The Effect of Formal Mechanism Reduction on Simulated Propane Autoignition and a Quantitative Assessment of the Impact of Uncertainties in Parameter Values

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Abstract

Numerical simulations of a comprehensive propane/oxygen model are used to demonstrate the ranges of behaviour such as oscillatory cool flames and multiple stage ignitions found in a closed vessel. The model is evaluated by a construction of the closed vessel pressure – ambient temperature (p-T_a) ignition diagram and comparing it with experimental results. The model is then formally reduced using the techniques of sensitivity, rate of production and principal component analyses. A reduced chemical mechanism is produced which retains the main types of dynamic behaviour exhibited by the full model as well as their position within the p-T_a diagram. Global uncertainty analysis methods are used to establish the main contributors to uncertainties in output predictions. Results from application of a Monte Carlo uncertainty analysis are reported here.

Introduction

Industrial explosion hazards can occur during the processing of hydrocarbons under partial oxidation conditions when fuel and oxidiser mixtures come into contact with hot surfaces or reside in hot chambers. Fluctuations in feed composition can also lead to operating conditions that may become dangerous due to the occurrence of cool flames at low temperatures and pressures. These cool flames can initiate ignitions and cause explosions. The use of computational fluid dynamics codes, in which direct chemical effects and phenomena are coupled to the flow dynamics, can be used to identify and predict explosion hazards. This offers a significant advance in hydrocarbon processes safety. It can also be of economic benefit and can contribute to the minimisation of atmospheric pollution. However, detailed combustion mechanisms contain very large numbers of chemical species and reactions. The scale and stiffness of the resulting simultaneous equations makes their incorporation into complex three dimensional reactive flows extremely difficult at present and for the foreseeable future. Therefore, there is a strong need for much reduced but accurate combustion kinetic models for application to process hazards mitigation and also in other areas such as engine research and development [1]. It is currently possible, using mathematical techniques, to identify species and reactions which can be systematically removed from large mechanisms without detriment to the output, thus creating a more compact and computationally efficient model [2].

The quantitative tests for the validity of combustion models include isothermal comparisons of the predicted yields of intermediates and products with experiment and of ignition delays during non-isothermal reaction, generally at high pressure. Only very rarely have there been tests based on the cool flame and ignition phenomena mapped in the pressure – ambient temperature (p-T_a) diagram, yet in many respects this is the primary data which should be the first indication for the existence of a potential industrial combustion hazard.

In this paper we use a comprehensive kinetic scheme to simulate numerically the combustion of propane and oxygen in equimolar mixtures in a closed vessel over a range of temperature at sub-atmospheric pressure. A number of quantitative reduction techniques, which are known to be reliable, are applied to the mechanism consecutively and the effect of the formal reduction on the mechanism is investigated by the comparison of p-Ta diagrams at varying stages of reduction. Uncertainty analysis is also used to characterise the model output as a result of imprecisely known input parameters. Propane is the simplest of the alkanes to exhibit the full richness of the low temperature, non-isothermal phenomena in closed vessels. These include multiple cool flames, two-stage and multiple stage ignitions. Whether in full or reduced form, a kinetic scheme must be capable of reproducing these complex reaction modes [3].

Numerical models and methods

The comprehensive model on which the analysis is based was derived at CNRS – DCPR, Nancy [4] for propane oxidation over the temperature range 600 – 2000K comprising 122 species in 1137 reactions. The

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resulting system of ordinary differential equations was solved using the SPRINT integration package [5]. A p-T_a ignition diagram was constructed from predictions of the time dependent behaviour over the ambient temperature range T_a = 500 – 650 K, based on the full kinetic scheme. This was then used as the benchmark against which the reduced models were tested.

The first stage in the reduction was the identification of necessary species. These include selected important species as defined by the user, and other species for which realistic concentrations are required in order to reproduce the concentrations of important species or important reaction features. Their identification is based on an iterative analysis of the system Jacobian [6] using KINALC [7-9]. The union of identified necessary species was taken at selected time points and the reactions of all redundant species removed.

Rate of production analysis was then used at several reaction times, to find both the redundant fast reversible pairs of reactions and the unimportant reactions that made only minor contributions to the production rates of necessary species (e.g. below a minimum contribution threshold). Local rate sensitivity analysis was also used to identify redundant reactions in the usual way [2].

The merit of local rate sensitivity analysis is that sensitivity coefficients can be calculated easily and efficiently, as empirical functions of species concentrations, reaction rates or stoichiometries [2]. However, there can be difficulties in using such a local linear analysis to evaluate uncertainties in output predictions if uncertainties in inputs are large and models are highly non-linear. More importantly, the validity of the information obtained is restricted to the specific time and or species concentrations at which the analysis is performed. This constraint means that the impact of parameter changes on non-local features such as time to ignition, for which the entire history of the chemical evolution has to be monitored, cannot be assessed.

Local linear methods, such as sensitivity analysis, can be extended to a non-local environment, as is the case in the linear "brute force" method. An initial simulation is performed with all parameters at their base values. Then a small change in each kinetic parameter or species heat of formation is made individually with no variation of any other parameter, a new simulation is performed, and the outcome is compared with that from the base case. Although expensive in terms of computational effort because an additional simulation has to be performed for each parameter change, non-local effects such as changes in concentrations or temperature over time and or space can be assessed using this method. However, only small variations to parameters about their base values can be evaluated and, most importantly for the development and subsequent application of satisfactory numerical models, the inter-relationship between variations in parameter values and how combinations of choices may optimise the response cannot be established.

Uncertainty analysis has to be further extended to global methods, such as Monte Carlo simulations and the Morris method [10, 11] if the interactive effects of input parameters are to be revealed. The merits, procedure and results of the application of the Morris method are discussed elsewhere [12]. For reasons of brevity here we present an application of the Monte Carlo method.

In the Monte Carlo method, the property of interest is computed while each of the selected variables is varied randomly over a specific range within each simulation. A sufficiently large number of simulations must be performed to get convergence of the mean value and the standard deviation of each output quantity. Where large number of input parameters exist, often thousands of simulations are required. The number is governed largely by the number of significant input parameters, which is likely to be much less than the total number of parameters tested [12]. Once the output statistics have converged, the distribution of the output values can then be plotted as a function of each of the relevant input parameters over their range of variation. A very clear distribution usually emerges from the scatter plots for those parameters that exhibit either strong linear or nonlinear responses that are, themselves, only weakly interactive. Strong interactions can often be difficult to interpret, necessitating application of the Morris method.

Results from model evaluation and reduction

First, we present a comparison of predictions obtained from the full scheme with experimental results. The p-T_a ignition diagram for equimolar propane + oxygen has been simulated using a heat transfer coefficient appropriate to a 1 dm^3 closed vessel for the comprehensive Nancy scheme and is shown in Fig.1.

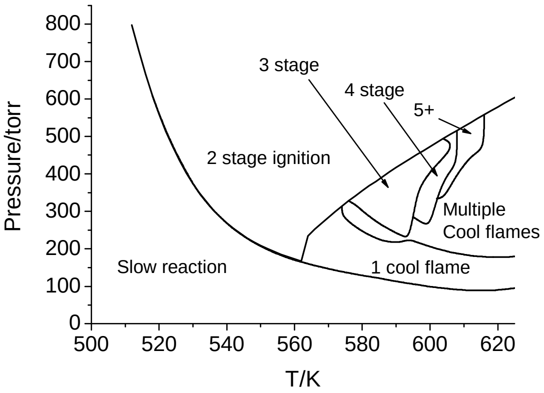

Fig. 1 Full Nancy scheme simulated p-Ta ignition diagram for equimolar C_3H_8 + O_2 in a closed vessel under spatially uniform conditions. This, and also the other ignition diagrams were computed at 2K intervals using an automatic generation procedure, giving precision of the boundary to ± 0.5 torr.

The qualitative characteristics in Fig. 1 compare well with the experimental ignition diagram shown in Fig. 2 [13], in terms of position and shape within the diagram, although there are fundamental quantitative differences. In particular, the minimum pressure at which a 2-stage ignition occurs in the simulation is 167 torr, which is appreciably below that of the experiments, at 280 torr. Moreover, a p-T_a diagram for C_3H_8 + O_2 obtained from the comprehensive C_7 model developed by Westbrook and co–workers [14], in reduced form comprising 92 species and 952 reactions, shows the same anomaly (Fig. 3).

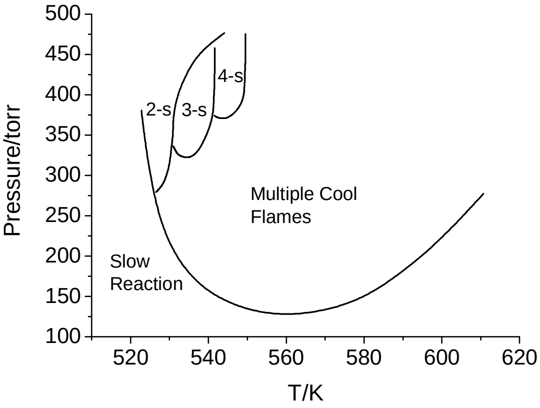

Fig. 2 Experimentally determined p-Ta ignition diagram for equimolar C_3H_8 + O_2 in a 1 dm^3 spherical vessel [13].

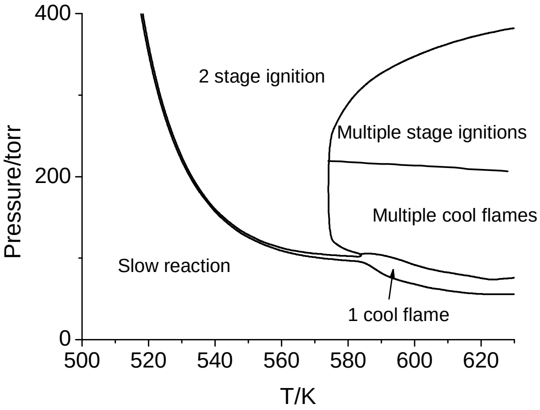

Fig. 3 p-Ta ignition diagram for equimolar C_3H_8 + O_2 in a closed vessel under spatially uniform conditions using a kinetic scheme derived from the comprehensive model of Westbrook *et al.* [14].

After reduction by investigation of the Jacobian to identify necessary species, the Nancy scheme (then comprising 60 species and 687 irreversible reactions) generated a p-T_a diagram that matched that of the full scheme extremely well, there being only minor variations of the boundary positions (Fig. 4).

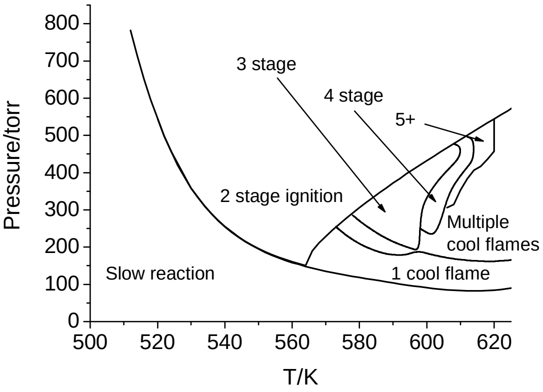

Fig.4 Intermediate reduced Nancy scheme simulated p-T_a ignition diagram for equimolar C_3H_8 + O_2 in a closed vessel under spatially uniform conditions.

A further level of simplification was achieved by investigation of the Jacobian at reduced tolerances, and this yielded a mechanism comprising 43 species in 427 reactions. Further species removal relying solely on this technique yielded a mechanism whose behaviour over the range of operating conditions gave increasing quantitative departures from the behaviour predicted using the full scheme. Nevertheless, more progress was possible by identifying and removing pairs of fast reversible reactions, which, combined with principal component analysis and rate of production analysis, to give a scheme of 41 species in 191 reactions (Fig. 5).

This skeleton mechanism represents the main types of dynamic behaviour exhibited by the full system. Some of the detail of multiple stage ignitions is lost in the reduction and there are minor quantitative differences with the full scheme. However this was considered to be an acceptable compromise between a minimum number of variables and a satisfactory description of the behaviour shown by the full model over the range of operating conditions.

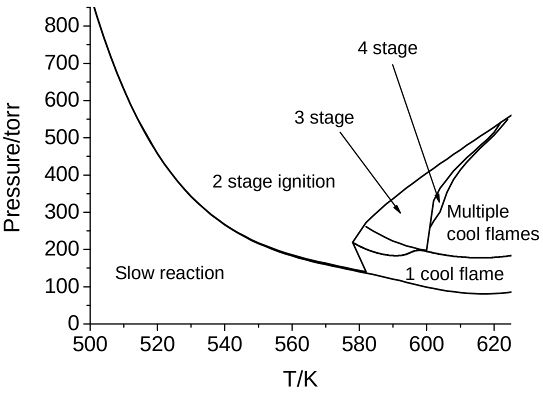

Fig.5 Simulated p-Ta ignition diagram for equimolar C_3H_8 + O_2 in a closed vessel under spatially uniform conditions from the final, Nancy scheme, comprising 41 species in 191 reactions,.

It remains the case that not only the reduced mechanisms but also the comprehensive scheme exhibits a reactivity that is somewhat higher than that observed experimentally. The main cause for concern lies in the pressure location for the two-stage ignition boundary, which flags up the transition from cool flame reaction to ignition as an appropriate basis for evaluation. Consequently, using the intermediate, 60-species reduced mechanism, global non-linear uncertainty analysis has been applied in order to investigate the potential origins of the discrepancies. We have addressed three global features, namely the temperature reached in the first stage of two-stage ignition (on the basis that it is a fundamental aspect of the transition process [15]), the induction time to the first stage (τ_1) and the induction time of the second stage (τ_2).

Results from the Monte Carlo uncertainty analysis

In this brief paper we use, but do not report in detail, the Morris method to determine an ordered ranking of the main contributors to output uncertainties in the selected features, We then focus on the analysis of the Monte Carlo simulations based on the most important parameters [15]. This allows a demonstration of how combinations of variations in parameter values may optimise the response. It was computationally viable to base this analysis on the intermediate reduced scheme, rather than the final 41 species scheme, as shown in Fig.4. A set of conditions was chosen for the Morris and Monte Carlo methods constituting an equimolar propane + oxygen mixture at 400.79 torr (diluted with nitrogen to 1 atmosphere total pressure) at T_a = 593K. Adiabatic conditions were maintained so that 2-stage ignition occurred rapidly on a reasonable timescale regardless of the adjustments made either to species heats of formation or to rate coefficients.

Where possible, the uncertainty of each individual ΔH^o_f was taken from the work of Afeefy *et al* [16]. However, in most cases there were no data available and, therefore, an approach was taken in which simple species were assigned a ± 5 kJ mol^{-1} range, intermediate species such as n-propylperoxy (n-$C_3H_7O_2$), a ±10 kJ mol^{-1} range, and complex species such as n-peroxyhydroperoxypropyl (n-$O_2C_3H_6OOH$), a ±15 kJ mol^{-1} range. Given that the initial values in these cases all come from group additivity calculations in the generation of the mechanism [4], it is reasonable to assume such levels of uncertainty. Using the Morris uncertainty analysis, strong sensitivities were detected with respect to ΔH^o_f of the following species,, in descending order, n-$O_2C_3H_6OOH$, n-$C_3H_7O_2$, i-$C_3H_7O_2$, n-C_3H_6OOH and CH_3O_2 radicals, and ethyl hydroperoxide (C_2H_5OOH).

The emphasis here is on the effect of heats of formation (ΔH^o_f), although rate coefficient adjustments made in the Morris method, using a ±25% range from their initial value, showed that the three criteria, the first stage temperature and the time dependences (τ_1 and τ_2), were highly sensitive to the magnitude of the pre-exponential term of three reactions in particular:

$$C_3H_8 + OH = n\text{-}C_3H_7 + H_2O \qquad (1)$$

$$C_3H_8 + OH = i\text{-}C_3H_7 + H_2O \qquad (2)$$

$$HO_2 + HO_2 = H_2O_2 + O_2 \qquad (3)$$

To examplify the inter-relationship between some of the main controlling heats of formation, the sensitivities of the temperature reached in the first stage of two-stage ignition and the time interval τ_1 with respect to variations in ΔH^o_f for n-$O_2C_3H_6OOH$ ($\underline{+}$15 kJ mol^{-1}), n-$C_3H_7O_2$ and i-$C_3H_7O_2$ ($\underline{+}$10 kJ mol^{-1}), derived from 5000 Monte Carlo simulations, are shown in Figs. 6-11.

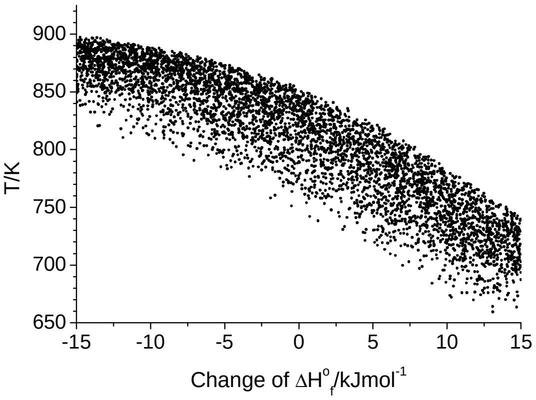

Fig. 6 Monte Carlo uncertainty analysis showing the dependence of the first stage temperature on ΔH^o_f of n-$O_2C_3H_6OOH$

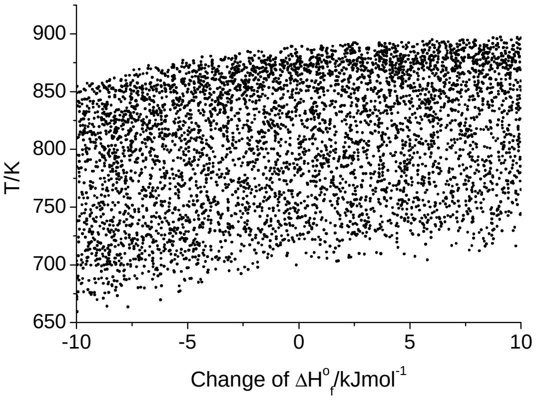

Fig. 7 Monte Carlo uncertainty analysis showing the dependence of the first stage temperature on ΔH^o_f of n-$C_3H_7O_2$

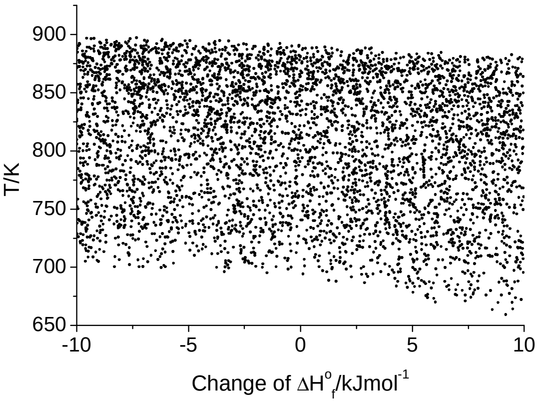

Fig. 8 Monte Carlo uncertainty analysis showing the dependence of the first stage temperature on $\Delta H^o{}_f$ of i-$C_3H_7O_2$

Figures 6-8 may be interpreted as follows. If $\Delta H^o{}_f$ for n-$O_2C_3H_6OOH$ is not varied from its base value then the temperature reached in the first stage of two-stage ignition is restricted to the range 750 - 850 K, regardless of the values of $\Delta H^o{}_f$ taken for the other two species. Whereas if $\Delta H^o{}_f$ for n-$O_2C_3H_6OOH$ is changed by +15 or -15 kJ mol^{-1} then the possible range for the first stage temperature is automatically restricted to 660 - 740 K or 830 - 900 K respectively. However, if $\Delta H^o{}_f$ for n-$C_3H_7O_2$ is changed by -10kJ mol^{-1} then the maximum temperature is restricted to 850 K. Conversely, if $\Delta H^o{}_f$ for n-$C_3H_7O_2$ is changed by +10kJ mol^{-1} the lowest possible temperature is approximately 720 K. There is a lower sensitivity to variations of $\Delta H^o{}_f$ for i-$C_3H_7O_2$. Nevertheless at the extremes shown in fig. 8 the maximum and minimum temperatures are restricted to 880 K at +10 kJ mol^{-1} and 700 K at -10kJ mol^{-1} even when the other parameters are optimised. The extreme upper temperature of 900 K can only be reached by simultaneous adjustment of all 3 parameters, -15 kJ mol^{-1} for $\Delta H^o{}_f$ of n-$O_2C_3H_6OOH$, +10 kJ mol^{-1} for $\Delta H^o{}_f$ of n-$C_3H_7O_2$, and -10 kJ mol^{-1} for $\Delta H^o{}_f$ of i-$C_3H_7O_2$. Conversely the extreme lower temperature of 660 K can only be reached by simultaneous adjustment of all 3 parameters in the opposite direction, +15 kJ mol^{-1} for $\Delta H^o{}_f$ of n-$O_2C_3H_6OOH$, -10 kJ mol^{-1} for $\Delta H^o{}_f$ of n-$C_3H_7O_2$, and +10 kJ mol^{-1} for $\Delta H^o{}_f$ of i-$C_3H_7O_2$. Figure 6 not only confirms the importance of n-$O_2C_3H_6OOH$ derived in the Morris analysis, but also quantifies the effect.

A similar interpretation can be made for the time to the first stage (τ_1) and the time from the first stage to the second stage of ignition (τ_2), as illustrated with respect to τ_1 in figs 9 to 11. $\Delta H^o{}_f$ for n-$O_2C_3H_6OOH$ and for n-$C_3H_7O_2$ have similar, but opposed, effects on τ_1. That is, if $\Delta H^o{}_f$ for n-$O_2C_3H_6OOH$ is raised by 15 $kJmol^{-1}$ whereas $\Delta H^o{}_f$ for n-$C_3H_7O_2$ is simultaneously lowered by 10 $kJmol^{-1}$ then τ_1 can be in the range from 5.3 to approximately 20 s. However, the change +15 $kJmol^{-1}$ imposed on n-$O_2C_3H_6OOH$ but with no change to $\Delta H^o{}_f$ for n-$C_3H_7O_2$ limits τ_1 to the range 5.3 to approximately 11 s.

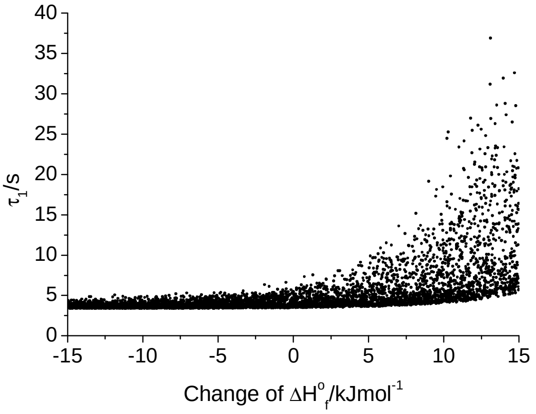

Fig. 9 Monte Carlo uncertainty analysis showing the dependence of τ_1 on $\Delta H^o{}_f$ of n-$O_2C_3H_6OOH$

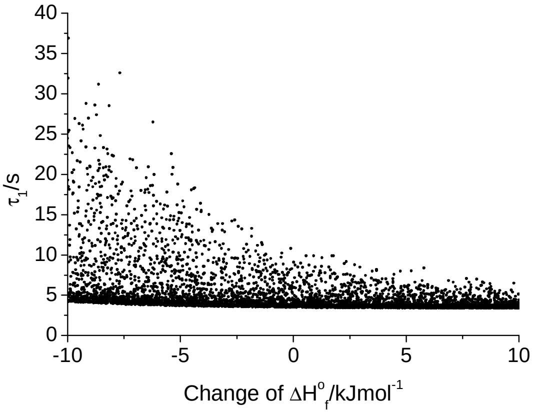

Fig. 10 Monte Carlo uncertainty analysis showing the dependence of τ_1 on $\Delta H^o{}_f$ of n-$C_3H_7O_2$

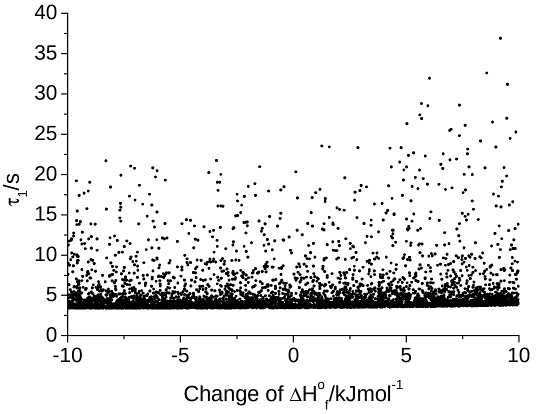

Fig. 11 Monte Carlo uncertainty analysis showing the dependence of τ_1 on $\Delta H^o{}_f$ of i-$C_3H_7O_2$

The dependence of τ_1 on ΔH^o_f for i-$C_3H_7O_2$ as shown in Fig. 11 is less pronounced, with a weak bias towards higher τ_1 times as ΔH^o_f is increased. The time to the first stage, τ_1, shows a different behaviour to that of the temperature. To obtain significant deviation above the base case value of below 5 s requires both an increase in ΔH^o_f for n-$O_2C_3H_6OOH$ and a decrease in ΔH^o_f for n-$C_3H_7O_2$, consequently there is a strong bias towards low values of τ_1 for the 5000 random simulations.

Discussion and conclusions

A comprehensive scheme for the combustion of equimolar propane + oxygen in a closed vessel at low temperature and pressure has been qualitatively evaluated. An approach for the systematic reduction of kinetic models has been shown to successfully reduce the numbers of species and reactions in the scheme. The reduced computational cost associated with a smaller scheme has facilitated the use of global methods for assessing the impact of uncertainties in the main input parameters within the scheme on the simulation of auto-ignition.

Although only scratching the surface of the issues, this example shows that in evaluating kinetic models it is prudent to address the interactions of uncertainties in rate parameters in a quantitative way. It should be noted also that the heats of formation, even of the $C_3H_7O_2$ radicals, are unlikely to be known to a precision better than $\pm$ (5 - 8) kJ mol^{-1} [17], and that for the n-$O_2C_3H_6OOH$ will certainly be less precise. Amongst the three, ΔH^o_f for n-$O_2C_3H_6OOH$ is the most important, and the question then arises as to the extent to which the p-T_a ignition diagram is affected if its heat of formation alone is increased. As an example Fig. 12 demonstrates that when ΔH^o_f for n-$O_2C_3H_6OOH$ is raised by only 12.5 $kJmol^{-1}$ there is a very pronounced effect, increasing the minimum pressure for 2-stage ignition by 180 torr, taking it higher than that found experimentally (Fig. 2).

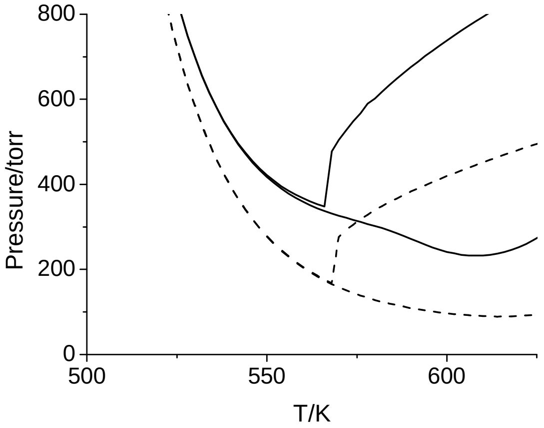

Fig. 12 Comparison of 2-stage and 1 cool flame boundarys. Dashed line - unadjusted thermodynamics, Solid line - +12.5kJ to ΔH^o_f of n-$O_2C_3H_6OOH$.

By virtue of the corresponding influence of this (and the other) heats of formation on the time dependence for the development of 2-stage ignition, the predictions for ignition delay, as might be used in the interpretation of the performance of fuels in e.g. HCCI engine combustion, would also be in error as a consequence of the same uncertainties. On the basis of the evidence from simulations for n-heptane combustion [18], the problem is not confined to propane combustion (although this is the simplest case to resolve) but is generic to the alkanes.

Acknowledgement

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