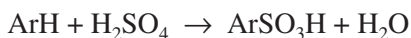


SULFONATION

Sulfonation is the introduction of a sulfonic acid group ($-\text{SO}_3\text{H}$) into an organic compound as, for example, in the production of an aromatic sulfonic acid from the corresponding aromatic hydrocarbon.



The usual sulfonating agent is concentrated sulfuric acid, but sulfur trioxide, chlorosulfonic acid, metallic sulfates, and sulfamic acid are also occasionally used. However, because of the nature and properties of sulfuric acid, it is desirable to use it for nucleophilic substitution wherever possible.

For each substance being sulfonated, there is a critical concentration of acid below which sulfonation ceases. The removal of the water formed in the reaction is therefore essential. The use of a very large excess of acid, while expensive, can maintain an essentially constant concentration as the reaction progresses. It is not easy to volatilize water from concentrated solutions of sulfuric acid, but azeotropic distillation can sometimes help.

The sulfonation reaction is exothermic, but not highly corrosive, so sulfonation can be conducted in steel, stainless-steel, or cast-iron sulfonators. A jacket heated with hot oil or steam can serve to heat the contents sufficiently to get the reaction started, then carry away the heat of reaction. A good agitator, a condenser, and a fume control system are usually also provided.

1- and 2-naphthalenesulfonic acids are formed simultaneously when naphthalene is sulfonated with concentrated sulfuric acid. The isomers must be separated if pure α - or β -naphthol are to be prepared from the product mix. Variations in time, temperature, sulfuric acid concentration, and acid/hydrocarbon ratio alter the yields to favor one particular isomer, but a pure single substance is never formed. Using similar acid/hydrocarbon ratios, sulfonation at 40°C yields 96% α isomer, 4% β , while at 160°C the proportions are 15% α -naphthol, 8.5% β -naphthol.

The α -sulfonic acid can be hydrolyzed to naphthalene by passing steam at 160°C into the sulfonation mass. The naphthalene so formed passes out with the steam and can be recovered. The pure β -sulfonic acid left behind can be hydrolyzed by caustic fusion to yield relatively pure β -naphthol.

In general, separations are based on some of the following consideration:

1. Variations in the *rate* of hydrolysis of two isomers
2. Variations in the solubility of various salts in water
3. Differences in solubility in solvents other than water
4. Differences in solubility accentuated by common-ion effect (salt additions)
5. Differences in properties of derivatives
6. Differences based on molecular size, such as using molecular sieves or absorption.

Sulfonation reactions may be carried out in batch reactors or in continuous reactors. Continuous sulfonation reactions are feasible only when the organic compounds possess certain chemical and physical properties, and are practical in only a relatively few industrial processes. Most commercial sulfonation reactions are batch operations.

Continuous operations are feasible and practical (1) where the organic compound (benzene or naphthalene) can be volatilized, (2) when reaction rates are high (as in the chlorosulfonation of paraffins and the sulfonation of alcohols), and (3) where production is large (as in the manufacture of detergents, such as alkylaryl sulfonates).

Water of reaction forms during most sulfonation reactions, and unless a method is devised to prevent excessive dilution because of water formed during the reaction, the rate of sulfonation will be reduced. In the interests of economy in sulfuric acid consumption, it is advantageous to remove or chemically combine this water of reaction. For example, the use of reduced pressure for removing the water of reaction has some technical advantages in the sulfonation of phenol and of benzene.

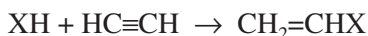
The use of the partial-pressure distillation is predicated upon the ability of the diluent, or an excess of volatile reactant, to remove the water of reaction as it is formed and, hence, to maintain a high concentration of sulfuric acid. If this concentration is maintained, the necessity for using excess sulfuric acid is eliminated, since its only function is to maintain the acid concentra-

tion above the desired value. Azeotropic removal of the water of reaction in the sulfonation of benzene can be achieved by using an excess of vaporized benzene.

The use of oleum ($\text{H}_2\text{SO}_4 \cdot \text{SO}_3$) for maintaining the necessary sulfur trioxide concentration of a sulfonation mixture is a practical procedure. Preferably the oleum and organic compound should be added gradually and concurrently to a large volume of cycle acid so as to take up the water as rapidly as it is formed by the reaction. Sulfur trioxide may be added intermittently to the sulfonation reactor to maintain the sulfur trioxide concentration above the value for the desired degree of sulfonation.

VINYLATION

Unlike ethynylation, in which acetylene adds across a carbonyl group and the triple bond is retained, in vinylation a labile hydrogen compound adds to acetylene, forming a double bond.



Catalytic vinylation has been applied to the manufacture of a wide range of alcohols, phenols, thiols, carboxylic acids, and certain amines and amides. Vinyl acetate is no longer prepared this way in many countries, although some minor vinyl esters such as vinyl stearate may still be manufactured by this route. However, the manufacture of vinyl-pyrrolidinone and vinyl ethers still depends on acetylene as the starting material.