Chemistry 310S

• Environmental Chemistry •

MidTerm Examination

February 25, 2010

DO NOT OPEN UNTIL INSTRUCTED TO BEGIN!!!

Answer all questions in ink; simply cross out mistakes. There should be NO talking or conversing or discussions of politics during the test. If you have questions please raise your hand. Please leave as quietly as possible so that others may continue to take their tests without interruption. Thank you and have a good time.

"The joy of discovery is certainly the liveliest that the mind (of man) can ever feel"

Claude Bernard

Hammett Substituent Constants

<table>
<thead>
<tr>
<th>Group</th>
<th>$\sigma_{\text{para}}$</th>
<th>$\sigma_{\text{meta}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_2$</td>
<td>-0.57</td>
<td>-0.16</td>
</tr>
<tr>
<td>OH</td>
<td>-0.38</td>
<td>0.13</td>
</tr>
<tr>
<td>OCH$_3$</td>
<td>-0.28</td>
<td>0.11</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>-0.14</td>
<td>-0.16</td>
</tr>
<tr>
<td>H</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Phenyl</td>
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<td>0.05</td>
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<tr>
<td>F</td>
<td>0.15</td>
<td>0.34</td>
</tr>
<tr>
<td>Cl</td>
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<td>0.37</td>
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<tr>
<td>Br</td>
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<tr>
<td>I</td>
<td>0.28</td>
<td>0.35</td>
</tr>
<tr>
<td>COOH</td>
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<td>0.35</td>
</tr>
<tr>
<td>CF$_3$</td>
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<td>0.43</td>
</tr>
<tr>
<td>CN</td>
<td>0.70</td>
<td>0.61</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>0.81</td>
<td>0.71</td>
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</tbody>
</table>

Total: 86 Pts; 9 Questions; only 5.5 pages
1. (6 Points). Perfluoroisobutene is toxic and is also a powerful greenhouse gas. However, it is capable of undergoing reasonably fast decomposition in the atmosphere. Please indicate the reaction mechanism of oxidation by OH in the presence of NOx to produce the first two stable products we would expect to observe.

2. (8 Points). Interestingly, this perfluoroketone appears to undergo hydrolysis rather quickly in similar fashion to that of the iodoform reaction. a) Please propose a mechanism for this hydrolysis showing all products; and then b) for the non-acid product, of this hydrolysis, please take it through all the expected atmospheric reactions to yield trifluoroacetic acid.
3. (18 Points). Please provide short answers for each of the queries below and do illustrate with figures, schemes, structures where that helps illustrate your point.

a) what determines the rate of an SN2 reaction? SN1? Illustrate each with an appropriate example:

\[ \text{SN1: } R_2 \text{C}^+ \cdot \text{R}^1 + X^- \rightarrow R_2 \text{C} \text{X} \quad \text{1st order} \]

\[ \text{SN2: } Y \cdots C \cdots X \rightarrow \text{product} \quad \text{2nd order} \]

3 points

Rate $\propto$ $X^-$ leaving group ability
$\propto$ stability of $C^+$ carbocation

Ex: $CH_3 - C - I \rightarrow CH_3 - C^+ + I^-$

Eto-P-OH $\rightarrow$ OEt

3 points

Rate $\propto$ nucleophilicity of $Y$
$\propto$ electrophilicity of $C$
$\propto$ $X^-$ leaving group ability
$\propto$ steric effects

Ex: Eto-P-O-C(NO$_2$)$_2$ $\rightarrow$ OEt

b) 1) what is quantum yield? 2) What are the four ways excited state energy can be dissipated? 3) Give a reasonable example for a compound you expect to be photolabile in surface waters exposed to actinic radiation and show your expected reaction (4).

1. Quantum yield: efficiency term, # of excited states leading to bond scission, fluorescence, etc.

$\Phi = \frac{\# \text{photons leading to a reaction}}{\# \text{photons absorbed}}$ 2 points

2. Bond breakage $A^* \rightarrow B + C$

3. Release of hν, ie, fluorescence $A^* \rightarrow A$ 2 points

3. Quenching $A^* + B \rightarrow B^* + A$

4. Vibrational relaxation

3. $\text{Cl}_2 \rightarrow \text{Cl}^+ + \text{Cl}^-$ 2 points

c) what are the dominant controls on $[\cdot \text{OH}]_a$ in surface waters?

Sources of OH:

$\text{NO}_3^- \xrightarrow{h\nu} \text{NO}_2 + O^- \xrightarrow{H^+} \text{OH}$

$\text{DOC} \xrightarrow{h\nu} \text{DOC}^* + \text{OH}$

$\text{FeO} \xrightarrow{h\nu} \text{Fe}^{2+} + \text{OH}$

$\text{Fe}^{2+}/\text{Cu}^+ + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+}/\text{Cu}^{2+} + \text{OH} + \text{O}_2$

$\text{H}_2\text{O}_2 \xrightarrow{h\nu} 2\text{OH}$

4 points for mentioning 4 of these 5 sources

Consumption of OH:

$\text{OH} + \text{CO}_3^{2-} \rightarrow \text{CO}_3^{-} + \text{OH}$ 1 point

$\text{OH} + \text{DOC} \xrightarrow{D_2} \text{DOC-O-O}^* + \text{H}_2\text{O}$

$[\text{OH}]_{ss} \propto \frac{\text{production rate}}{\text{scavenging rate}}$ 1 point
4. (5 Points). Please arrange the following in order of relative rates of reaction with hydroxyl radical with (1 = fastest; 4 = slowest):

- each

- each

5. (6 Points). Please indicate the expected linear change in rate by drawing a line in relation to the “hammett sigma” on each of the three graphs. Then provide the expected product of each reaction.

6. (8 Points). Chlorinated terpene mixtures (ex. C_{19}H_{28}Cl_{10}) are the main ingredient in the insecticide toxaphene which was banned due to high persistence in the environment. Would it be a good idea for someone to invent “fluorinated toxaphene”? Why or why not (be explicit)?

- Oxidation → only primary H abstraction → No addition to double bonds

- Hydrolysis → doesn’t occur

- Elimination → no acidic H with β leaving group → SN1 – poor leaving group → SN2 – steric hindrance

- Reduction → poor leaving group → low reduction potential (only 2Fs per carbon)
7. (8 Points). Please give the lewis structures for the following:

a) ozone:

b) bicarbonate ion:

c) nitrogen trioxide:

d) nitrogen containing product of the reaction of species in ‘c’ reaction with propane:

8. (11 Points). For each oxidative reagent shown on the right please show how each, from the first step, is generated.

9a. (6 Points). Please explain, with the necessary structures, why the hydrocarbon below would likely be persistent in a wastewater treatment plant?
9b. (10 Points). Please provide the step by step (5) microbial degradation pathway of the 4:2 polyfluoroalkylphosphate (used as paper coatings) to the corresponding perfluorinated acid (1):

\[
\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{O}-\text{P}-\text{OH} \xrightarrow{\text{microbial hydrolysis}} \text{CF}_3\text{CF}_2\text{CF}_2\text{COOH}
\]

2 points \[\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{O}_2} \text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{C}=\text{O} \]

2 points \[\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{CoA}} \text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2\text{C}=\text{O} \]

1 point \[\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2\text{C}=\text{O} \xrightarrow{-\text{HF}} \text{CF}_3\text{CF}_2\text{CF}_2\text{C}(-\text{CH}_2\text{C})=\text{O} \]

6 points for recognizing microbial hydrolysis of phosphate & oxidizing the resulting alcohol to carboxylic acid

You're Done!

4 points for taking through B-oxidation.