1. (15 points). Please give the ratio of OH addition to H-Abstraction for each of the following compounds. Your are to normalize to 1 for the slowest component.

<table>
<thead>
<tr>
<th>Calculation</th>
<th>H-Abstraction: Addition</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Chemical Structure" /></td>
<td>$k_{abs} = 1.36 \times 10^{-13} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td><img src="image" alt="Chemical Structure" /></td>
<td>$k_{abs} = k_{prim} F(C_j) F(C_j)$</td>
</tr>
<tr>
<td><img src="image" alt="Chemical Structure" /></td>
<td>$k_{abs} = k_{prim} F(C_j) \times 2 + k_{tert} F(C_j) F(C_j)$</td>
</tr>
<tr>
<td><img src="image" alt="Chemical Structure" /></td>
<td>$k_{abs} = k_{tert} F(C_j) F(F) F(F) + k_{prim} F(OR)$</td>
</tr>
</tbody>
</table>
2. (15 points). Please give the atmospheric lifetime (in days) with respect to OH reaction for each compound below and use \(1 \times 10^6\) molecule/cm\(^3\) as your OH concentration.

\[
\text{Calculation}
\]

\[
\begin{align*}
\text{no abstraction} \\
\log k_{\text{add}} &= -1.71 - 1.34 (\sigma_{\text{Br}}) \\
&= -1.71 - 1.34 \times 0.15 \\
k_{\text{add}} &= 1.22 \times 10^{-12} \text{ cm}^3/\text{molecule s}
\end{align*}
\]

\[
\text{Lifetime} \quad \tau = \frac{1}{[\text{OH}]_s \times k_{\text{add}}} \\
= \frac{1}{1 \times 10^6 \times 1.2 \times 10^{-12}} \\
= 815 \times 10^3 \text{ s} \\
= 9.4 \text{ d}
\]

\[
\begin{align*}
\text{no abstraction} \\
\log k_{\text{add}} &= -1.71 - 1.34 (\sigma_{\text{CH}_3} + \sigma_{\text{Br}} + \sigma_{\text{OCH}_3}) \\
&= -1.71 - 1.34 (-0.78 - 0.06 + 0.15) \\
k_{\text{add}} &= 1.3 \times 10^{-12} \text{ cm}^3/\text{molecule s}
\end{align*}
\]

\[
\begin{align*}
\text{no abstraction} \\
k_{\text{tot}} &= 1.63 \times 10^{-11} + 1.3 \times 10^{-12} \text{ cm}^3/\text{molecule s} \\
&= 1.8 \times 10^{-11} \text{ cm}^3/\text{molecule s}
\end{align*}
\]

\[
\begin{align*}
\tau &= \frac{1}{[\text{OH}]_s \times k_{\text{tot}}} \\
&= \frac{1}{1 \times 10^6 \text{ molecule/cm}^3 \times 1.8 \times 10^{-13} \text{ cm}^3/\text{molecule s}} \\
&= 0.66 \text{ d}
\end{align*}
\]

\[
\begin{align*}
F_3C-CH_2-O-CHF_2 \\
k_{\text{abs}} &= k_{\text{sec}} F(C(\text{CH}_3)) F(OCH_2CHF_2) + k_{\text{tert}} F(F)_2 F(\text{CF}_2) \\
&= 9.34 \times 10^{-13} \times 0.17 \times 0.032 + 1.94 \times 10^{-12} \times (0.094)^2 \times 0.44 \\
&= 1.8 \times 10^{-14} \text{ cm}^3/\text{molecule s}
\end{align*}
\]

\[
\begin{align*}
\tau &= \frac{1}{[\text{OH}]_s \times k_{\text{abs}}} \\
&= \frac{1}{8.1 \times 10^6 \text{ molecule/cm}^3 \times 1.8 \times 10^{-14} \text{ cm}^3/\text{molecule s}} \\
&= 5.31 \times 10^7 \text{ s} \\
&= 615 \text{ d}
\end{align*}
\]

\[
\begin{align*}
\text{no add} \\
\text{(no double bond)} \\
k_{\text{abs}} &= k_{\text{prim}} F(\text{CH}_2) + k_{\text{tert}} F(\text{CH}_2)^2 + 2k_{\text{tert}} F(\text{CH}_2) F(\text{CH}_2)^2 + 2k_{\text{tert}} F(\text{CH}_2) F(X) \\
&= 8.7 \times 10^{-12} \text{ cm}^3/\text{molecule s}
\end{align*}
\]

\[
\tau = 1.33 \text{ d}
\]

RING FACTORS
3. (6 points). Please indicate the following OH driven oxidations by showing the reagents, any intermediates (be thorough), and the first stable product that is isolatable from the following structures (some are arguably odd!).

![Chemical structures and reactions]

4. (4 points). Please discuss mechanistically the stability for the following compound with respect to hydrolysis under environmental conditions. Use chemical sketches, etc as you see fit. Do give a sense of how persistent you think this compound will be.

![Chemical structures and reaction]

slow k1 because by bulky cyclopentane and CF3
5. (6 points). Carbofuran, show below, is a widely used carbamate insecticide, though it is rather hazardous to nontarget organisms. A few years ago, it was the causative agent in the Withrow Park dog poisonings that gripped my Riverdale neighborhood. From what you’ve learned in class so far involving environmental photochemistry and hydrolysis, please explain (in chemical detail) why when we look for this compound in surface waters downstream of its use in corn fields we typically find the following three carbofuran degradation products: a) an alcohol, b) a ketone; and c) a product that has both alcohol and ketone functionality. [do provide the three structures as well]

6. (4 points). Please use appropriate chemical structures/figures to explain why one of the two benzoic acids derivatives is more acidic than the other.

- CN is an electron withdrawing group: it pulls electrons out of ring making the H more acidic (or the carboxylate more stable)

- SC(\text{H}_3) is an electron donating group: it pushes electron density toward the COOH group making the H less acidic.