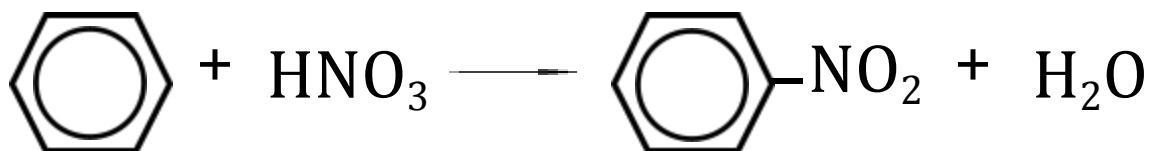


Substitution Reactions

Substitution reactions are organic and inorganic reactions involving the replacement of a functional group in a hydrocarbon by another compound. Being a replacement reaction, the substitution reaction takes in and outputs two reactants and products. Often hydrogen is the functional group replaced. Most endothermic substitution reactions give way to products with higher enthalpy than reactants. Given their predictable nature, substitution reactions can be used in a broad variety of applications such as production of phenol and hydrochloric acid. These and other characteristics make the substitution reaction an essential key to understanding chemistry.

Substitution reactions are reactions involving the replacement of a functional group in a compound by another functional group. Often hydrogen is the group being replaced and negatively charged ions serve as the replacement. When a halogen replaces the functional group, it is referred to as halogenation. These sort of reactions are common when diatomic halogen gas dissolves into aromatic alkene solutions. When the same compounds are nonaromatic, addition reactions are more likely to occur. For example

$C_6H_6(\text{aromatic}) + Cl_2 \xrightarrow{FeCl_3} C_6H_5Cl + HCl$ is more likely to occur with aromatic compounds while $H_2C = CH_2 + Cl_2 \xrightarrow{FeCl_3} H_2ClCH_2CH_2Cl$ is more probable with aliphatic hydrocarbons.



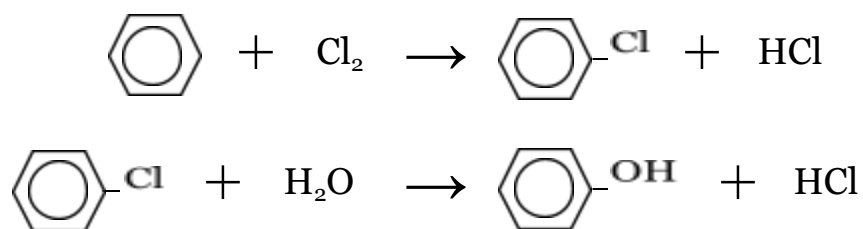
Benzene plus Nitric acid yields Nitrobenzene plus Water

Substitution reactions are a subset of single replacement reactions. However, they apply to *functional groups* being replaced usually in organic compounds, while single replacement deals with generic ions. For example: $2NaCl + F_2 \rightarrow 2NaF + Cl_2$ is a single replacement reaction. $C_6H_6 + C_2H_5Cl \rightarrow C_6H_5C_2H_5 + HCl$ is also a single replacement reaction, but in addition, it is a substitution reaction due to the replacement of functional group hydrogen with ethyl. Another marked distinction in substitution reactions is that the functional group being replacing the previous one does not have to have the same charge as the previous. Phenol, for instance has a 1- charge on its functional group, yet a 1+ charge was borne by the hydrogen that once stood in the hydroxide's place. This is made evident in reaction 1 where nitrite has a 1- charge while hydrogen has a 1+ charge. Single replacement reactions, in general however, only replace ions of the same charge.

Substitution reactions effect many aspects of the reactant hydrocarbon. This includes polarity, molecular size, and solubility. Since most aromatic hydrocarbons primarily consist of hydrogen on their outer ring, addition of a non-hydrogen functional group alters the shape of the molecule. It is no longer symmetrical. The imbalance of charge may create a dipole moment that effects other characteristics of the molecule. The more polar a molecule is, the better it dissolves in polar solvents such as water. Also, any unpaired electrons on the functional group, if all facing one direction can create a net magnetic moment. When under a magnetic field, the functional groups of all the hydrocarbons will line up parallel to the flux lines. If the

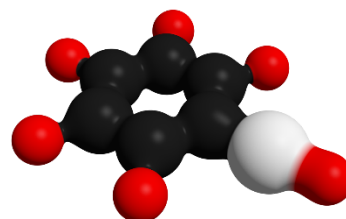
functional group ends with nitrogen, oxygen, or fluorine, as opposed to other non-hydrogen atoms, hydrogen bonding takes over and the boiling point of the hydrocarbon is rapidly raised.

The substitution reaction is seen in many organic applications. Acetone, phenol, and a broad variety of molecules are industrially produced using substitution reactions. The following reaction details production of phenol from diatomic chlorine and water:



Reaction 1: Production of phenol

Substitution reactions alter the physical and chemical properties of their reactants in several ways. Considering the example above, benzene contains only hydrogen functional groups while phenol has hydroxides. As a result of asymmetrical functional groups, phenol has a dipole moment. This dramatically lowers its vapor pressure compared to benzene while raising its heat of vaporization, the energy required to break the hydrogen bonds. Also, while dispersion forces do hold benzene together reasonably well as a liquid, hydrogen bond creates a tighter, more ordered, lower entropy liquid. This means that benzene is less dense than phenol. A colored ball model of phenol is pictured to the right.



Substitution reactions serve a broad variety of applications in organic chemistry. They replace functional groups in hydrocarbons and thus enlist themselves to the production of phenol, acetone, and many more compounds. Future technology may one day implement

substitution reactions in the manufacture of highly compact data storage units. A long alkane chain with either hydroxide or hydrogen functional groups can store bits in a manner even more compact than D.N.A. and much compactor than modern day MOS-Phet transistors. And regardless of whatever future technology quantum advancements may bring, organic creation will always be indebted to substitution reactions to function.

References

Brown, T. L., LeMay, H. E., Bursten, B. E., Murphy, C. J., & Woodward, P. M. (2012). p.1017, 1018, 1020, 1021. *Chemistry The Central Science*. Prentice Hall.

Organic Chemistry Portal. (n.d.). Nucleophilic Substitution (SN1SN2). Retrieved May 10, 2017, from <http://www.organic-chemistry.org/namedreactions/nucleophilic-substitution-sn1-sn2.shtm>.

Reichle, W. (1970). The nature of the hydrolysis of chlorobenzene over calcium phosphate apatite [Abstract]. *Journal of Catalysis*, 17(3), 297-305.
doi:10.1016/0021-9517(70)90104-1.