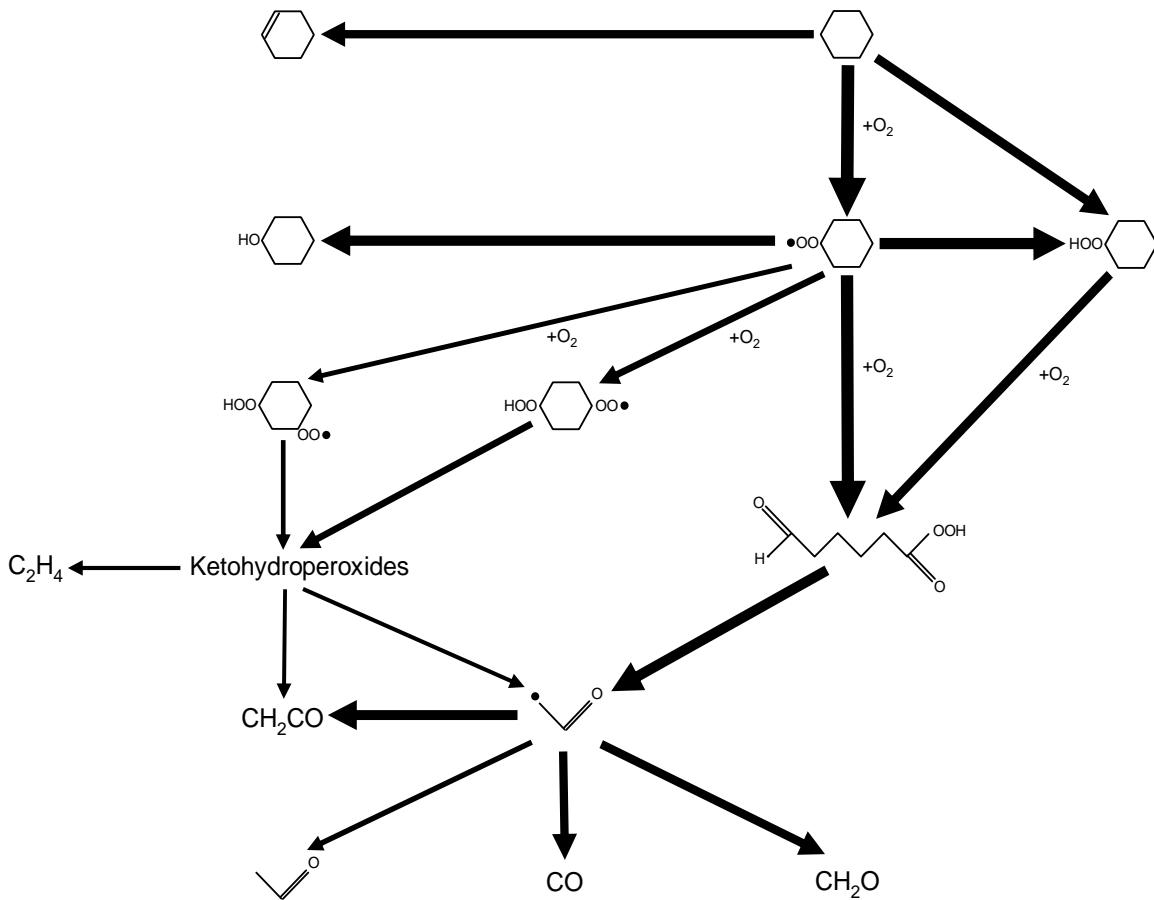


Fig. 4. Schematic of major carbon fluxes during isothermal oxidation of the QSSA reduced mechanism comprising 35 species and 323 reactions. Simulated at 470 K, 1 atm and cyclohexane + air in the molar proportions 1:2.

with only 45 species in 323 reactions, with 193 of these reactions requiring new algebraic formulations for rate parameters, embedded in a customized version of the integration software.

A further level of simplification was achieved by amalgamating redundant products into one 'dummy' species. In addition to the 8 redundant products identified by the iterative analysis of the Jacobian matrix, 2 more species became candidates for the species lumping procedure by virtue of having all their consuming reactions eliminated at the reaction removal stage using principal component analysis. The 10 product species were then amalgamated into one species which had the same thermodynamic properties of carbon dioxide because amongst the product only species this is in the highest concentration. With this simplification, mass balance and accurate heat release calculations are no longer preserved. However, in practice, the procedure leads to mechanisms which still give excellent reproduction of temperature profiles. This resulted in the creation of mechanism comprising of 35 species and 323 reactions (reactions unchanged). The performance of this mechanism is evaluated by the comparison of its p - T_a ignition diagram (Fig. 5) and temperature profiles (Fig. 6) to those of the full mechanism and also to those of the QSSA reduced

mechanism without this further level of simplification invoked.

The scale of the reduction via application of the QSSA is shown diagrammatically in Fig. 4 via an element flux diagram under isothermal conditions. Fig. 4 shows the mechanistic implications of eliminating the QSSA species via reaction lumping. Notable eliminations can be drawn from the comparison of Figs. 3 and 4, they are; the cyclohexyl radical, various isomers of the cyclohexyl peroxy radical, the cyclohexyl alkoxy radical, the ring breakage of this molecule and subsequent numerous additions of oxygen and isomerizations.

Discussion and Conclusions

A comprehensive scheme for the oxidation of stoichiometric cyclohexane + air in a closed vessel at low temperature and pressure has been systematically reduced to a skeleton mechanism with the use of automated sensitivity software. Comparisons of the p - T_a ignition diagrams of full and reduced kinetic models have shown that the numbers of species and reactions in the scheme have been successfully reduced. Further reductions have been achieved using the QSSA to lump reactions and further reduce species.

Computational speed-ups resulting from the removal of species from a chemical scheme are expected to scale

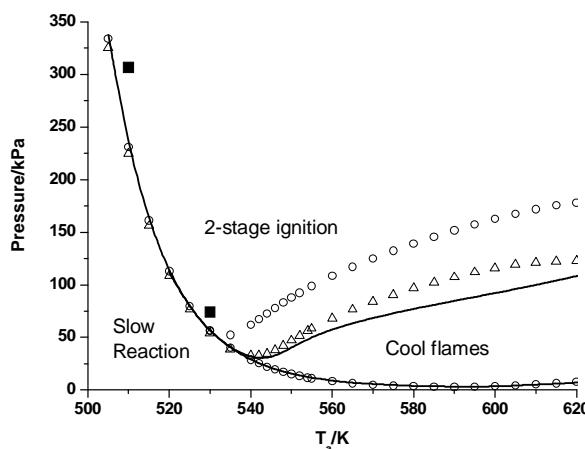


Fig. 5. Comparison of the p - T_a ignition diagrams produced by the full mechanism and reaction lumped 35 species mechanism. Conditions are for a stoichiometric cyclohexane + air mixture. Solid line; full mechanism. Open circles; QSSA reduced mechanism comprising 45 species and 323 reactions. Open triangles; QSSA reduced scheme with amalgamated products comprising 35 species and 323 reactions. Black squares, operating conditions of reduction.

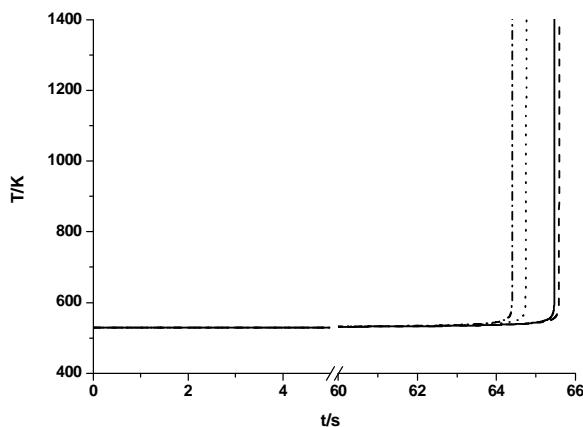


Fig. 6. Comparison of temperature profiles produced by the full mechanism (solid line), skeleton 60 species mechanism (dashed line), QSSA reduced mechanism comprising 45 species and 323 reactions (dotted line) and QSSA reduced scheme with amalgamated products comprising 35 species and 323 reactions (dash-dot line) at 530 K and 74 kPa.

with N^2 , where N is the number of species in the mechanism. The smallest QSSA reduced mechanism presented in this paper (35 species, 238 reactions) has a computational run time corresponding to 0.5% of that of the full mechanism. This substantial speed-up is in excellent accord with the estimate obtained from assuming runtime $\propto N^2$ which is also equal to 0.5% that of the full mechanism. The speed-up quoted pertains to zero-dimensional kinetic calculations. The application of the QSSA reduced scheme in CFD could achieve a further reduction in computational time in comparison to the kinetic speed-up, due to the simplification of transport calculations for these species.

Acknowledgement

The authors gratefully acknowledge financial support from the EU (EVG1-CT-2002-00072-SAFEKINEX) and from EPSRC (GR/R42726/01).

References

- [1] K.J. Hughes, J.F. Griffiths, M. Fairweather and A.S. Tomlin, *Phys. Chem. Chem. Phys.*, **8** (2006) 3197-3210.
- [2] F. Buda, B. Heyberger, R. Fournet, P.A. Glaude, V. Warth and F. Battin-Leclerc, Article in press.
- [3] J.L. Jackson, *Ind. Eng. Chem.*, **43** (1954) 2869-2870.
- [4] T. Turányi, <http://www.chem.leeds.ac.uk/Combustion/kinalc.htm>
- [5] <http://garfield.chem.elte.hu/Combustion/fluxviewer.htm>
- [6] F. Battin-Leclerc, <http://www.ensic.u-nancy.fr/DCPR/Anglais/GCR/softwares.htm>
- [7] M. Berzins and R.M. Furzland, Shell Research Ltd., TNER 85058, 1985.
- [8] R. Porter, M. Fairweather, J.F. Griffiths, K.J. Hughes and A.S. Tomlin, (July 2006), *16th European Symposium on Computer Aided Process Engineering*, Garmisch-Partenkirchen, Germany, p. 383-388.
- [9] <http://www.safekinex.org>, Public deliverable 37
- [10] T. Turányi, A.S. Tomlin and M.J. Pilling, *J. Phys. Chem.* **97** (1993) 163-172.
- [11] L.E. Whitehouse, A.S. Tomlin and M.J. Pilling, *Atmospheric Chemistry and Physics*, **4** (2004) 2025-2056.
- [12] <http://www.maplesoft.com>
- [13] J. Revel, J. C. Boettner, M. Cathonnet and J. S. Bachman, *J. Chim. Phys. Phys.-Chim. Biol.* **91** (1994) 365-382.
- [14] I. P. Androulakis, *Comp. & Chemical Engineering*, accepted for publication (2006).
- [15] T. Lu and C.K. Law, *Combust. Flame*, **144** (2006) 24-26.