1. (10 points). HFC 134a was a good refrigerant replacement for the more recalcitrant CFCs that were banned due to stratospheric ozone depletion problems. Currently, 134a is being phased out due to concerns regarding its global warming potential – C-F bonds absorb strongly in the IR and particularly so in the relatively opaque ‘atmospheric window’ region of which we’ll hear more about later in the term. In considering persistence alone, do you think the suggested replacement HFO 1234yf, shown below, is a good alternative? Explain your answer by comparing lifetimes of each and the most probable products of OH initiated oxidation. Show your calculations, rxn pathways, and note that you will need to use the Kwok & Atkinson paper to calculate OH addition to a compound with a double bond.

![Chemical structures]

\[
\begin{align*}
\text{F}_3\text{C} - \text{CH}_2\text{F} & \quad \text{HFC 134a} \\
\text{F} & \quad \text{H} \\
\text{F} & \quad \text{H} \\
\text{F} & \quad \text{H} \\
\text{NO}_2 & \quad \text{O}_2 & \quad \text{F} \\
\text{F} & \quad \text{H} \\
\text{F} & \quad \text{H} \\
\text{F} & \quad \text{H} \\
\text{H}_2\text{O} & \quad \text{H}_2\text{O}
\end{align*}
\]

\[
\begin{align*}
\text{F}_3\text{C} & \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \\
\text{F} & \quad \text{C} \\
\text{F} & \quad \text{C} \\
\text{F} & \quad \text{C} \\
\text{F} & \quad \text{C} \\
\text{H}_2\text{O} & \quad \text{H}_2\text{O}
\end{align*}
\]

\[
k_{\text{obs}} = \frac{k_{\text{REC}} F(\text{F}) F(\text{CF}_3)}{k_{\text{OH}}} = 9.34 \times 10^{-13} (0.094)(0.071) = 6.23 \times 10^{-15} \text{cm}^3 \cdot \text{molec}^{-1} \cdot \text{sec}^{-1}
\]

\[
T = \frac{1}{k_{\text{obs}}[\text{OH}]} = 18.6 \text{ 0.9 days}
\]

\[
\begin{align*}
\text{F}_3\text{C} & \quad \text{C} \quad \text{CH}_2\text{OH} \\
\text{F} & \quad \text{H} \\
\text{F} & \quad \text{H} \\
\text{F} & \quad \text{H} \\
\text{F} & \quad \text{H} \\
\text{H}_2\text{O} & \quad \text{H}_2\text{O}
\end{align*}
\]

\[
k_{\text{add}} = k (\text{CH}_3 = \text{CXY}) (\text{CXY}) = (5.14 \times 10^{-12})(0.16)(0.76) = 1.73 \times 10^{-12} \text{cm}^3 \cdot \text{molec}^{-1} \cdot \text{sec}^{-1}
\]

\[
T = 6.7 \text{ days}
\]

Both lead to same product, TFA, but HFO 1234yf has a much shorter atmospheric lifetime than HFC 134a: a good replacement.

2. (6 points). Fill in the products of the indicated rxns and give the lifetime for each:

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{Cl} & \quad \text{•OH/O}_2 & \quad \text{O}_2\text{N} \\
\text{Cl} & \quad \text{OH} & \quad \text{O}_2\text{N} & \quad \text{Cl}
\end{align*}
\]

**Lifetime** = 74.7 days

\[
k_{\text{add}} = 10 \\
= 1.55 \times 10^{-15} \text{cm}^3 \cdot \text{molec}^{-1} \cdot \text{sec}^{-1}
\]

\[
k_{\text{obs}} = \text{[1.3-1.34 (0.11+0.23)]} \\
= 1.35 \text{ days}
\]

\[
\text{O}_2\text{N} & \quad \text{Cl} & \quad \text{•OH/O}_2 & \quad \text{O}_2\text{N} \\
\text{Cl} & \quad \text{OH} & \quad \text{O}_2\text{N} & \quad \text{Cl}
\]

**Lifetime** = 12.5 days

\[
k_{\text{add}} = 10 \\
= 9.3 \times 10^{-13} \text{cm}^3 \cdot \text{molec}^{-1} \cdot \text{sec}^{-1}
\]

\[
k_{\text{obs}} = \text{[1.3-1.34 (0.11+0.23)]} \\
= 8.5 \times 10^{-12} \text{cm}^3 \cdot \text{molec}^{-1} \cdot \text{sec}^{-1}
\]
3. (18 points). Please give the atmospheric lifetime (in days) with respect to OH reaction for each compound below and use $1 \times 10^6$ molecules/cm$^3$ as your OH concentration.

<table>
<thead>
<tr>
<th>Calculation</th>
<th>Lifetime</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CF$_3$CF$_2$CF$_2$CH$_2$OH</strong></td>
<td>$T = 2.87$ days</td>
</tr>
<tr>
<td><strong>CH$_3$CH$_2$CH$_2$OH</strong></td>
<td>$T = 2.17$ days</td>
</tr>
<tr>
<td><strong>$\text{H}_3\text{C}$</strong></td>
<td></td>
</tr>
<tr>
<td><strong>$\text{C}_6\text{H}_5\text{NH}_2$</strong></td>
<td>$T = 1.82$ days</td>
</tr>
<tr>
<td><strong>$\text{Cl}$</strong></td>
<td></td>
</tr>
<tr>
<td><strong>$\text{C}=\text{O}$</strong></td>
<td>$T = 19$ days</td>
</tr>
<tr>
<td><strong>$\text{O}$</strong></td>
<td></td>
</tr>
<tr>
<td><strong>$\text{C}=\text{O}$</strong></td>
<td></td>
</tr>
<tr>
<td><strong>$\text{OH}$</strong></td>
<td></td>
</tr>
<tr>
<td><strong>$\text{H}_3\text{C}$</strong></td>
<td></td>
</tr>
<tr>
<td><strong>$\text{C}_6\text{H}_5$</strong></td>
<td></td>
</tr>
<tr>
<td><strong>$\text{CH}_3$</strong></td>
<td></td>
</tr>
</tbody>
</table>

**OH ADDITION:**

$\text{k}_\text{abs} = 9.34 \times 10^{-18} (3.5) (1.23) + 9.34 \times 10^{-13} (1.23) (0.018)$

$= 4.04 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$

$\text{k}_\text{add} = 10^{[\text{H}^+ + 3.54(-0.018)]}$

$= 10^{[\text{H}^+ + 3.34(-0.018)]}$

$= 1.36 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$

$\text{k}_{\text{TOT}} = 0.38 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$

$\text{k}_\text{TOT} = 10^{[\text{H}^+ + 3.41(-0.018)]}$

$= 3.44 \times 10^{-7}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$

$\text{k}_\text{add} = 10^{[\text{H}^+ + 3.41(-0.018)]}$

$= 0.337$ days

$k_{\text{add}} = 10^{[\text{H}^+ + 3.41(-0.018)]}$

$= 6.41 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$

$k_{\text{TOT}} = 6.05 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$

$k_{\text{TOT}} = 0.29$ days

$\text{k}_\text{abs} = 2(1.36 \times 10^{-13})(1.6)$

$= 4.35 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$

$\text{k}_\text{add} = 10^{[\text{H}^+ + 3.41(-0.018)]}$

$= 1.2 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$

$\text{k}_{\text{TOT}} = 6.05 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$

$\text{k}_{\text{TOT}} = 0.29$ days

$\text{k}_\text{abs} = 2(1.36 \times 10^{-13})(1.23)$

$= 3.35 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$

$\text{k}_\text{add} = 10^{[\text{H}^+ + 3.41(-0.018)]}$

$= 4.54 \times 10^{-14}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$

$\text{k}_{\text{TOT}} = 4.57 \times 10^{-14}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$

$\text{k}_{\text{TOT}} = 0.29$ days
4. (10 points). The structure below functions as a heat transfer fluid. Experimental data suggest it is photo-labile under actinic conditions and that homolytic cleavage is on either side of the carbonyl carbon. 1) which is most likely a or b? and 2) based upon your reading of the paper FTOH Atmo Fate (see web site), what do you propose the ultimate final degradation products are for this ketone? You need to take the reaction from the most likely two products of photolysis and carry them all the way through subsequent atmospheric reactions to the final products; and finally 3) a minor pathway will lead to perfluoropropanionic acid...show how this might proceed? **Hint:** the bottom right side of Fig. 1 in the paper might be helpful; also J Phys Chem A108:6325-6330 has a nice explanation of mechanism as well.

\[
\begin{align*}
\text{CF}_3\text{CF}_2\text{C} & \to \text{CF}_3\text{CF}_2-\text{C}^- + \cdot\text{F}^- \\
\text{CF}_3 & \to \text{O}_2 \\
\text{CF}_3 & \to \text{NO}_2 \\
\text{CF}_3 & \to \text{NO}_2 \\
\text{CF}_3 & \to \text{CF}_3 \\
\text{CF}_3 & \to \text{CF}_3 \\
\text{CF}_3 \text{CF}_2 \text{C} & \to \text{CF}_3 \text{CF}_2 \text{C} + \text{O}_2 \\
\text{CF}_3 & \to \text{CO}_2 \\
\text{CF}_3 & \to \text{NO}_2 \\
\text{CF}_3 & \to \text{NO}_2 \\
\text{CF}_3 & \to \text{H}_2\text{O}
\end{align*}
\]

1) **CLEAVAGE AT BIND B IS MORE LIKELY, BECAUSE**

- CF\text{3} AS A 2° RADICAL IS MORE STABLE THAN CF\text{3}
- CF\text{3} CF\text{2} AS A 1° RADICAL.

\[
\begin{align*}
\text{CF}_3\text{CF}_2\text{C} & \to \text{CF}_3\text{CF}_2\text{C}^- + \cdot\text{H}\text{O}_2 \\
\text{CF}_3 & \to \text{CF}_3 \\
\text{CF}_3 & \to \text{CF}_3 \\
\text{CF}_3 \text{CF}_2 \text{C} & \to \text{CF}_3 \text{CF}_2 \text{C}^- + \cdot\text{H}\text{O}_2 \\
\text{CF}_3 & \to \text{CF}_3 \\
\text{CF}_3 & \to \text{CF}_3 \\
\text{CF}_3 \text{CF}_2 \text{C} & \to \text{CF}_3 \text{CF}_2 \text{C}^- + \cdot\text{H}\text{O}_2 \\
\text{CF}_3 & \to \text{CF}_3 \\
\text{CF}_3 & \to \text{CF}_3 \\
\text{CF}_3 \text{CF}_2 \text{C} & \to \text{CF}_3 \text{CF}_2 \text{C}^- + \cdot\text{H}\text{O}_2
\end{align*}
\]

PERFLUOROBENZOPROPIONIC ACID

\[
\begin{align*}
\cdot\text{F}^- & \to \cdot\text{H}\text{O}_2 \\
\cdot\text{F}^- & \to \cdot\text{H}\text{O}_2 \\
\cdot\text{F}^- & \to \cdot\text{H}\text{O}_2 \\
\cdot\text{F}^- & \to \cdot\text{H}\text{O}_2
\end{align*}
\]

5. (4 points). Use resonance structures to 'show' why one of the structures "R" below is considered a good leaving group for the addition-elimination reactions for base catalyzed hydrolysis while the other would be relatively poor.

\[
\begin{align*}
\text{Cl}_3\text{C} & \to \text{Cl}_3\text{C}^- \\
\text{R} = \text{S}-\text{CH}_3 & \to \text{S}-\text{CH}_3 \\
\text{S}-\text{CH}_3 & \to \text{S}-\text{CH}_3 \\
\text{S}-\text{CH}_3 & \to \text{S}-\text{CH}_3
\end{align*}
\]

GOOD LG : " RESONANCE STABILIZATION

POOR LG : " RESONANCE STRUCTURE IS ELECTRONICALLY DESTABILIZED
6. (8 points). Fenthion is an organophosphate insecticide that was widely used a few decades ago. Please review the paper by Huang & Mabury (on the 310 web site) describing a research project which was inspired by a CHM 310 final exam question. With structures, schemes or other illustrations, and brief text please answer the following: a) what role does pH play in influencing the mechanism of hydrolysis? and b) would the hydrolytic fate of Fenthion in sunlit natural waters be different than in buffered 'pure' water?

![Chemical Structure of Fenthion]

\[ \text{H}_3\text{CO}-\text{P}^-\text{O}-\text{SCH}_3 \rightarrow \text{HO}-\text{P}^-\text{O}-\text{SCH}_3 + \text{CH}_3\text{OH} \]

a) At pH 7: \[ \text{H}_3\text{CO}^-\text{P}^-\text{O}-\text{SCH}_3 + \text{H}_2\text{O} \rightarrow \text{HO}-\text{P}^-\text{O}-\text{SCH}_3 + \text{CH}_3\text{OH} \]

At pH 9: \[ \text{H}_3\text{CO}^-\text{P}^-\text{O}-\text{SCH}_3 + \text{OH}^- \rightarrow \text{HO}-\text{P}^-\text{O}-\text{SCH}_3 + \text{H}_2\text{O} \]

b) In sunlit natural waters, \[ [\text{CO}_3^-] >> [\text{OH}^-] \]. \text{CO}_3^- \text{ dominates in most of rxs in s-oxidation of Fenthion.} \]

At basic pH: \[ \text{H}_3\text{CO}^-\text{P}^-\text{O}-\text{SCH}_3 \rightarrow \text{HO}-\text{P}^-\text{O}-\text{SCH}_3 + \text{CH}_3\text{OH} \]

More electrophilic \[ \text{P}^-\text{OH} \text{ can attack} \]

More good Lb: \[ \text{H}_3\text{CO}^-\text{P}^-\text{O} + \text{HO}-\text{P}^-\text{O}-\text{SCH}_3 \]

At pH 9, \[ [\text{OH}^-] \text{ is higher.} \text{ OH}^- \text{ is dominant nucleophile and much stronger than H}_2\text{O.} \text{ Conform ion pair with electrophilic P and can attack P to cleave P-O bond. Faster degradation at basic pH.} \]

7. (9 points). Please give the ratio of hydroxyl addition: H-abstraction rate constants for each of the following compounds. Always normalize to "1" for either addition or abstraction, whichever is smaller.

**Calculations**

H-abstraction:

\[ k_{\text{obs}} = 2 \left( 3.6 \times 10^{-13} \right) \] (1.23) + 
\[ 9.3 \times 10^{-13} \left( 1.00 \right) \times \left( 1.23 \right) \] + 
\[ 9.3 \times 10^{-13} \left( 1.23 \right) \times \left( 9.3 \right) \] = \[ 2.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \]

OH addition:

\[ k_{\text{add}} = 10^{-11} \times \left( 1.23 \right) \times \left( 1.00 \right) \times \left( 1.23 \right) \times \left( 9.3 \right) \] = \[ 4.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \]

Add: H-abstraction

**Calculations**

\[ k_{\text{obs}} = 2 \left( 1.36 \times 10^{-13} \right) \times \left( 9.3 \right) \] = \[ 2.53 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \]

\[ k_{\text{add}} = 10^{-4} \times 1.23 \times \left( 0.38 \right) \times \left( 0.69 \right) \] = \[ 4.7 \times 10^{-3} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \]

**Add: H-abstraction**

**Calculations**

\[ k_{\text{obs}} = 1.94 \times 10^{-2} \times \left( 0.38 \right)^2 \times \left( 1.0 \right) \times \left( 0.69 \right) \] = \[ 5.8 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \]

\[ k_{\text{add}} = 10^{-8} \times 1.23 \times \left( 0.38 \right) \times \left( 0.69 \right) \] = \[ 2.09 \times 10^{-8} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \]