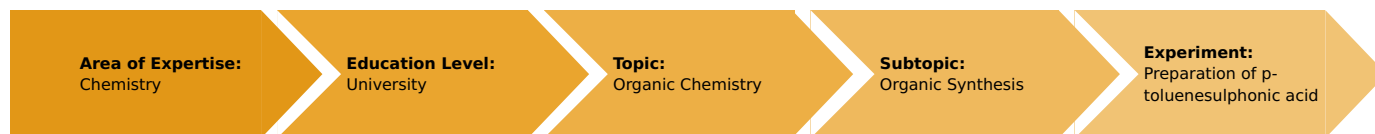


Preparation of p-toluenesulphonic acid (Item No.: P3101500)

Curricular Relevance



Difficulty



Intermediate

Preparation Time



1 Hour

Execution Time



1 Hour

Recommended Group Size



2 Students

Additional Requirements:

Experiment Variations:

Keywords:

Toluene, Sulphuric acid, Sulphonation, Electrophilic substitution, Aromatic compound, Azeotropic distillation

Task and equipment

Introduction

Principle

p-Toluenesulphonic acid and its salts are used as catalysts for reactions such as esterifications, dehydrations, and polymerisation reactions. They are more gentle reagents than sulphuric acid and, as powders, they can be dosed better. The sulphonation of toluene is an electrophilic substitution at the aromatic compound. The sulphonating reagents can be the free sulphur trioxide or the HSO_3^+ cation, which is present in the concentrated sulphuric acid in equilibrium. Unlike most other electrophilic substitutions, sulphonation is a reversible reaction. If water is present at higher temperatures, hydrolysis is mostly successful. In order to displace the equilibrium towards the desired product, the generated water must be bound or removed from the reaction mixture by way of azeotropic distillation.

Safety instructions



Toluene is a volatile, water-insoluble, highly flammable liquid. Its vapours are heavier than air but they can form explosive mixtures in combination with air. Toluene is harmful (low level of toxicity) and it has a strong irritating effect on the mucous membranes. A narcotic effect is possible.

First aid: Wash the affected skin areas with water and soap. Let splashes to the eyes evaporate with the lid gap wide open (blow carefully into the eyes). Then, rinse the eyes with water.

If inhaled: Fresh air.

Disposal: Collect flammable, halogen-free, organic solvents and solutions in a collecting vessel that is marked accordingly.

Concentrated acids are highly caustic. They burn the skin and destroy textile fabrics. For diluting, first add the water, then the acid (protective glasses, laboratory coat, gloves).

First aid: Rinse the affected skin areas and eyes with the lid gap wide open thoroughly with plenty of water.

Disposal: Solutions must be diluted with water, neutralised (pH 6-8), and flushed away.

Toluenesulphonic acid (sodium salt)

H315: Causes skin irritation.

H319: Causes serious eye irritation.

H335: May cause respiratory irritation.

P261: Avoid breathing dust/fumes/gas/mist/vapours/spray.

P280: Wear protective gloves/protective clothing/eye protection/face protection.

Sulphuric acid, 95-98%

H290: May be corrosive to metals.

H314: Causes severe skin burns and eye damage.

P280: Wear protective gloves/protective clothing/eye protection/face protection.

Toluene

H225: Highly flammable liquid and vapour.

H304: May be fatal if swallowed and enters airways.

H315: Causes skin irritation.

P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.

P331: Do NOT induce vomiting

Equipment

Position No.	Material	Order No.	Quantity
1	Support base DEMO	02007-55	1
2	Support rod, stainless steel, l = 600 mm, d = 10 mm	02037-00	2
3	Retort stand, h = 750 mm	37694-00	1
4	Right angle boss-head clamp	37697-00	3
5	Universal clamp	37715-00	3
6	Round bottom flask, 100ml, GL 25/12	35841-15	1
7	Water separator GL25/12	35790-15	1
8	Condenser, Dimroth type GL25/12	35815-15	1
9	Graduated cylinder 100 ml	36629-00	1
10	Beaker, high, BORO 3.3, 150 ml	46032-00	1
11	Beaker, high, BORO 3.3, 250 ml	46027-00	1
12	Buchner funnel, i.d. = 70, porcelain	32707-00	1
13	Circular filter, d 70 mm, 100 pcs	32977-02	1
14	Filter flask, 500ml, PN 34.5	34419-01	1
15	Rubber gaskets, conical, set of 8	39265-00	1
16	Water jet pump, plastic	02728-00	1
17	Porcelain dish, 75ml, d = 80 mm	32516-00	1
18	Funnel, glass, top dia. 55 mm	34457-00	1
19	Heating mantle f. roundbottom flask, 100 ml	49541-93	1
20	Clamp for heating mantle	49557-01	1
21	Power regulator	32288-93	1
22	Desiccator, vacuum, diam. 150 mm	34126-00	1
23	Porcelain plate f. desiccator 150mm	32474-00	1
24	Rubber tubing, i.d. 6 mm	39282-00	2
25	Rubber tubing, vacuum, i.d. 6mm	39286-00	1
26	Hose clip, diam. 8-16 mm, 1 pc.	40996-02	2
27	Glass rod, boro 3.3, l=300mm, d=7mm	40485-05	1
28	Wash bottle, plastic, 500 ml	33931-00	1
29	Spoon, special steel	33398-00	1
30	Crucible tongs, 200 mm, stainless steel	33600-00	1
31	Boiling beads, 200 g	36937-20	1
32	Silica gel, orange, granular, 500 g	30224-50	1
33	Silicon grease Molykote, 50 g	31863-05	1
34	Toluene 250 ml	30236-25	1
35	Sulphuric acid, 95-98% 500 ml	30219-50	1
36	Sodium chloride, 500 g	30155-50	1
37	Water, distilled 5 l	31246-81	1

Task

Prepare p-Toluenesulphonic acid from toluene and concentrated sulphuric acid.



Set-up and procedure



Set-up

The experiment is set up as per Fig. 1 and Fig 2.

Fill the 100 ml round bottom flask with 50 ml of toluene and 10 ml of concentrated sulphuric acid. Boil the reaction mixture for 15 minutes with a return flow at the water separator. Then, let it cool. In the meantime, prepare a saturated sodium chloride solution and pour it into the cool reaction mixture (if necessary, dilute it carefully beforehand with a little water). If the sodium salt of the p-toluenesulphonic acid does not crystallise immediately, prepare some initial crystallisation nuclei by rubbing with a glass rod. Filter the precipitated salt by suction and fill it into an evaporating dish. Dry it at 105°C to 110°C in a drying cabinet and let it cool in a desiccator.



Fig. 1

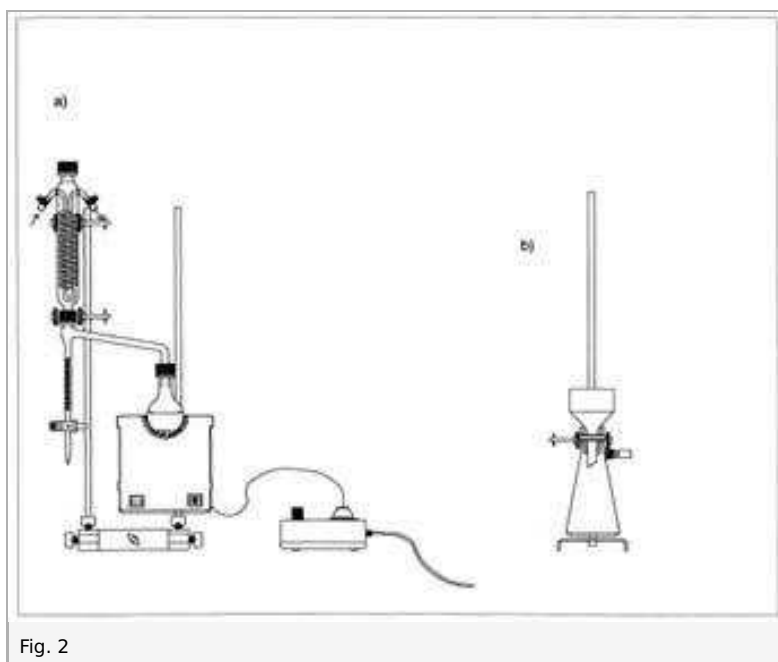


Fig. 2

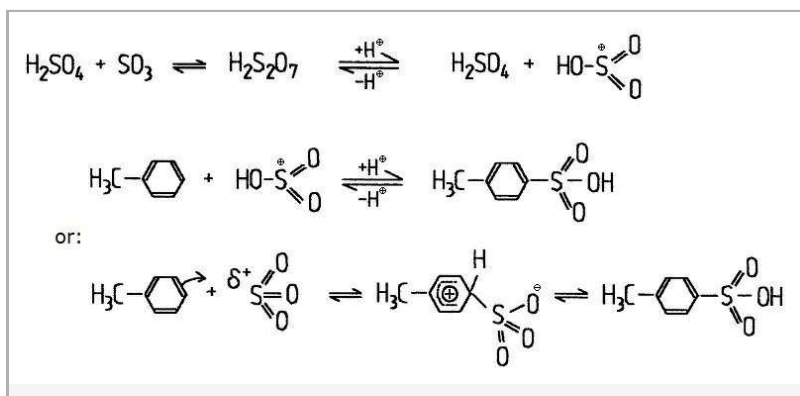
Results and evaluation

Results

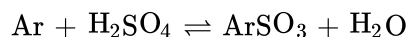
During boiling, the water is separated at the water separator. When the mixture cools, a thick paste may precipitate. This paste dissolves again when water is added carefully. From the saturated sodium chloride solution, which was poured into the product, p-toluenesulphonic acid sodium salt crystallises out in the form of white, glossy crystals.

Evaluation

The sulphonation of toluene is an electrophilic substitution at the aromatic compound. The sulphonating reagents can be the free sulphur trioxide or the HSO_3^+ cation, which is present in the concentrated sulphuric acid in equilibrium.



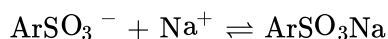
Unlike most other electrophilic substitutions, sulphonation is a reversible reaction. If water is present at higher temperatures, hydrolysis is mostly successful.



In order to displace the equilibrium towards the desired product, the generated water must be bound or removed from the reaction mixture by way of azeotropic distillation.

Pure p-toluenesulphonic acid is highly hygroscopic. The stoichiometric addition of water to the cool mixture or any water residues that are still present enable the targeted isolation of the p-toluenesulphonic acid monohydrate. Normally, however, the free sulphonic acid is not isolated. Instead, it is converted directly into sodium salt.

When the cool reaction mixture is added to a saturated sodium chloride solution, the sodium salt of the p-toluenesulphonic acid precipitates out. Arylsulphonic acids are strong acids. Their acidic strength can be compared to that of hydrochloric acid. This is why the acid is dissociated to a large extent. Due to the surplus of sodium ions in the saturated sodium chloride solution, the solution equilibrium is shifted to such an extent that sodium sulphonate precipitates out.



p-toluenesulphonic acid and its salts are used as catalysts for reactions such as esterifications, dehydrations, and polymerisation reactions. They are more gentle reagents than sulphuric acid and, as powders, they can be dosed better.

· p-toluenesulphonic acid:	
Molar mass:	172.20 g/mol
Melting point:	38 °C
· p-toluenesulphonic acid monohydrate:	
Molar mass:	190.22 g/mol
Melting range:	103-104 °C
Solubility in $\text{H}_2\text{O}/20\text{ °C}$:	670 g/l
· p-toluenesulphonic acid sodium salt:	
Molar mass:	194.19 g/mol