

Notes on the reactions of Benzene

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1 Introduction

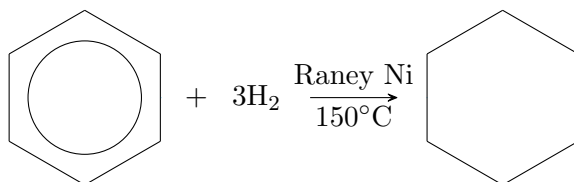
Benzene is an organic compound with the chemical formula C_6H_6 which has the structure of a ring. Each carbon atom is connected to two other carbon atoms and one hydrogen atom.

2 Theory

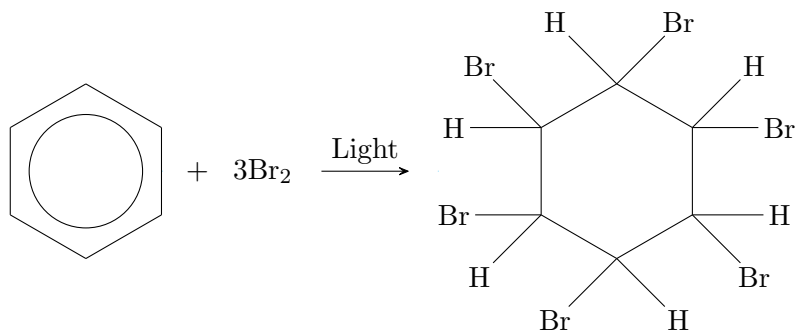
Benzene burns in oxygen or air to produce carbon dioxide and water:



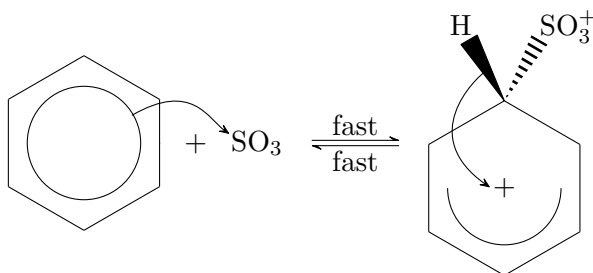
As you can see, there is a large amount of oxygen required to undergo this reaction. It is therefore important to note that in the combustion of benzene, it is likely that the oxygen supply is insufficient, often resulting in an incomplete combustion producing a yellow, smoky flame. When benzene is mixed with hydrogen in the presence of a Raney Nickel catalyst at a temperature of 150°C , it will undergo an addition reaction to form cyclohexane:



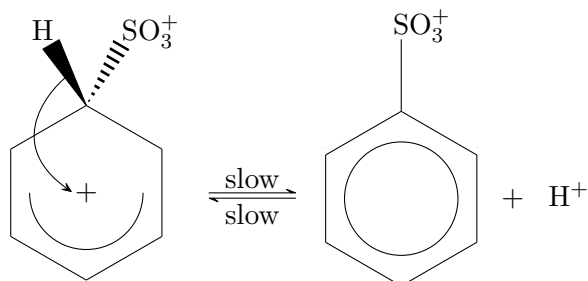
This is an important reaction for the production of nylon. Benzene undergoes addition reactions with bromine rapidly in the presence of ultraviolet light or bright sunlight to form 1,2,3,4,5,6 - hexabromocyclohexane:



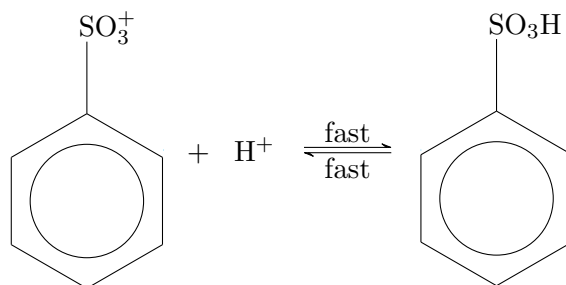
This is a free radical reaction and it bears all the hallmarks for a free radical reaction in that it requires light to overcome the activation energy and that it is a very rapid reaction. Fuming sulphuric acid reacts with benzene to produce benzenesulfonic acid, which is known as a sulfonation reaction and it takes place at room temperature and involves hazardous chemicals:



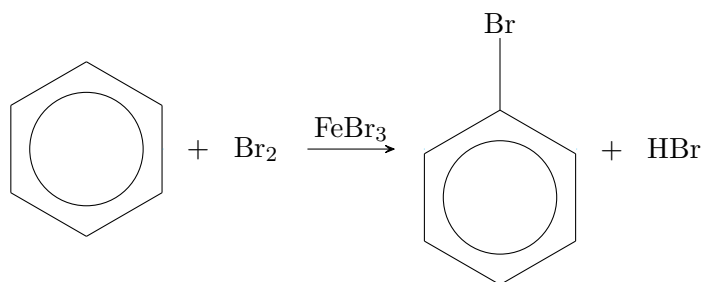
followed by:



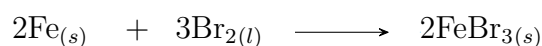
which is then followed by:



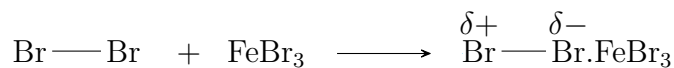
Benzene undergoes different reactions with halogens depending on the presence of light. In ultraviolet light, benzene undergoes a free radical addition reaction with halogens. In the absence of light, benzene undergoes an electrophilic substitution with halogens. This reaction does not occur unless there is a catalyst of iron (III) bromide or iron filings present. This catalyst is a halogen carrier, and the benzene, the halogen, and the halogen carrier are refluxed together to produce a halogeno-benzene:



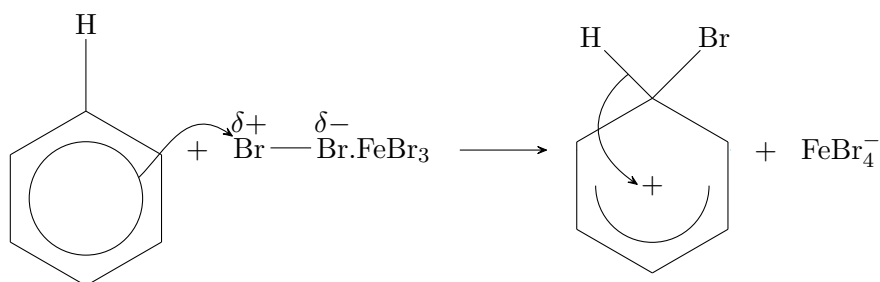
Iron filings can be used instead of iron (III) bromide since iron reacts with some of the bromine present to form iron (III) bromide:



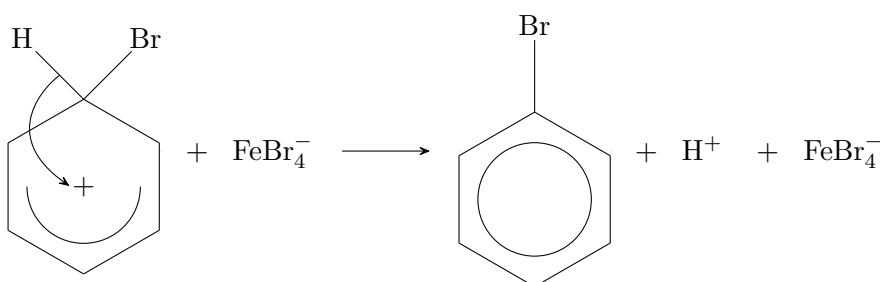
The iron (III) bromide polarises the bromine molecule, forming a complex:



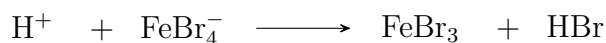
which acts as an electrophile, forming first a weak π complex, and then the more stable σ complex:



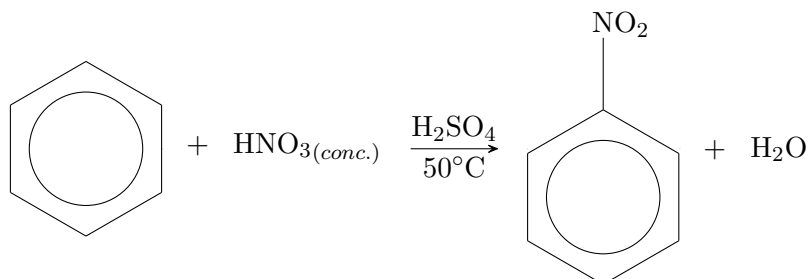
followed by the second step:



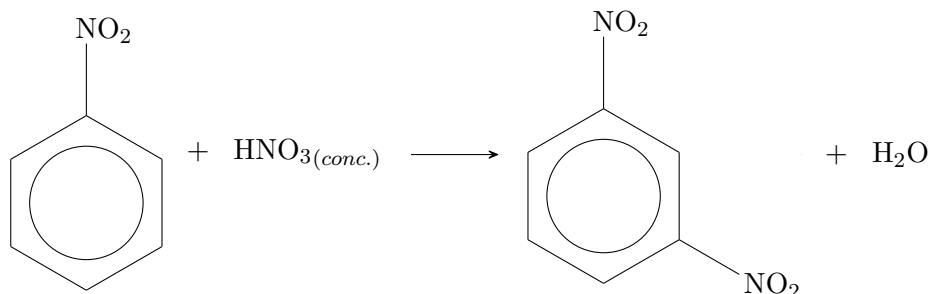
A proton is then lost and this reacts to regenerate the iron (III) bromide, forming HBr:



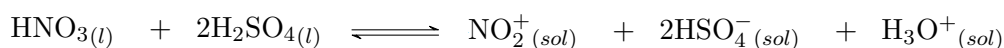
which shows that FeBr_3 is a catalyst. Benzene can react with something called a nitrating mixture, a mixture of concentrated nitric and concentrated sulfuric acid. In this reaction the product is nitrobenzene if the temperature is below 55°C :



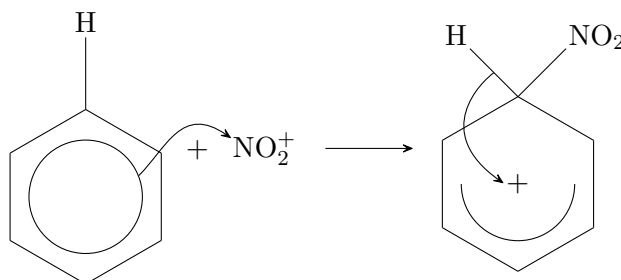
if the temperature is higher than 55°C, multiple substitution occurs and 1,3 - dinitrobenzene is formed, resulting in a mixture of products:



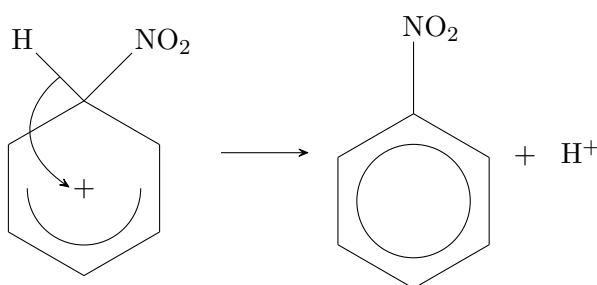
The first step of nitration involves the production of the NO_2^+ (nitronium) cation in the reaction of concentrated nitric acid and concentrated sulfuric acid:



The nitronium ion reacts with benzene like so:

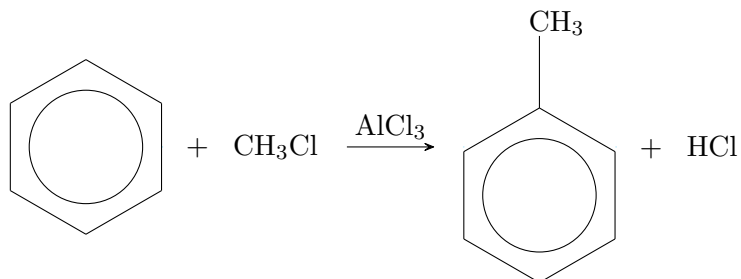


followed by:

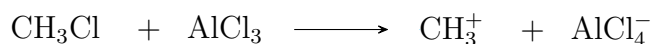


A round bottom reaction flask with the nitrating mixture is held in a beaker of cold water. The reaction flask has a tap funnel containing benzene. The benzene is added drop-by-drop to the mixture in the flask. The acids react with each other and then give out heat, as does the addition of benzene to the nitrating mixture, which is why the cold water and slow addition are needed.

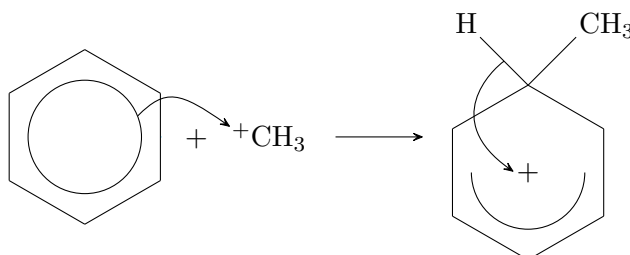
Refluxing benzene with a halogenoalkane in the presence of a halogen carrier catalyst, such as aluminium chloride provides a means of substituting an alkyl group in a benzene ring (known as alkylation):



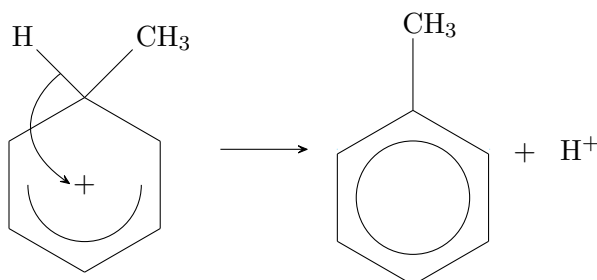
The halogen carrier polarises the halogenoalkane, forming an electrophilic alkyl cation. The cation is attracted to the benzene ring, forming a π complex, followed by a σ complex, which then breaks down to form the alkylbenzene product:



then the cation reacts with the benzene like so:



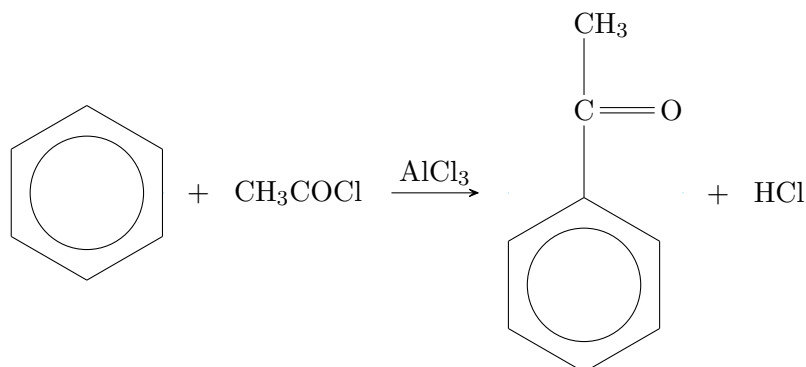
which is then followed by:



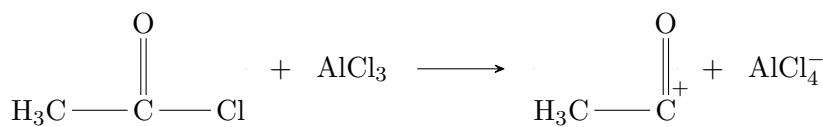
and the catalyst is reproduced in the end like so:



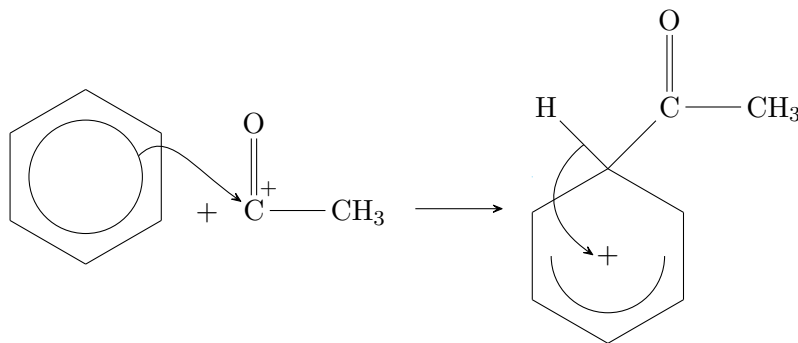
A similar reaction takes place when benzene is refluxed with an acyl chloride (known as acylation), where the product is a ketone:



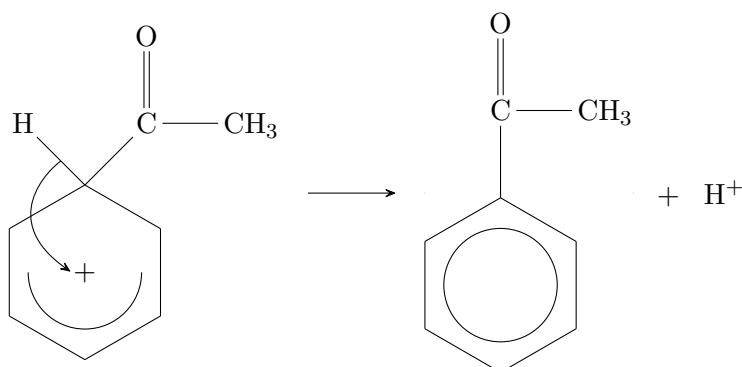
The product of this reaction is quite useful as it can be easily reduced to form a secondary alcohol, meaning it is used as an intermediate in the synthesis of organic chemicals. The mechanism of the reaction is very similar to that for alkylation. First, an electrophilic cation is produced from the acyl chloride:



Then the cation reacts with the benzene like so:



and then followed by:



and the catalyst is reproduced in the end like so:



The acylation and alkylation reactions shown are known as Friedel-Crafts reactions. Friedel-Crafts reactions are sometimes used in the synthesis of cross-linked polymers.

In all of these reactions, the substituted groups affect the electron density of the benzene ring. This affects the chemistry of the molecule. A substituent on the ring affects the rate of reaction on benzene for further substitutions.

For functional groups that donate electron density to the benzene ring, electrophilic substitution reactions will only get faster with further substitutions.

For functional groups that withdraw electron density from the benzene ring, electrophilic substitutions will only get slower with further substitutions if they were to occur in the first place.