Sulfonation Chemistry – more sustainable approaches

RSC Symposium, Basel, June 1-2, 2016

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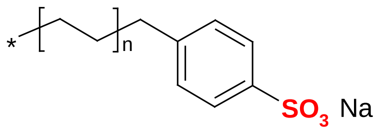
More sustainable sulfonations

Content

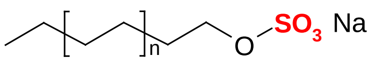
- Conventional sulfonation reactions
  - Where they are used, which products are manufactured, their benefits and disadvantages
- Alternative sulfonation reactions
  - What can be improved, what is more sustainable, benefits and disadvantages
- More sustainable sulfonation reactions
  - What they look like, their sustainable benefits

More sustainable sulfonations

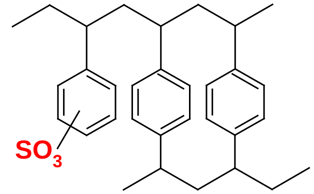
Introduction



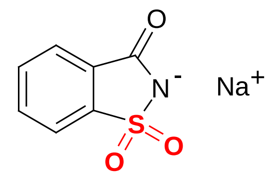
Linear Alkylbenzene sulfonate
Detergent



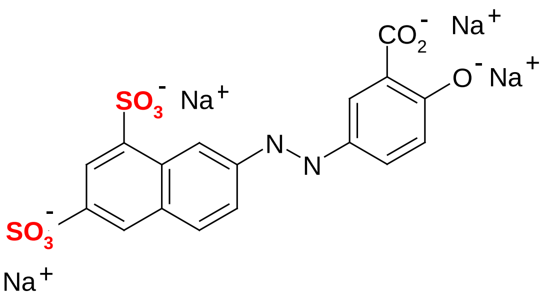
Fatty alcohol sulfate
Detergent



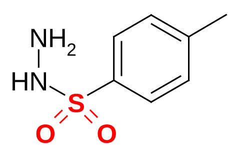
Sulfonated sytrene divinylbenzene copomylers
Ion exchange resins



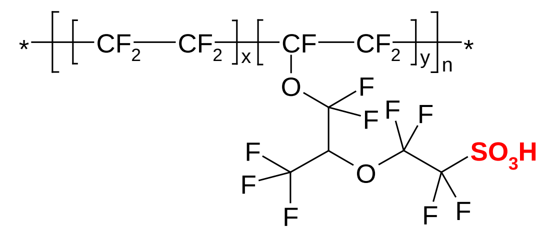
Saccharin
Artificial Sweetener



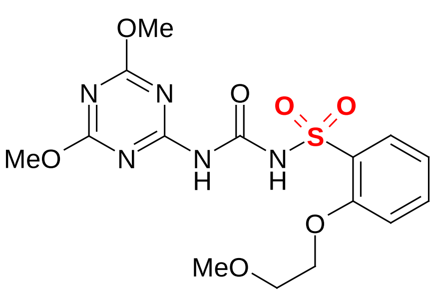
Mordant Yellow 20
Dye



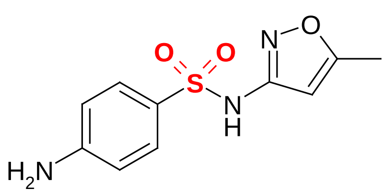
Toluenesulfonyl hydrazide
Blowing agent for rubber



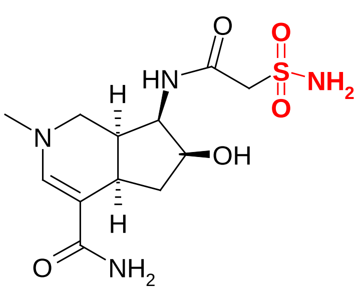
NAFIONTM (DuPont)
Sulfonated Polymer



Cinesulfuron ("Sailant")
Sulfonylurea Herbicide



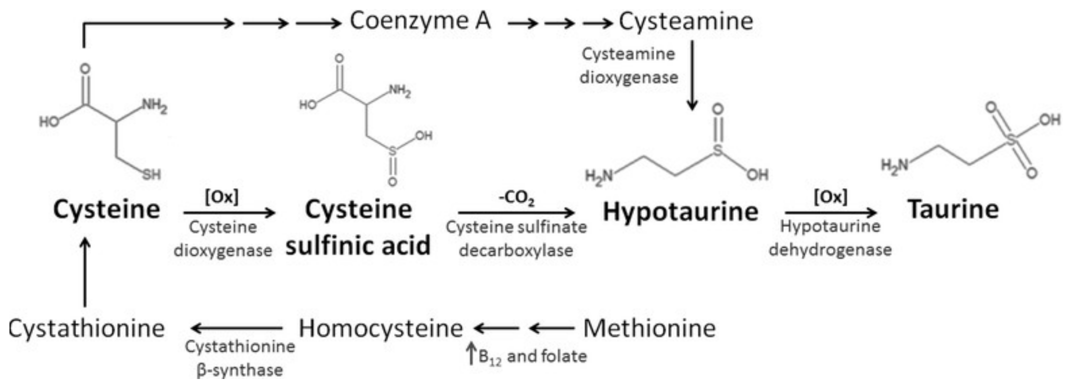
Sulfamethoxazol
Sulfonamide Antibiotic

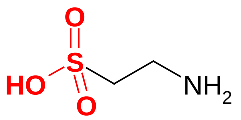


(-)-Altemicidin
Arcaricidal and antitumor activity

More sustainable sulfonations

Natural “sulfonations”





2-Aminoethanesulfonic acid
Taurine

- Synthesis of thioles:
  - R-X + NaSH → R-SH + NaX
  - Aryl-Grignard + sulfur
  - Diazonium salt + Na sulfide or Na xanthate
- → Nature is not a model for sustainable sulfonations

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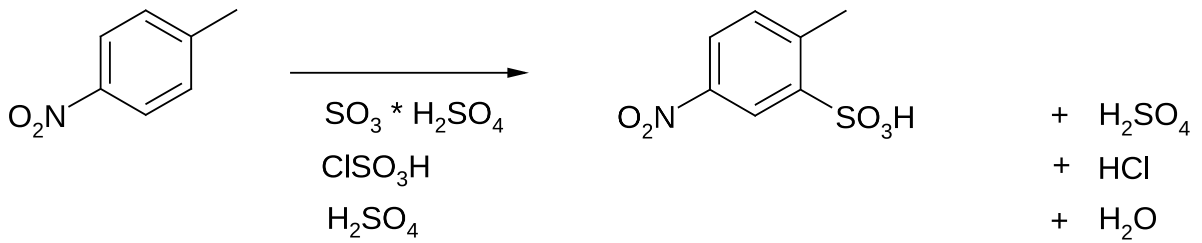
Conventional sulfonation



Difficulties:

- Sulfuric acid: dilution effect due to formation of water: (large) excess of reagent necessary
- Sulfone formation as side reaction can be prevented by high excess of reagent
- Waste waters need to be neutralised (and oxidised due to dissolved organic residues)
- Sulfonic acids mainly easily soluble in water and reagent: difficult to isolate
- Sulfochlorination and subsequent hydrolysis: sulfonic acids better to isolate

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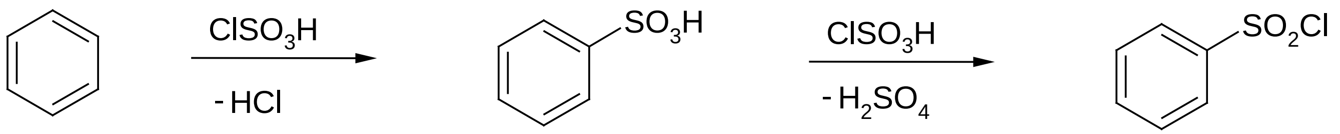
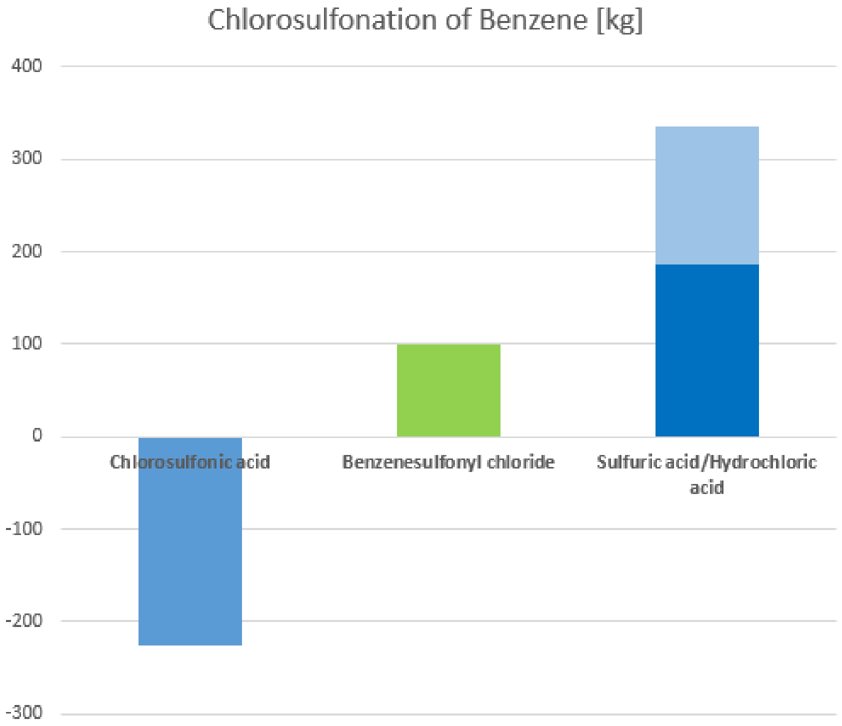
Conventional sulfonation





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Challenges

- Paper chemistry: introduction of pure SO_3 would be the most efficient method
  - No waste
  - No dilution
  - Reactivity remains unchanged
- Problem:
  - Handling and availability: SO_3 is normally not available and highly reactive
  - Sophisticated solutions exist for dedicated sulfonation plants but no smart development for multi purpose environment
- Scale and type of process
  - Sulfonation in dedicated equipment: in general waste is not a «problem»
  - Problems are sulfonations in multi purpose equipment in «mid scale»

Multi purpose	Dedicated / large volumes
API's	Ion exchange resins
AI's	Detergents
Dyes	
Polymers	

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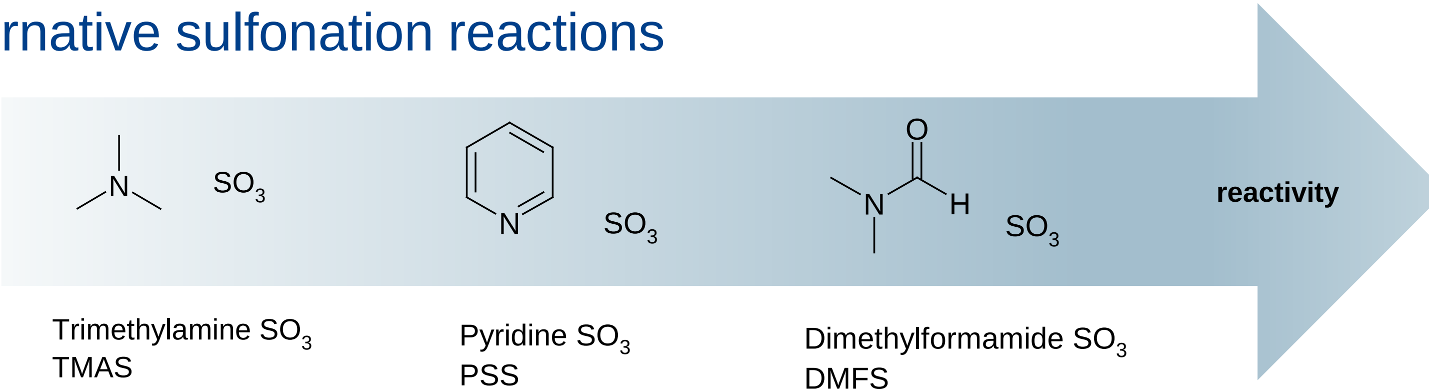
Alternative sulfonation reactions



Advantages	Disadvantages
Smooth reaction conditions	Expensive
No aqueous, acidic waste	Not suitable for every sulfonation reaction
Liquid amines can be distilled off and re-used	Use of amines as «reaction aids»
Ideal for sensitive substrates	Hazardous reagents
Reactivity according to base strength of amines	

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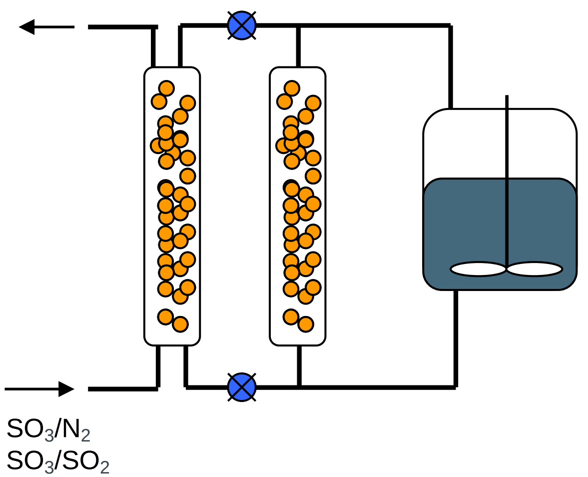
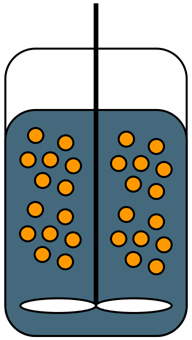
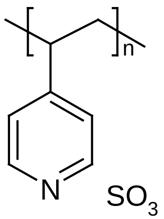
Sulfur trioxide on a polymeric carrier

continuous reaction, stationary phase, beads



batch reaction, granular carrier





PVPS

Polyvinylpyridine SO_3 complex

Advantages	Disadvantages
Moderated reactivity	Needs SO_3 source
«Rechargeable»	Liquid/dissolved substrates needed

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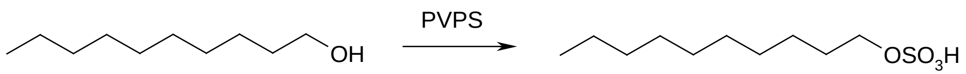
Sulfonation with PVPS

- Feasibility study:
  - Reaction of n-dodecanol with PVPS
  - Batch reaction
  - Feasibility confirmed: 80% conversion; no product isolation



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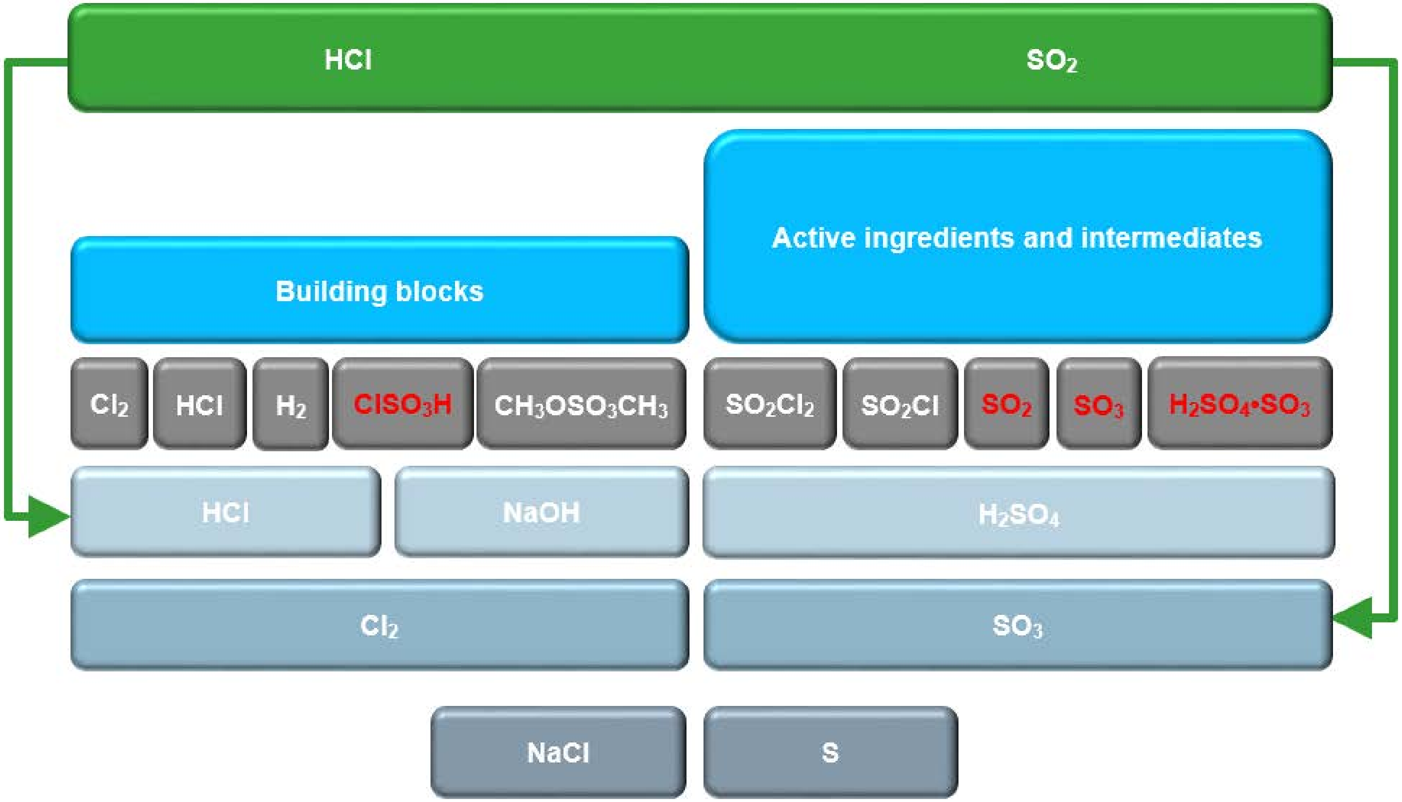
CABB‘s Verbund and recycling system



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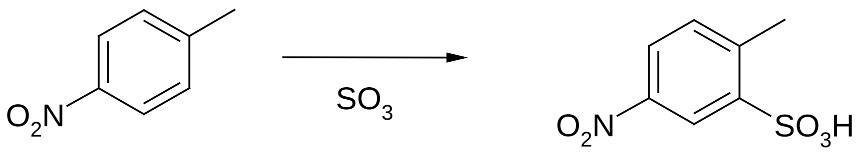
Sulfonation with SO_3 in a microreactor



- Commercially interesting reaction: sulfonation of an aromatic compound
- High reactivity, exothermic reaction: → microreactor
- Multi-purpose approach: → microreactor
- Challenges:
  - solid starting material
  - solid product
  - liquid range of SO_3 is between 18°C and 48°C
  - dosage of SO_3
  - quantitative analysis of SO_3 volume
  - analytical detection method of SO_3

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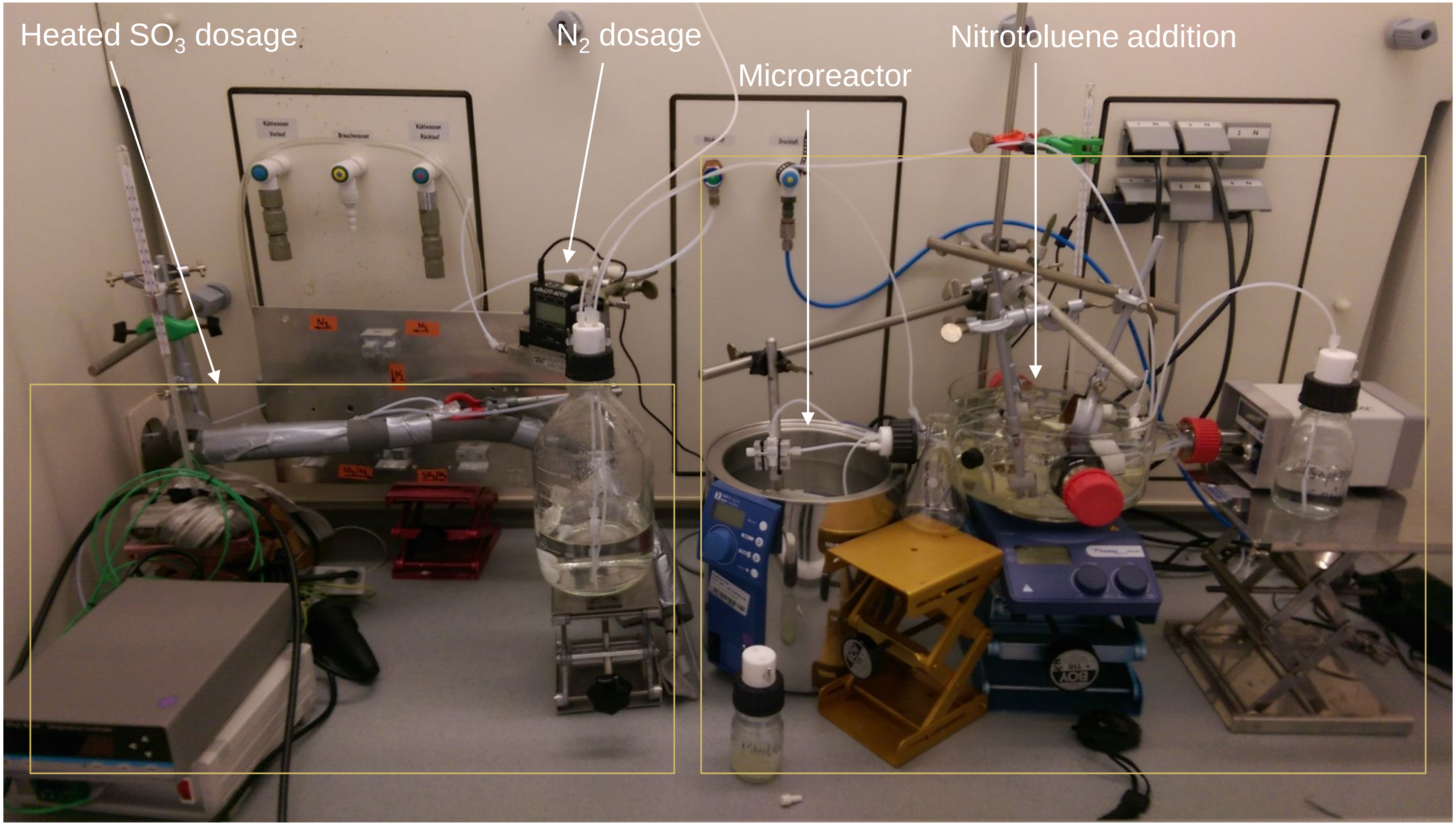
Sulfonation with SO_3 in a microreactor



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Sulfonation with SO_3 in a microreactor: results and learnings

- p-Nitrotoluene (PNT) was successfully reacted with SO_3 to yield p-Nitrotoluenesulfonic acid (PNTS)
  - PNT is heated to 75°C to obtain a liquid starting material
  - Dosage of liquid SO_3 with a syringe pump, evaporation of SO_3 before reaction with PNT
  - Reaction is fast; selectivity and yield depend on temperature and concentration parameters
  - A continuous reaction of PNT with SO_3 was carried out and analytical results determined at steady state
- Multi product approach possible for all starting materials with “low” melting points, or in solution

- → such kind of aromatic compounds are difficult to handle in a microreactor without a solvent
- → inert solvent for SO_3 sulfonation is difficult to find
- → microreactor is not the most suitable equipment for this reaction

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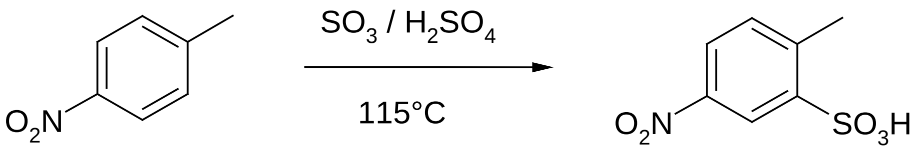
Continuous sulfonation with oleum/SO_3 in CSTR reactors



- Cascade of four reactors: two for reaction, two for work-up
- Preparation of a solution of PNTS via sulfonation of PNT with sulfuric acid to start the reaction
- Water resp. mother liquor is added and temperature lowered to precipitate PNTS
- Continuous process with recycling of mother liquor up to 4 times
  - Yield 98.5%
  - Disadvantage: use of oleum and dilution with water results in waste sulfuric acid

Advantages	Disadvantages
High yield	Needs SO_3 source
Continuous process for large volumes	No real multi purpose approach
	Formation of waste

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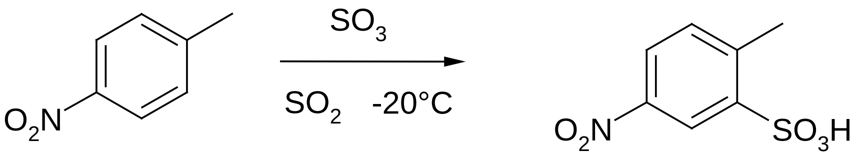
Batch sulfonation with SO_3 in liquid SO_2



- Reaction in heterogeneous phase
- Suspension of PNT in liquid SO_2
- Exothermic reaction upon addition of SO_3 and SO_2 under reflux
- Distillation of SO_2 lets PNTS precipitate
- 98.6% yield with >99% purity

Advantages	Disadvantages
No waste!	Needs SO_3 source
Multi-purpose approach	Needs SO_2 liquid
High yield and high purity	
Recycling of SO_2	

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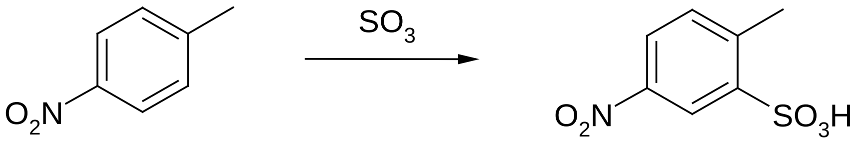
Calculation of PNT sulfonation processes



- Calculation of material and waste efficiency shows similar results of both processes
- Cost calculation of the two different processes shows surprisingly very similar process costs
- Better multi purpose approach: sulfonation in liquid SO_2 with SO_3 as reagent

	Continuous / oleum	Batch / SO_2 / SO_3
Process Mass Intensity (PMI)	1.78	1.03
E-factor	0.78	0.03

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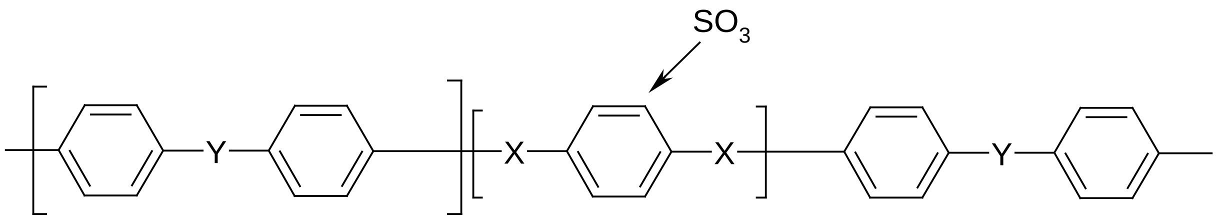
Sulfonation of polymers with SO_3 in SO_2



- Sulfonation of a polymer: pre- or postpolymerisation, homogeneous or heterogeneous
- Degree of sulfonation (dS) determines hydrophilicity
- Conventional process: solution of polymer in concentrated sulfuric acid
- Precipitation into water, extended washing: very large amounts of waste water
- Alternative sulfonation process: SO_3 in liquid SO_2

	Conventional (sulfuric acid)	SO_3 in SO_2
Benefits	Polymer partially soluble in SE	Heterogeneous reaction Better control of dS No chain cleavage No discoloration
Disadvantages	Cleavage of polymer, discoloration Large volumes of waste water Long washing process	Low solubility of polymer

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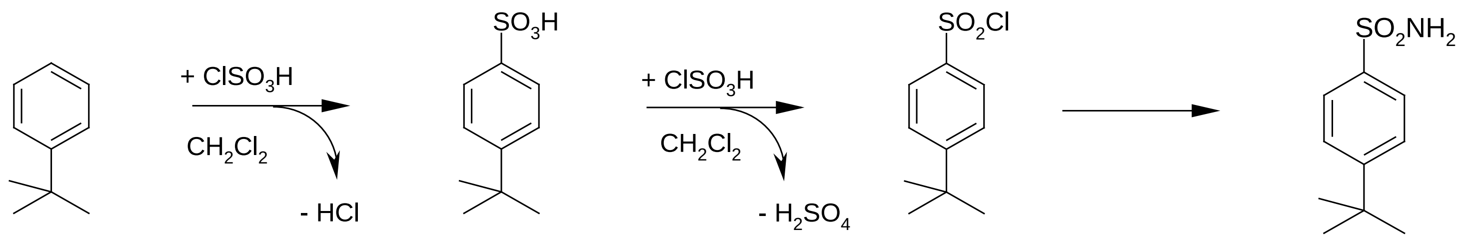
Sulfonamide: conventional sulfonation with $ClSO_3H$



Original process:

- Reaction of the aromatic compound with $ClSO_3H$ in dichloromethane at -5°C
- Subsequent reaction of intermediately formed sulfonic acid with $ClSO_3H$ to yield sulfonyl chloride
- Reaction of sulfonyl chloride with acqueous ammonia solution to yield sulfonamide

- HCl and H_2SO_4 are removed as aqueous waste
- Dichloromethane and toluene are completely recycled

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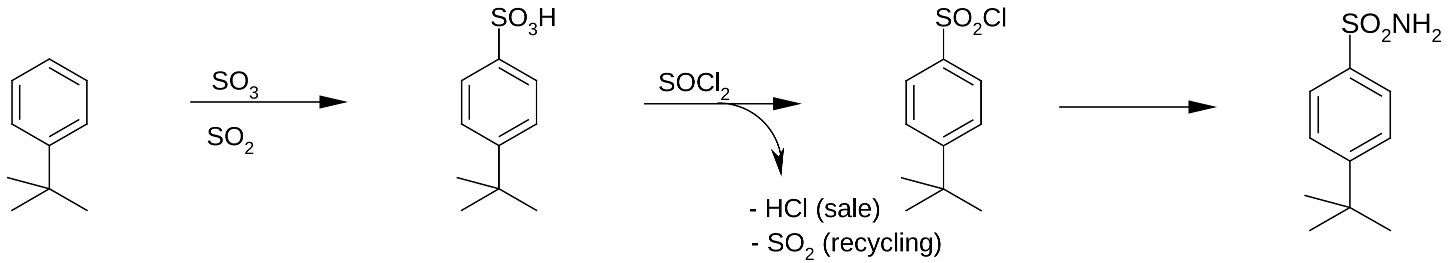
Sulfonamide: improved sulfonation with SO_3/SO_2



CABB's improved process

- Reaction of aromatic compound with SO_3 in liquid SO_2 at -20°C
- Reaction of sulfonic acid with thionyl chloride
- Reaction mixture is heated to 25°C which leads to evaporation of SO_2
- Reaction of sulfonyl chloride with acqueous ammonia solution in toluene
- SO_2 evaporates and is completely recycled
- HCl is converted into hydrochloric acid as commercial sales product
- One pot synthesis

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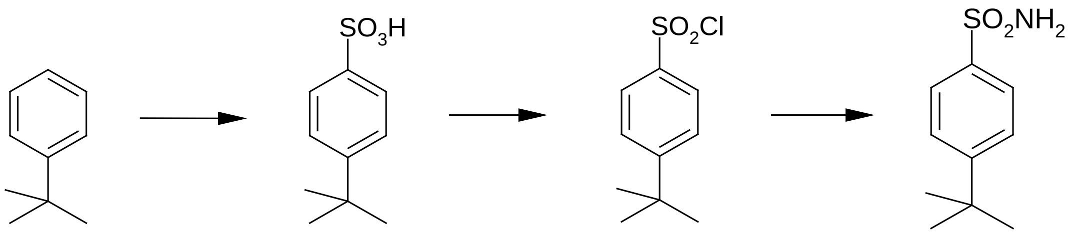
Sulfonamide: comparison of process efficiency



- No chlorinated nor other solvent necessary
- Sulfur dioxide comes out of the pipeline and is evaporated back into the Verbund system
- Different sulfonation technology: advantage of direct sulfonation with liquid sulfur trioxide
- Most efficient use of reagents (no loss of one molecule $ClSO_3H$ as sulfuric and hydrochloric acid)

	CH_3Cl / $ClSO_3H$	SO_2 / SO_3 / $SOCl_2$
Waste water	13 kg per kg product	5.9 kg per kg product
PMI	20.2	12.7
E-factor	19.2	11.7
Atom efficiency	44%	51%

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Conclusion

- Creation of waste in sulfonation reactions can be avoided using SO_3 as reagent
- Nearly no waste is formed using SO_3 in liquid SO_2 (E-factor almost zero)
- Sulfonations with SO_3 can be best controlled in continuous reactions (reactivity, exothermicity) or in liquid SO_2 (reactivity moderator) at low temperatures
- Sulfonations with SO_3 in SO_2 leads to better atom efficiency, lower PMI and lower E-factor values compared to other sulfonations (provided that the SO_2 is recycled)

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