The functional group of alkyl halides is a carbon-halogen bond, the common halogens being fluorine, chlorine, bromine and iodine. With the exception of iodine, these halogens have electronegativities significantly greater than carbon. Consequently, this functional group is polarized so that the carbon is electrophilic and the halogen is nucleophilic, as shown in the drawing below.

Two characteristics other than electronegativity also have an important influence on the chemical behavior of these compounds. The first of these is covalent bond strength. The strongest of the carbon-halogen covalent bonds is that to fluorine. Remarkably, this is the strongest common single bond to carbon, being roughly 30 kcal/mole stronger than a carbon-carbon bond and about 15 kcal/mole stronger than a carbon-hydrogen bond. Because of this, alkyl fluorides and fluorocarbons in general are chemically and thermodynamically quite stable, and do not share any of the reactivity patterns shown by the other alkyl halides. The carbon-chlorine covalent bond is slightly weaker than a carbon-carbon bond, and the bonds to the other halogens are weaker still, the bond to iodine being about 33% weaker. The second factor to be considered is the relative stability of the corresponding halide anions, which is likely the form in which these electronegative atoms will be replaced. This stability may be estimated from the relative acidities of the H-X acids, assuming that the strongest acid releases the most stable conjugate base (halide anion). With the exception of HF ($pK_a = 3.2$), all the hydrohalic acids are very strong, small differences being in the direction $\text{HCl} < \text{HBr} < \text{HI}$.

The characteristics noted above lead us to anticipate certain types of reactions that are likely to occur with alkyl halides. The following table summarizes the expected outcome of alkyl halide reactions with nucleophiles. It is assumed that the alkyl halides have one or more beta-hydrogens, making elimination possible; and that low dielectric solvents (e.g. acetone, ethanol, tetrahydrofuran & ethyl acetate) are used. When a high dielectric solvent would significantly influence the reaction this is noted in red.

**Note that halogens bonded to sp$^2$ or sp hybridized carbon atoms do not normally undergo substitution or elimination reactions with nucleophilic reagents.**

<table>
<thead>
<tr>
<th>Nucleophile</th>
<th>Ionic Nucleophiles</th>
<th>Anionic Nucleophiles</th>
<th>Neutral Nucleophiles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( Weak Bases: I$^-$, Br$^-$, SCN$^-$, N$_3^-$, CH$_3$CO$_2^-$, RS$^-$, CN$^-$ etc. )</td>
<td>$pK_a$'s &gt; 15</td>
<td>( H$_2$O, ROH, RSH, R$_3$N )</td>
</tr>
<tr>
<td>Alkyl Group</td>
<td>$pK_a$'s from -9 to 10 (left to right)</td>
<td>$pK_a$'s ranging from -2 to 11</td>
<td></td>
</tr>
</tbody>
</table>
### Primary RCH₂–

Rapid $S_N2$ substitution. The rate may be reduced by substitution of β-carbons, as in the case of neopentyl.

Rapid $S_N2$ substitution. $E2$ elimination may also occur. e.g. 

\[
CICH_2CH_2Cl + KOH \rightarrow CH_2=CHCl
\]

$S_N2$ substitution. ($N \approx S >> O$)

### Secondary RCH₂–

$S_N2$ substitution and / or $E2$ elimination (depending on the basicity of the nucleophile). Bases weaker than acetate ($pK_a = 4.8$) give less elimination. The rate of substitution may be reduced by branching at the β-carbons, and this will increase elimination.

$E2$ elimination will dominate.

### Tertiary R₃C–

$E2$ elimination will dominate with most nucleophiles (even if they are weak bases). No $S_N2$ substitution due to steric hindrance. In high dielectric ionizing solvents, such as water, dimethyl sulfoxide & acetonitrile, $S_N1$ and $E1$ products may be expected.

$E2$ elimination will dominate. No $S_N2$ substitution will occur. In high dielectric ionizing solvents $S_N1$ and $E1$ products may be formed.

Nitrogen and sulfur nucleophiles will give $S_N2$ substitution in the case of 1º and 2º-halides. 3º-halides will probably give $E2$ elimination with nitrogen nucleophiles (they are bases). In high dielectric ionizing solvents $S_N1$ and $E1$ products may be formed. Water hydrolysis will be favorable for 2º & 3º-halides.

### Allyl

Rapid $S_N2$ substitution for 1º and 2º-halides. For 3º-halides a very slow $S_N2$ substitution or, if the nucleophile is moderately basic, $E2$ elimination. In high dielectric ionizing solvents, such as water, dimethyl sulfoxide & acetonitrile, $S_N1$ and $E1$ products may be observed.

Rapid $S_N2$ substitution for 1º halides. $E2$ elimination will compete with substitution in 2º-halides, and dominate in the case of 3º-halides. In high dielectric ionizing solvents $S_N1$ and $E1$ products may be formed.

Nitrogen and sulfur nucleophiles will give $S_N2$ substitution in the case of 1º and 2º-halides. 3º-halides will probably give $E2$ elimination with nitrogen nucleophiles (they are bases). In high dielectric ionizing solvents $S_N1$ and $E1$ products may be formed. Water hydrolysis will be favorable for 2º & 3º-halides.

### Benzyl

Rapid $S_N2$ substitution for 1º and 2º-halides. For 3º-halides a very slow $S_N2$ substitution or, if the nucleophile is moderately basic, $E2$ elimination. In high dielectric ionizing solvents, such as water, dimethyl sulfoxide & acetonitrile, $S_N1$ and $E1$ products may be observed.

Rapid $S_N2$ substitution for 1º halides (note there are no β hydrogens). $E2$ elimination will compete with substitution in 2º-halides, and dominate in the case of 3º-halides. In high dielectric ionizing solvents $S_N1$ and $E1$ products may be formed.

Nitrogen and sulfur nucleophiles will give $S_N2$ substitution in the case of 1º and 2º-halides. 3º-halides will probably give $E2$ elimination with nitrogen nucleophiles (they are bases). In high dielectric ionizing solvents $S_N1$ and $E1$ products may be formed. Water hydrolysis will be favorable for 2º & 3º-halides.

### Contributors