

PP04: METHODOLOGIES FOR AUTOMATIC HYDROCARBON AUTOXIDATION MECHANISM GENERATION

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Abstract. Aviation fuel undergoes oxidation of the hydrocarbon components due to thermal stress, this degrades the fuels properties and causes deposits in the fuel and engine systems. Our research uses computational modeling techniques to understand how the chemical composition of a fuel effects its thermal stability. Computational chemistry techniques are used to calculate the thermodynamic and kinetic data for the oxidation reactions in the fuel.

Keywords: Fuel Oxidation, Modeling

INTRODUCTION

Aviation fuel has the dual purpose in modern aircraft of acting as the energy source and as a heat exchanger to remove excess heat from the engine systems. The increase in fuel temperature causes the aviation fuel to undergo oxidation and form insoluble deposits which can block the fuel systems (Kuprowicz et al 2007). The chemical composition of a fuel has been shown experimentally to effect its thermal stability, with the presence of polar species and high aromatic content increasing the oxidation rate (DeWitt et al 2014). This work attempts to better understand the mechanisms which govern the oxidation of the fuel and the role that changing chemical composition has on the global kinetics of these processes.

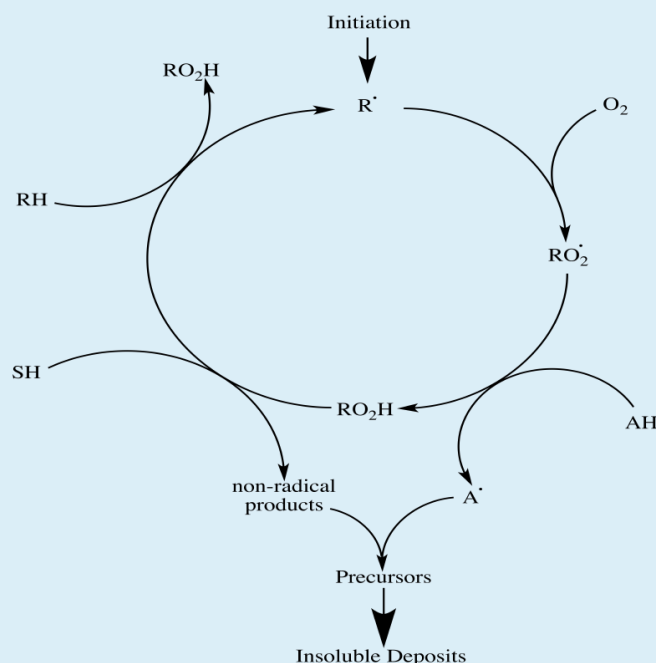


Figure 1. Simple reaction cycle for the formation of oxidation products

Aviation fuels properties are altered by changing the composition, with addition of aromatics increasing the energy density of the fuel, and the range of the aircraft. Increasing the aromatic content has also been linked to increasing the smoke and particulates produced from combustion. For this

reason it would be useful to increase the energy density of a fuel without increasing aromatic content. One solution would be to include higher amounts of cyclic hydrocarbons, as they should burn in the similar ways to normal paraffins (Amara et al 2016). The investigation into the effect that hydrocarbons composition has on the oxidation mechanisms was carried out using quantum chemistry models (Zabarnick et al 2006). The knowledge gained from these calculations builds on the role that each component has on the thermal stability problem. The work presented shows how cyclic hydrocarbons effect the oxidation rate, with the quantum mechanically calculated kinetics and thermodynamics compared to those of aromatic, and straight chain alkanes.

RESULTS AND DISCUSSION

The Calculations were carried out using the Gaussian 09 software, using Density Functional Theory. The calculations were carried out at the B3LYP/6-311G (d,p) level of theory, with electronic structure calculations of peroxides being carried out using CASSCF and CASPT2 theories. The results are compared to experiment and literature.

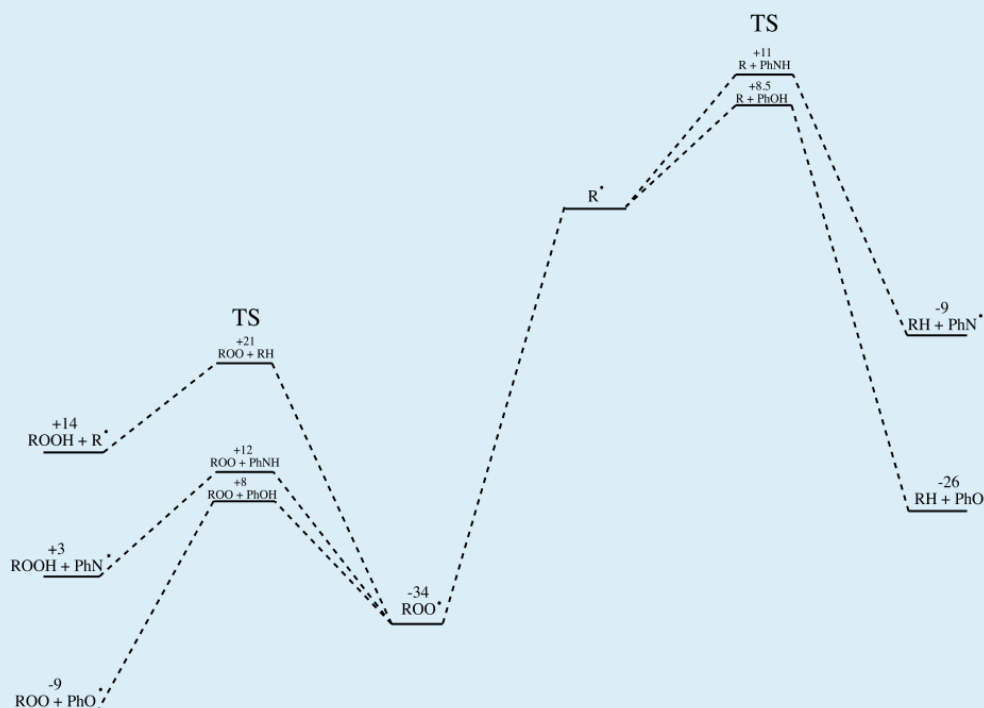


Figure 2. Potential energy surface of the oxidation reactions for dodecane

It was found that cyclic hydrocarbons were more stable to oxidation than aromatic hydrocarbons, with this being linked to aromatic hydrocarbon stabilising the radical species produced during the oxidation process through conjugation. Cyclic hydrocarbons were however more reactive than straight chain alkanes, due to the greater proportion of radical stabilising secondary and tertiary carbons. This supports what is seen in the experiments, with the rate of oxidation increasing as the percentage of cyclic hydrocarbons increase in the test sample. The aromatic and cyclic radicals were more stable and less reactive to further reactions due to the stabilising effects of the hydrocarbon structure. However more investigations are needed to identify the role that structure plays on oxidation rates and deposit formation.

Limitations of the calculations were found when the electron spin states of the species changed during a reaction. This is a particular problem for reaction such as the homolytic fission of peroxides, where it could lead to errors of up 7 Kcal mol⁻¹. This was solved by moving to a theoretical technique that better describes these systems, at greater computational expense.

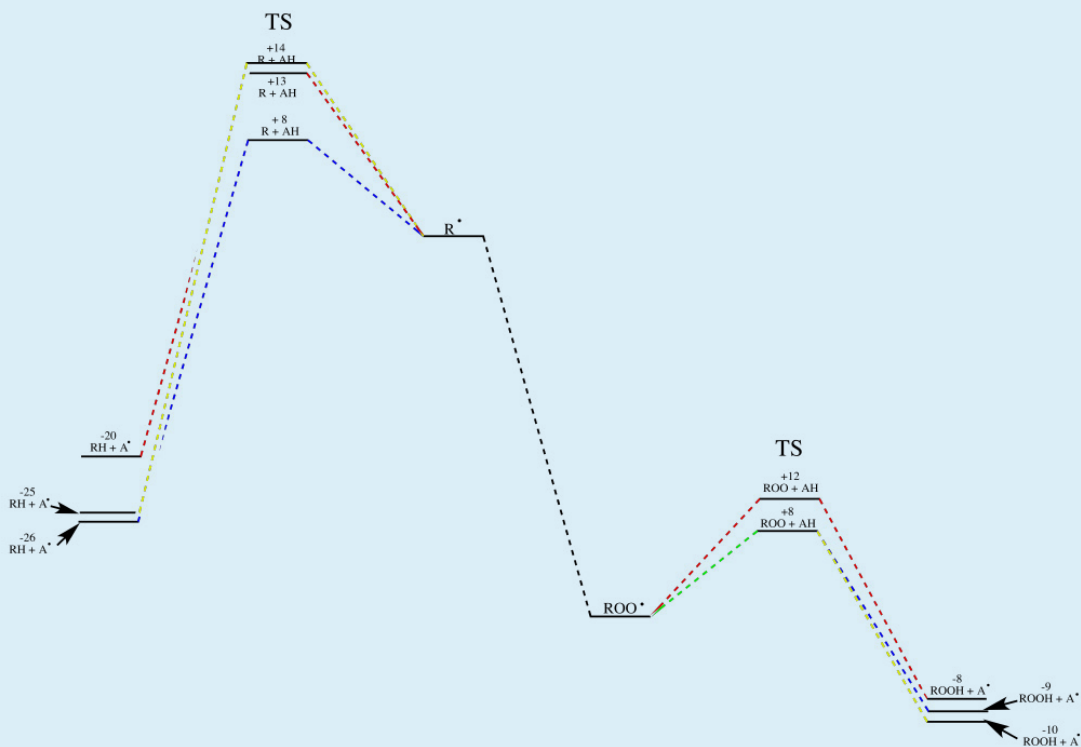


Figure 3. Potential energy surface of the oxidation reactions for dodecane – Blue, Toluene – Yellow and Decalin – Red

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