HALOGENATION

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I. INTRODUCTION

Halogenation may be defined as the process whereby one or more halogen atoms are introduced into an organic compound.

The preparation of organic compounds containing fluorine, chlorine, bromine, and iodine can be accomplished by a variety of methods. The conditions and procedures differ, not only for each member of the halogen family but also with the type and structure of the compound undergoing treatment.

The chlorine derivatives, because of the greater economy in effecting their preparation, are by far the most important of the technical halogen compounds and for this reason are given primary consideration. The bromine derivative, however, sometimes has certain advantages because of the greater ease in effecting the replacement of this halogen in subsequent reactions or because it possesses certain pharmaceutical or dyeing properties.

The fluorine derivatives are well established in the fields of refrigerants and aerosol propellants because of their stability and low boiling points.

As may be observed from the following examples, halogenations may involve reactions of (1) addition, (2) substitution, i.e., of hydrogen, (3) replacement, i.e., of groups, for example, the hydroxyl or sulfonic acid group.

$$HC{\equiv}CH + 2Cl_2 \xrightarrow{FeCl_3} Cl_2HC{-}CHCl_2 \qquad (1a)$$

$$C_6H_6 + 3Cl_2 \xrightarrow{h\nu} C_6H_6Cl_6 \qquad (1b)$$

$$CH_3COOH + Cl_2 \xrightarrow{PCl_3} CH_2ClCOOH + HCl \qquad (2)$$

$$C_2H_5OH + HCl \xrightarrow{ZnCl_2} C_2H_5Cl + H_2O \qquad (3)$$

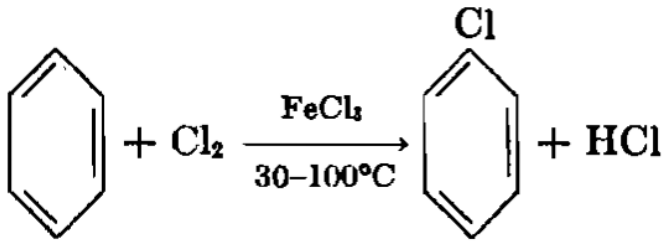
From the preceding formulations, it becomes clear that each type of reaction may involve not only a specific halogenating agent but also a suitable catalyst or activator. Many of the catalysts are halogen carriers. Iron, antimony, and phosphorus, which are able to exist in two valencies as halogen compounds, are used as they are less stable at the higher valence and give up part of their halogen during the process. In the presence of free halogen, such compounds alternately add on and give up halogen to carry on the reaction. Iodine, bromine, and chlorine which are capable of forming mixed halogens are also frequently employed as catalysts in halogenation processes. Active carbon, clays, and other compounds also serve to catalyze halogenation processes. Where the halogen is energized to an activated state by means of light, heat, nuclear energy, or free radicals, it may then proceed to react by addition as in reaction (1*b*) or by substitution without the need of a catalyst.

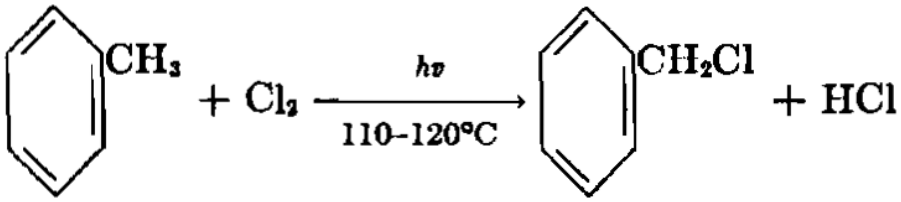
Chlorination. A number of methods are available for organizing the material relating to halogenation processes, all of which are necessarily complex. Here, as in other chapters, the principal classification is based on the (halogenating) agents employed. The most important methods for preparing chlorine compounds are the following:

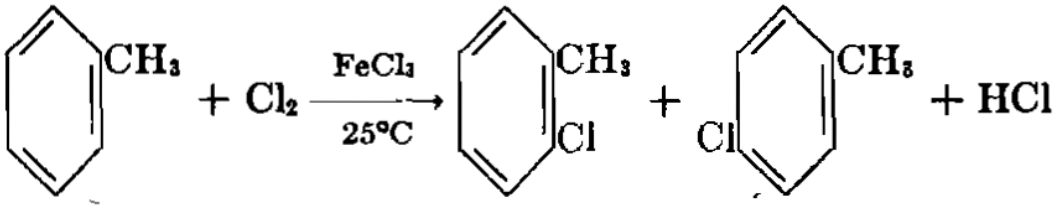
Direct Action of Chlorine Gas:

$$H_2C{=}CH_2 + Cl_2 \xrightarrow{FeCl_3} ClH_2CCH_2Cl$$

$$CH_4 + Cl_2 \xrightarrow{400\text{–}500°C} CH_3Cl + CH_2Cl_2 + HCl$$







Hydrochloric Acid as the Chlorinating Agent:

Addition reaction, direct action:

$$HC{\equiv}CH + HCl \xrightarrow{HgCl_2} H_2C{=}CHCl$$

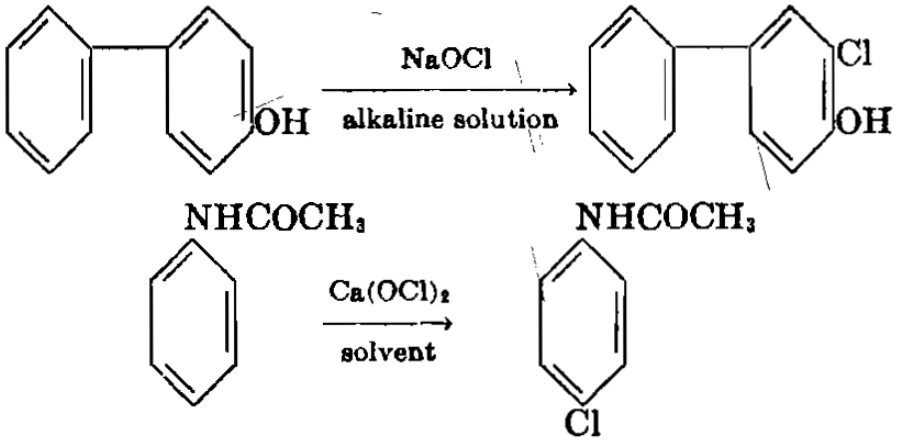
Substitution reactions, indirect action:

$$2C_6H_6 + 2HCl + O_2 \xrightarrow{CuCl_2 \text{ on } Al_2O_3} 2C_6H_5Cl + 2H_2O$$

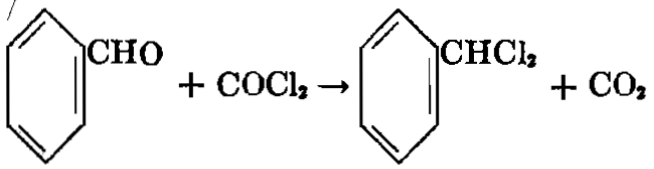
Replacement reactions:

$$C_2H_5OH + HCl \xrightarrow{ZnCl_2} C_2H_5Cl + H_2O$$

Sodium Hypochlorite as Chlorinating Agent:



Chlorination with Phosgene ($COCl_2$) *and Benzotrichloride* ($C_6H_5CCl_3$):



$$CH_3COOH + C_6H_5CCl_3 \rightarrow CH_3COCl + C_6H_5COCl + HCl$$

Chlorination with Sulfuryl Chloride (SO_2Cl_2):