CARBOXYLIC ACID UNKNOWN

A. Solubility Tests: Water, $NaHCO_3$, and NaOH

Test the solubility of your acid first in neutral water, in $NaOH/H_2O$, and in $NaHCO_3$. 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 $NaOH/H_2O$ to 30 drops. Swirl/mix well. Use of small stir bar helps.

- Water Test: Only acids with small numbers of carbons should be soluble.
- $NaOH/H_2O$: 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 1: if it is so small that it dissolves in neutral water, then dissolving in $NaOH/H_2O$ tells nothing extra.
  - Note 2: 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 $NaOH/H_2O$ to 30 drops, because if you put in more acid than you realized, and the hydroxide runs out, you won't get full dissolving.
- $NaHCO_3/H_2O$: An acid-base reaction should lead to solution, but the other unique thing is that acid-base protonation of bicarbonate leads to CO_2 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 $NaOH/H_2O$, solubility is often quite slow; often benefits from a larger portion of $NaHCO_3/H_2O$; 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

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

Weigh, as accurately as possible, around 200 mg (0.200g) of your acid into a 125 mL Erlenmeyer flask. You want 3-4 significant figures after the decimal for this, so the usual balances are unacceptable. Whether you have 200 mg or 220 or 180 doesn't matter, so long as you know exactly what your original mass is. If you have a liquid, add drops until you get to about the same mass. 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: If you do a titration twice and both results are pretty consistent, you'll have a much higher confidence in your accuracy! If you do it twice and the answers differ significantly, at least one of them must be in error.

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.
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Example of Molecular Weight Calculation:

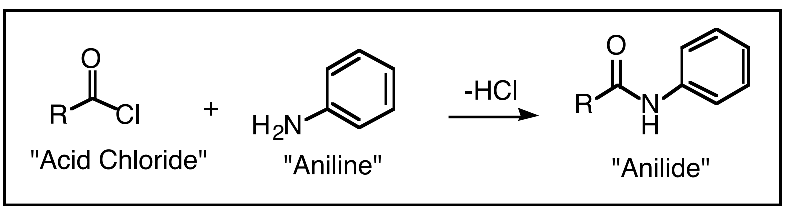
Measured data:

- 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 $= (14.50 mL)\left(\frac{1L}{1000 mL}\right)\left(\frac{.1005 mol}{1L}\right)$ = 0.001457 mol NaOH
- Moles of acid = moles of base = 0.001457 mol acid
- Molecular weight of acid = $\frac{0.2015 g}{0.001457 mol}$ =138.3 g/mol

D. Anilide Derivative



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 normally a good starting guess will be only 2 mL of ethanol. Add more as needed (which will be true in many cases). If no crystals form even after cooling, try adding an ice chip. (Or more than one ice chip.)

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. Add two pipets of HCl/water, swirl it around, and place it in an ice-bath. The residue will probably crystallize. If not, try to add an ice chip or scrape it with a rough stick. Scrape the reside out onto a Hirsch funnel, and rinse with some HCl/water and then some water to get your crude derivative. When you recrystallize, you will probably not need very much ethanol, and will probably need ice chips to help induce crystallization. But it should still work. If the material never really solidifies so that filtration isn't actually practical, just pour off the HCl/water, and do the recrystallization in the test-tube. Recrystallize using 1:1 ethanol/water rather than ethanol, and perhaps spike with ice chip if crystallization is difficult.

E. NMR ^{1}H will be useful. Don't bother with a ^{13}C 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.

Carboxylic Acid Candidates

Liquid Acid Unknowns	bp of Acid	mw of Acid (g/mol)	mp of Anilide 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

Solid Acid Unknowns	mp of Acid	mw of Acid (g/mol)	mp of Anilide 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 ($CH_3CH=CHCO_2H$)	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 ($PhCOC_6H_4CO_2H$)	127-128	226	195
Cinnamic Acid ($PhCH=CHCO_2H$)	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**

Unknown No. Name

1. Physical Examination of Starting Material

    a) Physical State________________b) Color________________

2. Solubility Tests on Starting Material

Solvent:	Water	If Insoluble in Water, Does it Float or Sink?	Aq NaOH	Aq NaHCO
Solubility:	_______	__________________	________	_________

3. Melting point or boiling point for starting material: Book value:

    Most Likely Candidates?

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

    Approximately ___________ g/mol. (Attach a separate sheet that details your weights, calculation!)

5. Derivative

	observed mp	literature mp
Crude		
Recrystallized		

6. H-NMR (attach, with assignments/interpretation)

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

8. Comments, difficulties, complaints, etc..