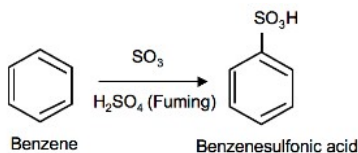


## 18.4: SULFONATION OF BENZENE (AN EAS REACTION)

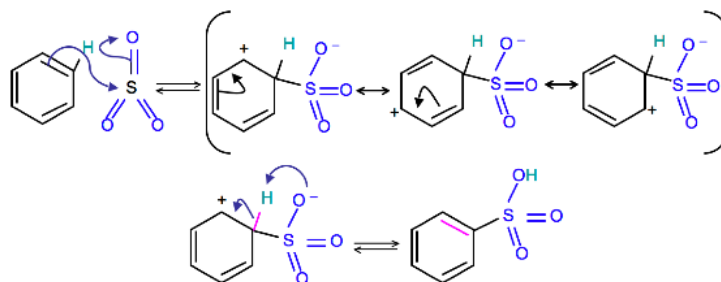
### SULFONATION OF BENZENE

Sulfonation is a reversible reaction that produces benzenesulfonic acid by adding sulfur trioxide and fuming sulfuric acid. It is important to note that the chemical formula of the sulfonic group is  $-\text{SO}_3\text{H}$ . The reaction is reversed by adding hot aqueous acid to benzenesulfonic acid to produce benzene.



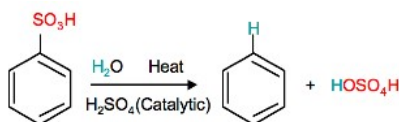
### MECHANISM

To produce benzenesulfonic acid from benzene, fuming sulfuric acid and sulfur trioxide are added. Fuming sulfuric acid, also referred to as *oleum*, is a concentrated solution of dissolved sulfur trioxide in sulfuric acid. The sulfur in sulfur trioxide is electrophilic because the oxygens pull electrons away from it because oxygen is very electronegative. The benzene reacts with the sulfur of sulfur trioxide to form the sigma complex. A subsequent proton transfer occurs to produce benzenesulfonic acid. All three steps are shown together in the mechanism below.

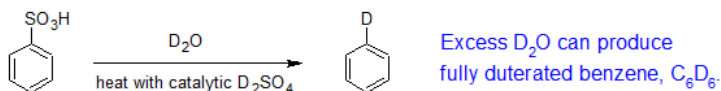


### REVERSE SULFONATION

Sulfonation of benzene is a reversible reaction. Sulfur trioxide readily reacts with water to produce sulfuric acid and heat. Therefore, by adding heat to benzenesulfonic acid in diluted aqueous sulfuric acid the reaction is reversed.

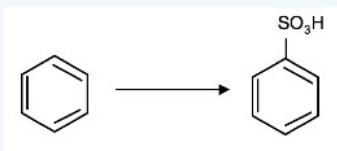


The reversibility of the sulfonation reaction creates an opportunity to prepare deuterated benzene. Isotopically labeled reagents can be useful in determining reaction mechanisms since the C-D bond is stronger than the C-H bond.

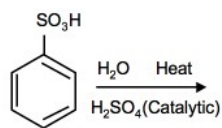


### Exercise

7. What is/are the required reagent(s) for the following reaction:



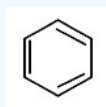
8. What is the product of the following reaction:



9. Why is it important that the nitration of benzene by nitric acid occurs in sulfuric acid?  
 10. Write a detailed mechanism for the sulfonation of benzene, including all resonance forms.

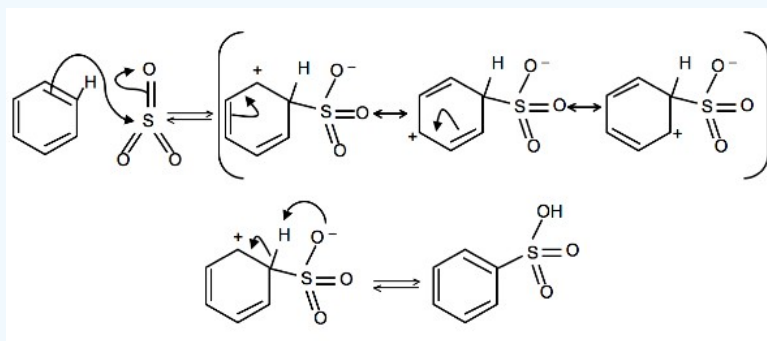
**Answer**

7.  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  (fuming)  
 8.



9. Sulfuric acid is needed in order for a good electrophile to form. Sulfuric acid protonates nitric acid to form the nitronium ion (water molecule is lost). The nitronium ion is a very good electrophile and is open to attack by benzene. Without sulfuric acid the reaction would not occur.

10.



## CONTRIBUTORS AND ATTRIBUTIONS

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- Prof. Steven Farmer ([Sonoma State University](#))
- William Reusch, Professor Emeritus ([Michigan State U.](#)), [Virtual Textbook of Organic Chemistry](#)
- Catherine Nguyen

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