Alcohols (R-OH) and Alkyl halides R-X (X = F, Cl, Br, I)

Alcohols

Alcohols contain a R-OH functional group.

Primary, secondary or tertiary?

<table>
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<th>OH</th>
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Nomenclature:

Suffix:

numbering scheme:

The number locating it is placed in front of the root name.

Other functional groups present the # for the -OH is placed before the –ol.

Prefix:

With higher priority functional groups use:

Number the longest chain of carbons using higher priority functional group
### Naming examples:

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Line Drawing</th>
<th>1° 2° 3°</th>
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<th>Line Drawing</th>
<th>1° 2° 3°</th>
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</table>
**Physical Properties:**  
- The H atom attached to the O  
- Volatility:
  - Melting points:
  - Boiling points:
  - Aqueous solubility:

**Reactivity:**  
Alcohols as bases or nucleophiles

**Nucleophiles** are electron rich species that react with electron poor ones.  
Alcohol oxygen atoms are ________ bases.

The C-OH is difficult to break, it needs to be assisted  
Alcohols are very weakly acidic  

\[
\begin{align*}
\text{Br} & \quad \text{H} & + & \quad \overset{\text{O}}{\text{H}} & \quad \overset{\text{H}}{\text{H}} & \quad \rightarrow & \quad \overset{\text{Br}}{\text{H}} & \quad + & \quad \overset{\text{O}}{\text{H}} & \quad \overset{\text{H}}{\text{H}} \\
\end{align*}
\]

Alcohols react with Na (or K) →  

\[
\begin{align*}
\text{H}_2\text{O}: & \quad \rightarrow \\
\text{ROH}: & \quad \rightarrow \\
\end{align*}
\]

Alkoxide:

Alkoxides are important bases in organic chemistry.  
Replace the H with another R' group →

Reaction with a carboxylic acid →

Reaction with hydrogen halides →
Alkyl halides

Nomenclature:
Functional group suffix =
Functional group prefix =

Primary, secondary or tertiary?

<table>
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<th>CH$_3$Cl</th>
<th>Br</th>
<th>Br</th>
<th>Br</th>
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</thead>
</table>

Physical Properties:
The carbon halogen bonds are typically quite polar

Volatile:
Melting points:
Boiling points:
Aqueous solubility:

Reactivity:
Polarity makes the C atom electrophilic.
The halogens (Cl, Br and I) are good leaving groups.

\[
\text{Nu} + \text{CR}_3-X \rightarrow \text{CR}_3-\text{Nu} + \text{X}
\]

Bases can remove β-hydrogens and cause 1,2-elimination

\[
\text{NaOR} 
\]

Insertion of a metal (esp. Mg) creates an organometallic species.

\[
\text{M}^+ + \text{CR}_3-X \rightarrow \text{CR}_3-\text{MX}^+
\]
Carbocations

Structure:

\[
\begin{array}{c}
\text{R} \\
\text{R} \\
\text{R} \\
\text{C} \\
\end{array}
\]

Stability:

Order of simple alkyl carbocations is:

\[
\begin{array}{cccc}
\text{CH}_3 & \text{C} & \text{C} & \text{C} \\
\text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{H} \\
\text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{H} \\
\text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{H} \\
\end{array}
\]

Alkyl groups are weakly electron donating

a) Inductive effects.

\[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_2 \\
\text{CH} \\
\end{array}
\]

b) Hyperconjugation

c) Resonance effects
Reactivity:
Act as electrophiles

Loss of $H^+$ can generate a $\pi$ bond.

Rearrangements: generates a more stable carbocation
a) 1,2-hyride shifts
b) 1,2-alkyl shifts

Reactions involving carbocations:
a) Substitutions via $S_N 1$
b) Eliminations via $E1$
c) Additions to alkenes and alkynes ($HX, H_3O^+$)

Mechanism:
This pathway is a multi-step process with the following characteristics:

Step 1:

Step 2:
Multi-step reactions have intermediates (I) and several transition states (TS).

SM = starting material
$TS_1$ = Transition State 1
I = Intermediate
$TS_2$ = Transition State 2
P = Products
Free Radicals

\[
\text{Br} - \text{Br} \quad \rightarrow \quad \text{BrH} + \text{BrH}
\]

Stability:

Order:

\[
\begin{align*}
\text{CH}_3 - \text{CH}_3 & \quad \text{CH}_3 - \text{H} \\
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{H}
\end{align*}
\]

Alkyl groups are weakly electron donating:

a)

b)

c)

Structure:
Reactivity:

Free radicals act as electrophiles:

Alternatively, loss of H⁻ can generate a pi bond

Rearrangements: Free radicals rarely rearrange

Radical Substitution:

\[ \text{X} - \text{X} + \text{C} \rightarrow \text{X} - \text{X} - \text{C} + \]

Substitution of R-H by \(-\text{X}\):

Alkane R-H relative reactivity order:

Halogen reactivity:

Mechanism:
Radical Chain Mechanism

Three distinct type of steps:

**Step 1 (Initiation)**

\[
\text{Br} + \text{Br} \rightarrow \text{Br} + \text{Br}
\]

**Step 2 (Propagation)**

(a) A halogen radical removes hydrogen atom

(b) The alkyl radical removes bromine atom from another \(\text{Br}_2\)

\[
\text{Br} + \text{H} - \text{CH}_3 \rightarrow \text{H} - \text{Br} + \text{CH}_3
\]

\[
\text{Br} + \text{CH}_3 \rightarrow \text{Br} + \text{Br} - \text{CH}_3
\]

**Step 3 (Termination):** Reactions between pairs of radicals,

\[
\text{CH}_3 + \text{CH}_3 \rightarrow \text{CH}_3 - \text{CH}_3
\]

\[
\text{Br} + \text{Br} \rightarrow \text{Br} - \text{Br}
\]

\[
\text{Br} + \text{CH}_3 \rightarrow \text{Br} - \text{CH}_3
\]
Selectivity

Selectivity of radical halogenations of alkanes is based on two factors:

1) Reactivity of the alkyl (R-H) system
   The bond strength of the R-H depends on H as 1°, 2° or 3°.
   \[ R-H \rightarrow R\cdot + H\cdot \]

   Bond dissociation energies for methyl 1°, 2° or 3° hydrogens

<table>
<thead>
<tr>
<th>Type</th>
<th>R-H</th>
<th>kJ/mol</th>
<th>kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>CH₃-H</td>
<td>435</td>
<td>104</td>
</tr>
<tr>
<td>1</td>
<td>CH₃CH₂-H</td>
<td>410</td>
<td>98</td>
</tr>
<tr>
<td>2</td>
<td>(CH₃)₂CH-H</td>
<td>397</td>
<td>95</td>
</tr>
<tr>
<td>3</td>
<td>(CH₃)₃C-H</td>
<td>380</td>
<td>91</td>
</tr>
</tbody>
</table>

2) Reactivity of the halogen (X•)
   \[ F\cdot \quad Cl\cdot \quad Br\cdot \quad I\cdot \]

   Reactivity determines selectivity:
   _______ reactive radicals are more selective

Selectivity of the radical reactions can be calculated using
   a) A reactivity factor, \( R_i \),
   b) A statistical factor, \( nH_i \).
How to calculate the ratio of products;

**Step 1:** What are the possible monosubstituted products?

**Step 2:** How many hydrogens that yield the same product? \( (nH_i) \)

**Step 3:** What is the reactivity \( (R_i) \) for the hydrogen and halogen type?

**Step 4:** Using the reactivity factors, what are the total possible structures?

**Step 5:** What is the percent of each hydrogen type per total hydrogens?

<table>
<thead>
<tr>
<th>( % P_i = \frac{100 \cdot nH_i \cdot R_i}{\sum_i nH_i \cdot R_i} )</th>
<th>( % P_i )</th>
<th>% yield of product &quot;i&quot;</th>
<th>( R_i ) at 25 °C</th>
<th>Br</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>( nH_i )</td>
<td>number of H of type &quot;i&quot;</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( R_i )</td>
<td>type &quot;i&quot; reactivity factor</td>
<td>2</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \sum_i )</td>
<td>sum for all types</td>
<td>3</td>
<td>3</td>
<td></td>
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</tr>
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</table>

What does the reactivity factors indicate?
You try: the chlorination of propane: \( \text{CH}_3\text{CH}_2\text{CH}_3 \)

**Step 1:**

**Step 2:**

**Step 3:**

**Step 4:**

**Step 5:**

What about bromination of propane?

Conclusions from this data:
Radical Halogenation of Alkanes

\[ \text{X--X} + \text{C} \rightarrow \text{C} + \text{C} \]

Reaction type:
Products:
Alkane R-H relative reactivity order :
Halogen reactivity:

Selectivity: Bromination
Chlorination

Mechanism:
More highly brominated by-products are possible if methyl bromide reacts with a bromine radical in the same fashion as methane does.

Draw the cycle that leads to the formation of dibromomethane.
Try this: Radical Halogenation
1. Calculate the predicted yields for all of the monohalogenated products produced by chlorination and bromination of butane.

For chlorination:

Bromination:
How to identify the original compound from the product ratios.

**Step 1:** What are the possible starting materials (isomers)?

**Step 2:** Which ones give the correct number of products?

**Step 3:** Calculate which has the correct ratios.

**Try this:** On radical chlorination, an isomer of hexane gave a mixture of monochlorides in the ratio 46: 39: 15. Identify the isomer.

**Step 1:**

**Step 2:**

**Step 3:**

1) 

2) 

**Answer:**