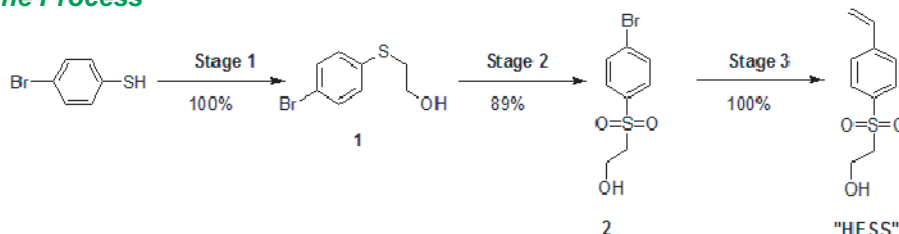


Case Study: Thermochemistry, Kinetics and Modelling Scale-up of a Highly Exothermic Oxidation

The Process



- Sulfone **2** is a key intermediate in the synthesis of HESS, a novel VOC-free crosslinking monomer. **2** is prepared by oxidation of sulfide **1**, itself obtained via nucleophilic addition of 4-bromothiophenol to 2-chloroethanol.
- A pilot facility had been identified for kilo-scale manufacture, however large-scale manufacturing issues had not been addressed as the client's focus had been to produce small quantities for materials testing.

Customer Requirements

- For pilot manufacture, quantification of exotherms that might occur under normal and abnormal operating conditions for stages **1** and **2** was needed
- An early assessment of feasible manufacturing conditions based on physicochemical properties of the process was also requested
- Stage 2 was known to be particularly exothermic. Hydrogen peroxide and perborate are strong oxidizing agents requiring special precautions; hydrogen peroxide can also decompose to form copious quantities of oxygen gas, presenting a potential over-pressure hazard. Since the rate of decomposition increases with increasing temperature, it was paramount to understand how control of the process temperature could be achieved on large-scale
- In particular, accumulation of the peroxide species in solution could be potentially very dangerous and must be avoided

Approach

- Reaction calorimetry was carried out on each of stages 1 and 2 and used to calculate ΔH_r
- Kinetic models based on the reaction chemistry were prepared and kinetic parameters were regressed to Qr data
- Reaction models were combined with detailed reactor model based on the chosen pilot facilities in order to construct predictive process models. These models were then used to calculate Maximum Temperature of the Synthesis Reaction under adiabatic conditions (MTSR) values and predict the effects of reagent accumulation under different scenarios
- A detailed process review based on laboratory procedures was also carried out. This entailed assessing the lab process according to key scale-up criteria (safety, permissibility, regulatory, environmental and economic factors)
- Detailed process flow-sheets and material balances were also prepared to assist the pilot manufacturer with equipment selection and construction of an operations list

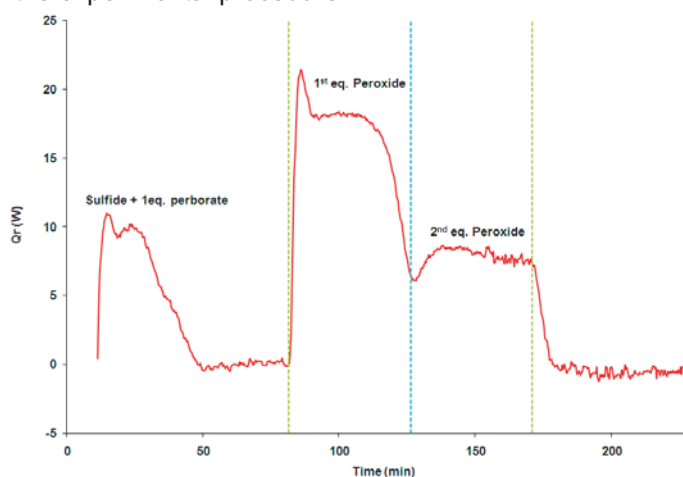
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Outputs for Stage 1:

- A significant exotherm was observed. The enthalpy of reaction, ΔH_r , as determined by the reaction calorimetry experiment, is $-9.59 \times 10^4 \text{ Jmol}^{-1}$ of bromothiophenol.
- The calorimetry data also indicated that the reaction was sufficiently fast that the accumulation of the dosed substrate was low
- Calculation of MTSR suggests that the effect of accumulation of unreacted 2-chloroethanol in the event of a cooling system failure (adiabatic operation) is to raise the temperature by less than 10°C ; in this case to a maximum of 54°C from an operating temperature of 45°C . This mild thermal runaway is due to both the rapid rate of the reaction keeping the level of accumulation to a low level and the relative dilution of the reaction system.

Outputs for Stage 2:

- Initial calorimetry experiments on stage 2 using the client's original lab procedures involved the addition of a molar equivalent of perborate to the sulfide, followed by an addition of more than two equivalents of peroxide. This produced Qr data as illustrated below, which revealed three exotherms corresponding to different phases of the experimental procedure:



- From these initial experiments, some process modifications were suggested, which were successfully trialled by the client in both lab and small-scale adiabatic experiments. Most notably, the oxidation procedure was changed to use catalytic perborate (or boric acid)
- ΔH_r for the oxidation was determined to be $-8.6 \times 10^5 \text{ Jmol}^{-1}$ of sulfide, an extremely high value
- Simulations however suggested that peroxide accumulation under experimental conditions was low and that MTSR resulting from a cooling failure was below that of the solvent boiling point
- Process modelling suggested the pilot facilities had sufficient heat transfer capability to handle the exotherms from stages 1 and 2, however, temperature control at the facility would be problematic until a proper feedback temperature control system was implemented
- As the project develops, models developed for stages 1 and 2 will be used to quickly test a variety of feed scenarios both for normal and abnormal conditions including for example cooling system failure, reagent under/over charge as well as other reactors/control systems and scale-up

Client Testimonial

"As part of a scale up programme for a polymer monomer synthesis, we needed an optimisation study and safety assessment of a three step process. LyraChem quickly and efficiently provided exactly what we needed and we received an excellent summary report at the end of the work. Importantly, this study did highlight the need for a major change in one reaction step to avoid potential thermal runaway, and now we're now routinely supplying customers as a direct of their efforts on the project"