1. Introduction
- Reduction of regulated pollutants emitted from alcohol based fuels as compared to traditional fossil fuels. [1]
- Increased unregulated emissions, such as carbonyls, from alcohol based fuels.
- Fewer studies into the atmospheric fate of longer chain alcohols such as the isomers of butanol.
- Butanols provide greater energy density than shorter chain alcohols.
- The hydroxyl radical (OH) is the most important oxidising agent in the troposphere.
- CI initiated chemistry also plays an important role in the tropospheric oxidation of VOCs, with oxidation mechanisms typically analogous with those of OH initiated oxidations, but with reaction rates several orders of magnitude larger.
- Comparing computer simulations and measurements is an excellent test of our current understanding of the chemical mechanisms occurring.

2. HIRAC[2]
- Highly Instrumented Reactor for Atmospheric Chemistry.
- 2.25 m³ cylindrical stainless steel chamber.
- Capable of temperature and pressure dependent studies (203 - 343 K and up to 1000 mbar).
- 8 quartz tubes house photolysis lamps.
- 4 mixing fans ensure total mixing time of ~70 s.
- Numerous analytical instrumentation available: FTIR and GCs for VOC measurements, FAGE for [OH] and [HO₂] measurements.

3. Experimental
Relative Rate:

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\text{Product Studies:}
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4. Results: Temperature Dependent Relative Rate Studies of n- and iso-butanol with CI

- Excellent agreement with room temperature literature rate constants.
- Negative temperature dependence over 298 - 345 K.
- Poor reproducibility of measurements CI + n-butanol likely due to increased influence of wall reactions at low temperatures.

5. Results: Products of CI Initiated Oxidation of iso-butanol Under Varying NO₃ Conditions

- Increased ozone production with increased initial [NO].
- As initial [NO] increases, HO₂ grows in at longer times due to increased competition between reactions R3 and R7/8. HO₂ is also suppressed by reaction R9.

6. Future Work
- Further investigation into low temperature relative rate measurements of CI + iso- and n-butanol.
- Further analysis of iso-butanol + CI oxidation reactions under varying NO₃ conditions.
- Modelling of iso-butanol + CI oxidation reactions is currently underway.
- Experiments of iso-butane + CI oxidation process for comparison of ozone formation potential under varying NO₃ conditions.
- Experiments to investigate the products and ozone formation potential under varying NO₃ conditions of the OH initiated oxidation of iso-butanol and iso-butanol.

7. References

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\text{Figure 1.1: iso-butanol}
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\text{Figure 1.2: n-butanol}
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\text{Figure 4.1: Temperature dependent measured rate constant for iso-butanol + CI at 1000mbar. Blue squares show rate constants measured by relative rate method, using cyclohexane as a reference compound, in HIRAC, averaged over several experiments. Green circles show rate constant measured by Wu et al. at 293.2 K and at 1 atm using reference compounds propane and cyclohexane. Purple triangles show rate constant measured by Anderson et al. at 298 K and at 10 Torr of NH₃.}
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\text{Figure 4.2: Temperature dependent measured rate constant for n-butanol + CI at 1000mbar. Blue squares show rate constants measured by relative rate method, using cyclohexane as a reference compound, in HIRAC, averaged over several experiments. Green circles show rate constant measured by Garzón et al. at 264.8 K and by laser photoysis/fluorescence. Green circles show IUPAC recommended values.}
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\text{Figure 5.1: Comparison of measured and calculated OH reactivity of iso-butanol + CI initiated oxidation of iso-butanol in the absence of NO.}
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\text{Figure 5.2: Contribution of , ,  and oxidation products - mainly aldehydes - to measured OH reactivity.}
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\text{Figure 5.3: Experimental and Results}
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\text{Figure 5.4: Contribution of , ,  and formed potentials.}
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\text{Figure 5.5: Experimental and Results}
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