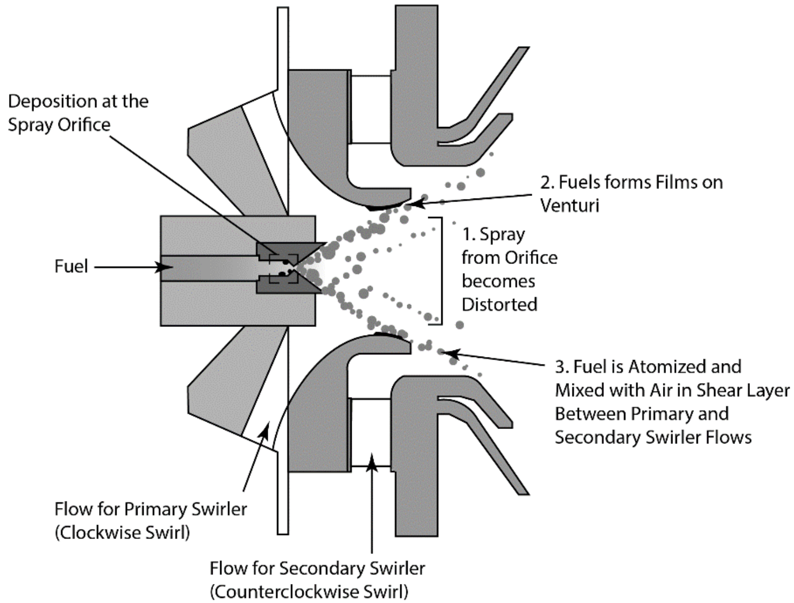
The University Of Sheffield.

Understanding Thermal Stability of Future Jet Fuels Using Computational Chemistry

Charlie Adams
Simon Blakey, Anthony Meijer, Ehsan Alborzi, Christopher Parks

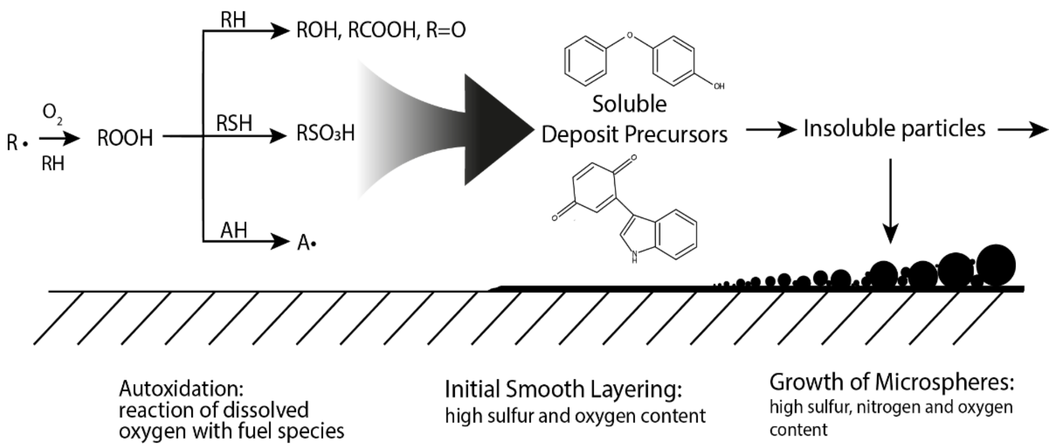
The Thermal Stability Problem

- Deposition on fuel injector and heat transfer of fuel-oil heat exchanger
- Thermal stability level defined in ASTM D3241 [1]
- Dependent on initial fuel chemistry, each fuel has **unique** fuel chemistry
- Future alternative fuels will **need** to meet these standards



Adapted from [2]

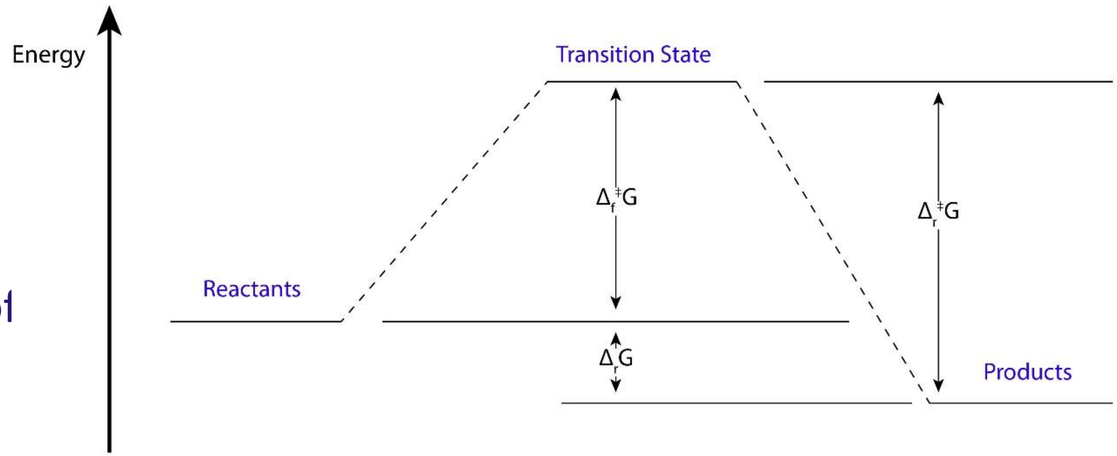
Chemical Background



- **Complex** series of chemical reactions
- **Prediction** of deposition is achieved by building **pseudo-detailed mechanisms**
- **Soluble Macromolecular Oxidatively Reactive Species (SMORS)** mechanism is main mechanism describing deposit formation

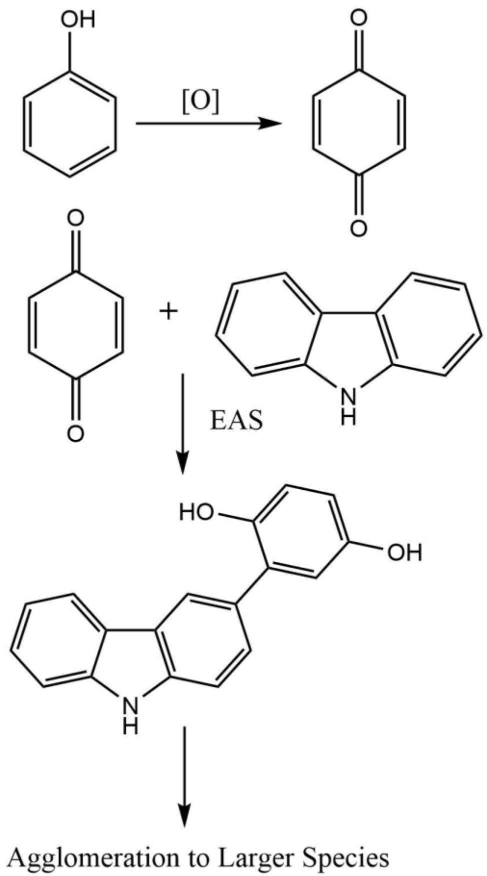
Computational Chemistry as a Predictive Tool

- **Molecular geometries** a function of the total electronic energy
- **Density functional theory (DFT)** provides a means of obtaining the electronic energy with a high degree of accuracy
- **Reactants, products and transition states** guessed and then the geometries optimized as a series of stationary points



A WORLD TOP 100 UNIVERSITY

SMORS mechanism [3]



- Electrophilic aromatic substitution (EAS) between oxidized **indigenous phenols** and **polar species**
- **Generalized** mechanism
- Extensive experimental investigation but little mechanistic scrutiny
- Computational details: B3LYP functional with a cc-PVDZ basis set, PCM model used with heptane chosen as a solvent

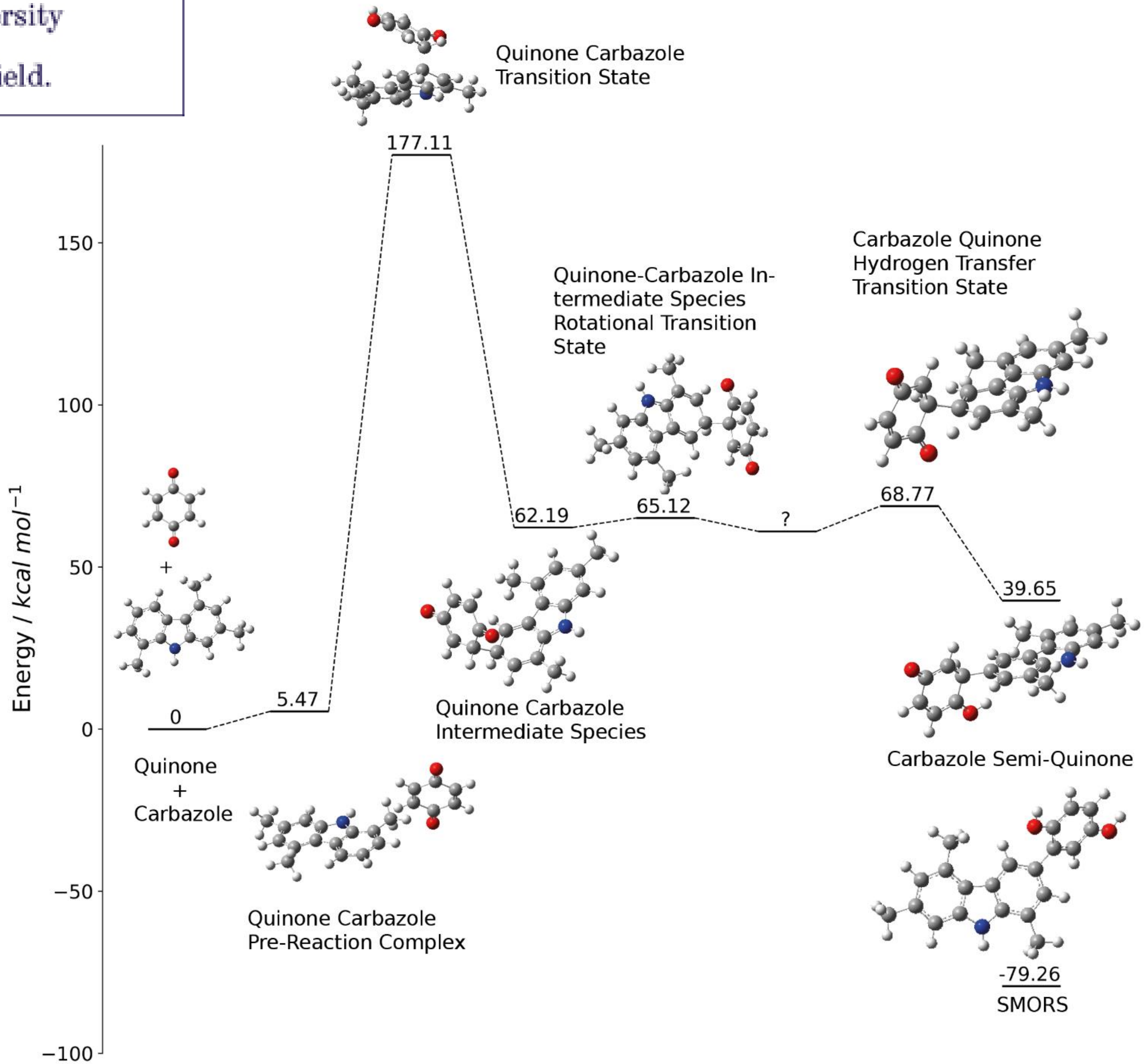
Proposed SMORS scheme

- **Oxidation of phenols to quinones was energetically favourable**, thermodynamically –7.15 $kcalmol^{-1}$ downhill.

- **No energetically favourable pathway** found to form the proposed SMORS at EAS step.

- Proton shuttle required to form final proposed species

Proposed SMORS scheme



Modified SMORS scheme

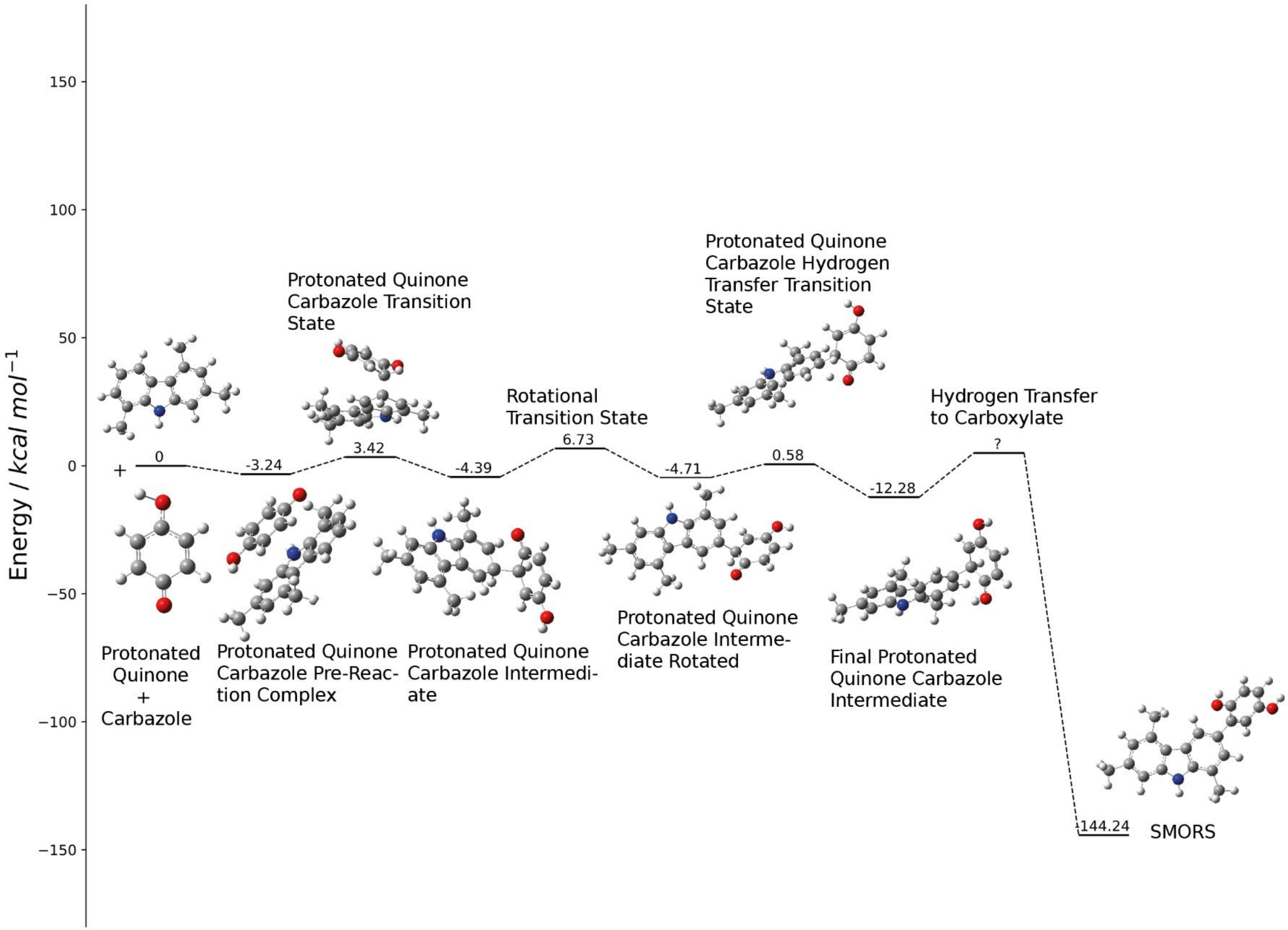
- Analogous reactions between quinones and indoles **all employ acid catalysts**

- **Acids are known to form** during the oxidation of bulk hydrocarbons (carboxylic acids) and indigenous sulfur compounds (sulfonic acids)

- Acid catalysed EAS reaction **lowers the barrier from +177.6kcal mol^{-1} to +6.7kcal mol^{-1}**

- Acids previously shown to have an adverse effect on thermal stability, small amounts of dissolved water could provide solvent for protonation to occur

Modified SMORS scheme



Conclusions

- No mechanistically feasible pathway found for original SMORS scheme using EAS

- Quantum chemistry shown to be a powerful mechanistic tool for understanding fuel properties

- Acids shown to be a possible catalyst to the formation of bulk insoluble

- Future alternative fuels **low/negligible amount of sulfur**, good news for the thermal stability.

References

[1] ASTM International. Journal of ASTM International. (2004). Web.

[2] Heneghan, S. P., Zabarnick, S., Ballal, D. R., & Harrison, W. E. (1996). JP-8+100: The Development of High-Thermal-Stability Jet Fuel. *Journal of Energy Resources Technology*, *118*(3), 170. https://doi.org/10.1115/1.2793859

[3] Beaver, B., Gao, L., Burgess-Clifford, C., & Sobkowiak, M. (2005). On the mechanisms of formation of thermal oxidative deposits in jet fuels. Are unified mechanisms possible for both storage and thermal oxidative deposit formation for middle distillate fuels? *Energy and Fuels*, *19*(4), 1574–1579. https://doi.org/10.1021/ef040090j

