**Lab Report for Carboxylic Acid Unknown: Pandemic-Modified**

**Summary of all of the key data, with links to the H-NMR data**

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| --- | --- | --- | --- | --- | --- |
| Student Last  Name Starts  with Letters: | Titration Data:  Grams of Acid | Titration Data:  mL of  0.1002 mol/L  NaOH | Starting  Material  Melting  Range | Derivative  Melting  Range | Acid NMR: |
| A | 0.2003 g | 13.3 mL | 179-184 | 165-170 | <http://web.mnstate.edu/jasperse/Chem365/NMR-Acid-A.pdf> |
| B-C | 0.2007 g | 16.5 mL | 119-122 | 155-161 | <http://web.mnstate.edu/jasperse/Chem365/NMR-Acid-B-C.pdf> |
| D-G | 0.2004 g | 24.0 mL | 68-73 | 111-117 | <http://web.mnstate.edu/jasperse/Chem365/NMR-Acid-D-G.pdf> |
| H-K | 0.1996 g | 13.6 mL | 131-134 | 146-151 | <http://web.mnstate.edu/jasperse/Chem365/NMR-Acid-H-K.pdf> |
| L-N | 0.2002 g | 12.9 mL | 136-141 | 113-117 | <http://web.mnstate.edu/jasperse/Chem365/NMR-Acid-L-N.pdf> |
| O-S | 0.2011 g | 14.9 mL | 104-109 | 120-124 | <http://web.mnstate.edu/jasperse/Chem365/NMR-Acid-O-S.pdf> |
| T-Z | 0.1998 g | 14.8 mL | 178-183 | 138-144 | <http://web.mnstate.edu/jasperse/Chem365/NMR-Acid-T-Z.pdf> |

Summary:

1. See the lab-report fill-in sheet, page 77.
2. You will analyze and identify one unknown carboxylic acid
3. Which acid to analyze is determined by the starting letter of your last name, see table above.
4. There will be four pieces of data from which to determine your structure:

* The molecular weight of your carboxylic acid, which can be calculated based on the titration information.
  + The data is taken from actual student work, and may not be perfect.
  + Assume that you can trust that the titration data will enable a molecular weight calculation that will be within ≤5 g/mol of the actual molecular weight.
  + But it might not be more accurate than that.
* The melting range for the starting carboxylic acid
* The melting range for the anilide derivative
* The H-NMR for the starting carboxylic acid.
  + Remember that the carboxylic acid hydrogen will NOT show up in your NMR.
  + It’s so far downfield, >10ppm, that it’s off scale.

1. There is a fill-in sheet page 77 where you can enter your data.
2. In addition, you’ll print and attach your NMR data, and you’ll need to write in a standard H-NMR summary (and interpretation) table
3. The actual experiment video is only 26 minutes!
4. No procedure writeup is required! ☺
5. Page 76 lists molecular weights and melting information for acids and derivatives.

CARBOXYLIC ACID UNKNOWN

**A. Solubility Tests: Water, NaHCO3, and NaOH. (Pandemic: Skipped!)**

Test the solubility of your acid first in neutral water, in NaOH/H2O, and in NaHCO3. For each test, add 15 drops of aqueous solution to a small test tube, and then add 2 drops of sample if it is a liquid, or a little spatula quantity if you have a solid. If you do have a solid, double your NaOH/H2O and NaHCO3 to 30 drops. Swirl/mix well. Use of small stir bar helps.

* Water Test: Only acids with small numbers of carbons should be soluble.
* NaOH/H2O: Carboxylic acids are ionized by NaOH, and the resulting sodium carboxylates are usually soluble (with some exceptions, if there are too many carbons present…).
  + Note: Solubility of solid acids is often quite slow, because the hydroxide may only be able to “attack” the acid at the surface. Trying this test in a large test tube with a stir-bar is sometimes helpful. But be sure to check after five or ten minutes have passed, not just initially. Also, sometimes it helps if you double your NaOH/H2O beyond 30 drops, because if you put in more acid than you realized, and the hydroxide runs out, you won’t get full dissolving.
  + NaHCO3/H2O: An acid-base reaction should lead to solution, but the other unique thing is that acid-base protonation of bicarbonate may lead to CO2 bubbles. If the solubility is poor the bubbles are small and slow, but even with a solid you can often see little bubbles forming. As with the NaOH/H2O, solubility is often quite slow; often benefits from a larger portion of NaHCO3/H2O; and often benefits from stirring with a stir bar.
  + Note: If you see the bubbles, it’s a firm proof of acid. But the failure to see bubbles isn’t proof to the contrary, that you don’t have an acid. Sometimes the bubbles are too small, or too slow, or you just can’t see them for whatever reason.

**B. Melting Point/Boiling Point. Pandemic: Yes, data included.**

If your carboxylic acid is a solid, take its melting point. If it is a liquid, take its micro-boiling point.

**C. Titration/Neutralization Equivalence🡪Molecular Weight Determination**. **Pandemic: Data included.**

Weigh, as accurately as possible, around 200 mg (0.200g) of your acid into a 125 mL Erlenmeyer flask. Use the balance nearest the acetone-hood. (You want 3-4 significant figures after the decimal for this, so the other balances are unacceptable.) Pre-tare the flask, then add sample directly into the flask and record the mass to avoid inaccuracy. (Adding to a boat, recording, and then pouring into Erlenmeyer will introduce error.) Whether you have 200 mg or 220 or 180 doesn't matter, so long as you know exactly what your original mass is. Dissolve your material in around 25 mL of ethanol. [Logic: It is vital that the solution be homogeneous, so you need ethanol to keep it dissolved. But the indicator needs water to work right.] Add 2 drops of phenolphthalein indicator solution. Titrate the solution with \_\_\_\_\_\_\_ M NaOH. (Copy the concentration down from the bottle!)

Summary of titration logic: Molecular weight (or "formula weight", FW) is the ratio of mass per mole. Having weighed your acid, you know the mass very precisely; but how do you know how many moles? By titrating against the precisely standardized base! From the precisely known volume of base and the molarity of the base, you can determine the # of moles of base used. Since the mole/mole stoichiometry is 1 mole of base per 1 mole of acid, the # of moles of base tells the # of moles of acid. Knowing mass of acid and moles of acid, the ratio gives you the formula weight.

Note: Do your titration once, and check the molecular weight value with me. If you get within 5 g/mol, I’ll tell you and you won’t need to repeat. If you don’t get within 5 g/mol, then you’ll need to do it again. (Normally several repeats for reproducibility would be in order.)

Molecular weight calculations like this are not perfectly reliable (even if you calculate right!). In general an error of up to five grams/mole is acceptable. Logical reasons for errors are shown below:

* + Reason 1: If you don’t see the color change right away and “overshoot” the amount of NaOH added, you will have added more moles of NaOH than necessary. The calculation assumes that the number of moles of acid is exactly the same as the number of moles of NaOH added; but if you overshoot the NaOH, this won’t actually be true. Your moles of acid will actually be slightly less than the number of moles of base. So when you are dividing mass of acid by moles of acid, you will have a slightly exaggerated number for the denominator. This will result in an underestimation of the grams/mole ratio, and will underestimate the actual molecular weight.
  + Reason 2: Not all of the acids are perfectly pure. For example, if the solid sample is only 95% pure, this will cause an error in the calculation! Since acids are somewhat hydrophilic, it’s not uncommon for acids to be somewhat wet and to give somewhat exaggerated molecular weight numbers.

Example of Molecular Weight Calculation:

Measured data:

* + - Weight of acid: 0.2015 g
    - Molarity of NaOH: 0.1005 M
    - Volume of NaOH to reach the titration end-point: 14.50 mL

Mathematical Calculation of Molecular Weight:

* + - Moles of NaOH == 0.001457 mol NaOH
    - Moles of acid = moles of base = 0.001457 mol acid
    - Molecular weight of acid = =138.3 g/mol

**D. Anilide Derivative. Pandemic: Yes, melting-range data included.**



Place 10 drops (or 0.10 grams, if it’s a solid) of the acid chloride into a large test tube. Add a stir bar, and add 1 pipet of ether. To this solution add 20 drops of aniline, dropwise (may spatter if you add it all at once) and stir for 5 minutes if it’s not already solid. The primary precipitate that forms is the aniline hydrochloride salt. If your reaction is so exothermic that the ether boils away and you end up with an unstirrable solid, then add another pipet of ether. After the five minutes is up, add 2 pipets of aqueous NaOH, and continue stirring for an additional five minutes. If some precipitate remains it is the derivative itself. Use a long pipet to remove the aqueous layer from the bottom of the test tube. (Any unreacted acid chloride should be removed by the basic water.) Then add 2 pipets of aqueous HCl, and stir vigorously. Use a long pipet to remove the aqueous layer. (The aniline should be removed in the process.) Cool your solution in an ice-bath.

If you have a significant amount of precipitate at this point, it is the desired derivative. Filter directly over a Hirsch funnel. Rinse with some HCl/water and then some water to get your crude derivative. If you don’t have a significant amount of precipitate, skip down to the instructions in bold.

Recrystallize the crude derivative from ethanol. Ideal volumes will vary depending on your unknown, but a suggested starting point is 2mL of ethanol and 10 drops of water. But the solubilities will vary greatly from unknown to unknown, so you need to make whatever adjustments are appropriate for your particular sample. You shouldn’t need these anymore, but several recrystallization reminders:

* Use a small Erlenmeyer, not a beaker, to reduce solvent evaporation.
* Make all your adjustment decisions while the solution is boiling hot.
* Heating your Erlenmeyer in a hot-water beaker is convenient, to provide more even heating than if you just stand it on a hot plate, and to avoid overheating on the hot-plate surface.
* You and your hood partner should also warm up some ethanol in case you need to add some
* Other than when you’re just starting, never add cold solvents.
* During cooling, cover the flask to avoid evaporation of the hot solvent.
* Supersaturation is quite common. If you think you’re at 50% water, probably stop and cool and see whether crystals will form.
* If no crystals form even after slowly cooling and then icing, try adding ice chip(s).
* Your rinse solvent should be very similar to what you think your actual solvent blend is.

If following the acid wash you do not have a precipitate (or don’t have very much precipitate), then much/all of the derivative is dissolved in the ether. Add a boiling stick and heat your test-tube to boil off the ether, either with a heat gun or in a hot-water bath. place it in an ice-bath. (Maybe consult with the instructor for fast help.) The residue will probably then crystallize. If not, try to add an ice chip and scrape it with a rough stick. Whether it actually crystallized or not, just recrystallize right in the large test tube. Start with around 1 mL of water. Heat it up in a hot water bath, and add as much hot ethanol as it takes to just barely get the product to just barely dissolve. Cool slowly, and perhaps stimulate crystal formation with an ice chip if necessary. Then harvest your crystals. Your wash solvent should probably be at least 50% water.

**E. NMR:** **Pandemic: Yes, data included.** 1H will be useful. Don’t bother with a 13C NMR, since solubility will probably be too low to get anything worthwhile. The OH hydrogen is often very broad, due to H-bonding, sometimes so broad that you won’t see it at all.

* Aromatic hydrogens ortho to a carbonyl are typically pushed downfield, toward 8 ppm. This is because a carbonyl group is a strong electron withdrawer, so it makes the ortho carbons more electron poor, which “deshields” the ortho hydrogens.
* A carboxylic acid hydrogen will normally be invisible, so don’t look for it. They are so broadened by hydrogen-bonding that they often just blend into the baseline. Even if you could see them, they appear down at 11-14 ppm, which is off-scale from our plots.
* Some solid carboxylic acids will have low solubility in CDCl3. If your sample is not completely soluble, you can run it anyway. But sometimes when there isn’t that much sample dissolved, background lines from components in the CDCl3 solvent can be misinterpreted for real sample lines. The two most common candidates are a line at 0.00 ppm (tetramethylsilane) and a singlet at 7.26 (CHCl3). These two components are always present when you use CDCl3 solvent, but their height in a printed spectrum looks much taller relative to other signals if the real sample is very dilute versus if the real sample is more concentrated.

### Carboxylic Acid Candidates

bp of mw of mp of Anilide

# Liquid Acid Unknowns Acid Acid (g/mol) Derivative

Ethanoic Acid 118 60 47

Propanoic Acid 141 74 103

Butanoic Acid 162 88 95

Pentanoic Acid 185 102 63

2,2-Dichloroethanoic Acid 194 129 118

Hexanoic Acid 202 116 95

Octanoic Acid 237 140 57

mp of mw of mp of Anilide

# Solid Acid Unknowns Acid Acid (g/mol) Derivative

Decanoic Acid 31-32 164 70

Bromoethanoic Acid 47-49 139 131

3-Phenylpropanoic Acid 47-49 150 92-98

2,2,2-Trichloroethanoic Acid 54-58 163.4 97

2-Chloroethanoic Acid 61-62 94.5 137

2-Butenoic Acid (CH3CH=CHCO2H) 71-73 86 118

2-Phenylethanoic Acid 76-79 136 118

3-Methylbenzoic Acid 108-110 136 126

Benzoic Acid 122-123 122 163

2-Benzoylbenzoic Acid (PhCOC6H4CO2H) 127-128 226 195

Cinnamic Acid (PhCH=CHCO2H) 133-135 148 153

2-Chlorobenzoic Acid 138-142 156.5 118

3-Nitrobenzoic Acid 140-142 167 155

2,2-Diphenylethanoic Acid 147-149 212 180

2-Bromobenzoic Acid 150 201 141

2,2-Dimethylpropanoic Acid 163-164 102 127

3,4-Dimethoxybenzoic Acid 179-182 182 154

4-Methylbenzoic Acid 180-182 136 145

4-Methoxybenzoic Acid 182-185 152 169-171

3-Hydroxybenzoic Acid 201-203 138 157

3,5-Dinitrobenzoic Acid 203-206 212 234

4-Nitrobenzoic Acid 239-241 167 211-217

* Note: Carboxylic acids are hydrophilic, and tend to absorb some water from the air. Some of the starting amines may also have trace isomeric impurities. The result of moisture and/or impurities means that some of the starting materials may have melting points that are a little bit depressed.

Unknown Report Sheet- **Carboxylic Acid** Name

1. Melting point or boiling point for starting material: List value:

* See the table on page 72 for the actual data
* See the table on page 76 for the list value

2. What is the approximate molecular weight (mw) of my sample, based on my titration?

* See the table on page 72 for the actual grams of acid used, and the actual volume of 0.2002 mol/L NaOH used to reach the endpoint.
  + Note: data is actual student data from last year. (And may not be perfect!)
* The molecular weight you can calculate will come within ≤5 g/mol of the actual molecular weight. ☺
* For listing of molecular weights, see table on page 76.

Grams of carboxylic acid. mL of 0.1002 mol/L NaOH.

Calculated molecular weight (in g/mol) for your carboxylic acid.

**Show your calculation work used to determine the molecular weight!**

* + Beware of ridiculous significant figures.

3. Melting Range for Derivative: Observed mp literature mp

* See the table on page 72 for the actual data
* See the table on page 76 for the list value

6. H-NMR (print and attach, with assignments/interpretation. Do analyze aromatic H’s)

* **On the proton spectrum, create a standard 4-column summary table of your H-NMR data, detailing chemical shifts, integrations, and splittings, and “source”.**
* Draw the structure of your molecule, with identifiers by each carbon (a, b, c…).
* Then on your standard summary table add a “source” column in which you explain which hydrogens (a, b, or c, etc…) are responsible for which signals. Note: if the sample is too concentrated, the splitting may in some cases get broadened and become problematic.
* Note: the carboxylic acid proton will NOT be visible in your spectrum. (It’s off-scale, >10ppm)

7. What is My Actual Unknown? (Letter and Draw Structure)