

Experiment 3 Synthesis and Column Chromatography of 3-Methylbutyl Acetate

Monday, March 12, 2007
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Title: Experiment 3: Synthesis and Column Chromatography of 3-Methylbutyl Acetate

Purpose: To synthesize and purify 3-methylbutyl acetate through equilibrium reaction of 3-methyl-1-butanol and acetic acid to 3-methylbutyl acetate and water with use of catalyst of para-toluenesulfonic acid.

Pre-lab:

Compound	Molecular weight	Hazards	Density	Mp/bp
Para-toluene sulfonic acid	190.22	Irritating to eyes, skin, and respiratory system.		mp: 103-106C
Glacial acetic acid	60.05	Corrosive, flammable, harmful with inhalation, contact with skin or eyes, and ingestion	1.049g/mL at 25C	Mp: 16.2 C
3-methyl-1butanol (isopentanol)	88.15	Harmful with inhalation, contact with skin or eyes, and ingestion	0.809g/mL at 25C	Mp: -117C Bp: 130C
3-methyl butyl acetate (isopentyl acetate)	130.18	Flammable, Harmful with inhalation, contact with skin or eyes, and ingestion	0.876 g/mL at 25 C	Mp: -78 C Bp: 142 C
acetone	58.08	Highly flammable, Harmful with inhalation, contact with skin or eyes, and ingestion.	0.791g/mL at 25C	Mp: -94 C

1. If the 3-methyl-1-butanol was from an older bottle and contained a significant amount of water from air absorption, then less of the product would form. Often times water does not affect equilibrium when dealing with acid base reactions; however, in this case water is taken into

account and does affect the equilibrium. By Le Chatelier's Principle, when adding additional water (product side) it will shift the equilibrium to the left toward the reactants.

2. Para-toluenesulfonic acid is the catalyst in this reaction. Changing the concentration of the catalyst will not affect the equilibrium position. It will only affect the rate of reaction.
3. 3-methylbutyl acetate has a boiling point of 142 C while 3-methyl-1butanol has a boiling point of 130 C. The compound with the lower boiling point (3-methyl-1butanol) will convert to gas phase first and be separated from the mixture before 3-methylbutyl acetate during gas chromatography.

Procedure:

Day 1

1. Put 50mg of para-toluenesulfonic acid 5mL microscale round bottom flask.
2. Estimate masses of 3-mythl-1butanol and glacial acetic acid
3. Weigh and record 5mL round bottom flask with para-toluenesulfonic acid.
4. Add 3-methyl-1butaonol. Find mass
5. Repeat for glacial acetic acid
6. Add 3 Teflon boiling chips
7. Assemble reflux apparatus
8. Clamp flask to rack in fume hood. Put bulb from flask inside wide-mouth bottle. Wide-mouth bottle is on hot plate.
9. Fill bottle with sand just to cover the bottom.
10. Turn on hot plate until vapor condenses
11. Complete reflux to instructor's designated time.
12. Contents of round bottom flask are put into microscale.
13. Place centrifuge with 1mL water into rack.
14. Gradually add 2mL of sodium bicarbonate and swirl
15. Repeat with adding 1mL of sodium bicarbonate until pH of the aqueous layer is greater than 7.
16. Remove aqueous layer and remaining is unreacted 3-methyl-1-butanol and 3-methylbutyl acetate.
17. Add sodium sulfate powder to tube and keep for day 2.

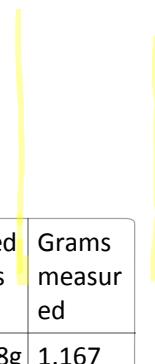
Day 2

1. Pipette filter product
2. Ad 1mL dichloromethane to pipette filter
3. Collect filtrate in scintillation vial and label as "crude product"
4. Setup chromatography
5. Put silica gel into 50mL Erlenmeyer flask.
6. Add petroleum ether until have free-flowing slurry.
7. Load sample into column and collect 15mL hexane eluent.
8. Switch solvent on column to 10% dichloromethane in petroleum ether.
9. Collect 5mL in 5 test tubes.
10. Spot tiny amount of eluent onto filter paper and note odor.
11. Get GC analysis on first and last fractions that contain 3-methylbutyl acetate.
12. Get tare weight of 125mL Erlenmeyer filter flask
13. Put contents of 3-methylbutyl acetate without 3-methyl-1-butanol into Erlenmeyer flask.
14. Remove solvent from filter flask

15. Record weight of flask with ester

Figure 1: GC Banana Ester This

Data/Results GC of 3-methylbutyl acetate provided Lab Product. It has two peaks at 10min (area=1219665, height=604273) and 3min (area=987818, height=404273). Our synthesized 3-methylbutyl will be compared to this GC as a tool to determine how successful the



Yellow = 3-methylbutyl acetate

Pink = 3-methyl-1-butanol

Green = one of the above or mixture of both

Experiment was	methyl mmol	mol	g/mol		
1butanol					

Glacial Acetic Acid

Figure 2: GC 3-methylbutyl acetate GC of 3-methyl-1-butanol

provided by instructor. Peak at one minute (area=1727166, height=680123) and at 1.6minutes (area=72858, height=29906). This 3-methylbutyl has strongest banana smell on the first vial. 5 is where we are measuring when the banana smell fades.

A good 3-methylbutyl acetate will not resemble this GC, because this was a reactant and was supposed to be separated by the column.

Yellow = 3-methylbutyl acetate

Pink= 3-methyl-1-butanol

Green= one of the above or mixture of both

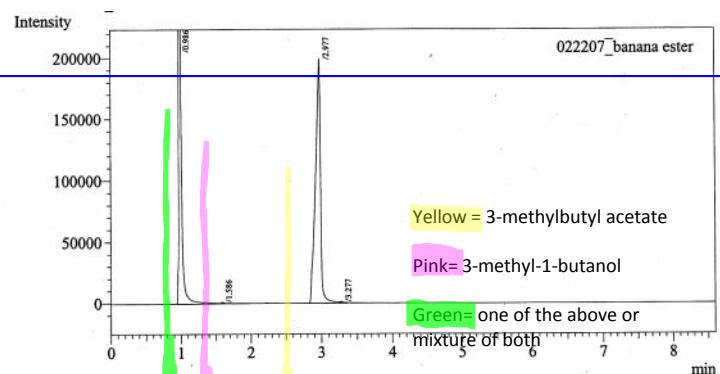
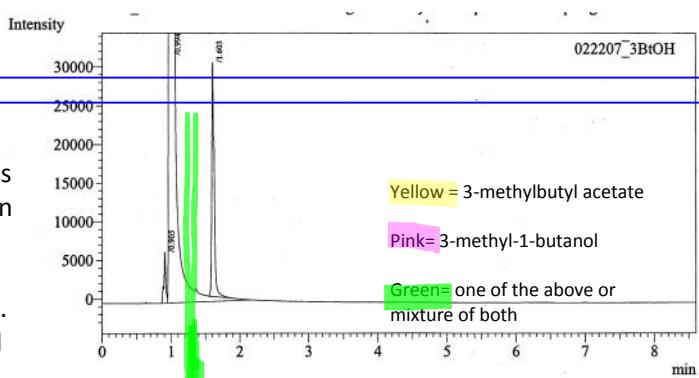


Figure 3: GC Crude GC of crude sample before running through column. The first peak originates from the presence of both 3-methyl-1-butanol and 3-methylbutyl acetate. The second peak is from 3-methyl-1-butanol only. The third peak is from 3-methylbutyl acetate. By comparing this GC to Figure 1 and Figure 2, we can conclude that the crude contains both 3-methyl-1-butanol and 3-methylbutyl acetate.

Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	Cmpd Name
1	0.986	1219665	604273	0.000	S		
2	1.586	1913	923	0.000		T	
3	2.977	987818	198533	0.000		S	
4	3.277	1214	784	0.000		T	
Total		2210610	804513				



Peak#	Ret.Time	Area	Height	Conc.	Unit	Mark	Cmpd Name
1	0.905	12275	6326	0.000			
2	0.994	1727166	680123	0.000		SV	
3	1.603	72858	29906	0.000		T	
Total		1812299	716355				

Figure 4: GC Third Sample This is the third eluent from the column which had banana odor. The results are not ideal since the only large peak is at one minute. It is strange that the second and third peak (1.6 minutes and 3 minutes) are so tiny, because they each originate from a different compound. The first peak is very large, but does not provide very conclusive data since it could be from either compound.

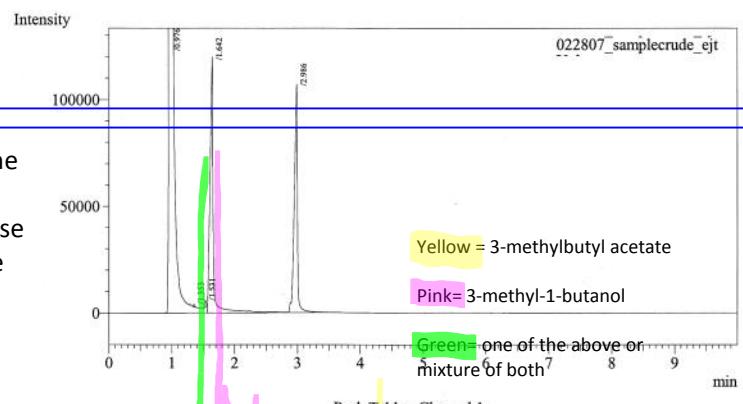


Yellow = 3-methylbutyl acetate

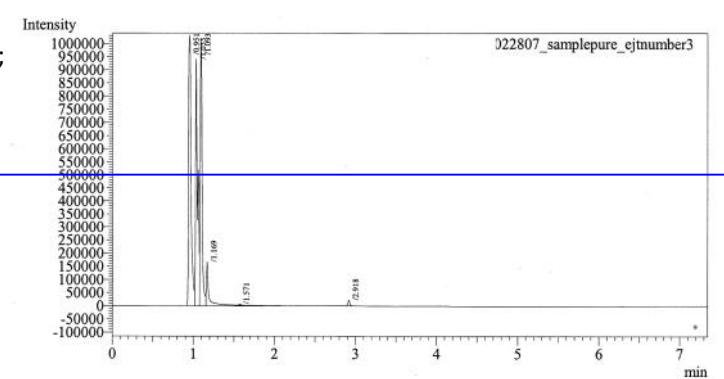
Figure 5: Sixth Sample This is the sixth eluent from the column which had no banana odor. These

provide very conclusive data since it could be from either compound.

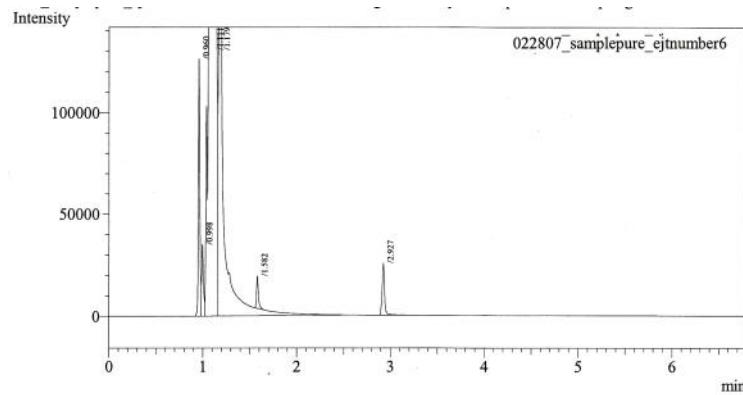
Figure 5: Sixth Sample This is the sixth eluent from the column which had no banana odor. These results are also strange because third peak would suggest that there would be more banana than the third eluent; however, our smelling of the samples contradicts this. It seems as though the amount of both 3-methylbutyl acetate and 3-methyl-1-butanol might have increased due to the more defined second and third peaks; however, the height and total area have decreased from the third eluent.



Peak Table - Channel 1			
Peak#	Ret.Time	Area	Height
1	0.976	3383235	1031199
2	1.353	1322	1148
3	1.531	5931	3083
4	1.642	434567	118884
5	2.986	368114	104194
Total		4193169	1258509



Peak Table - Channel 1					
Peak#	Ret.Time	Area	Height	Conc.	Unit
1	0.951	2329169	1030664	0.000	E
2	1.033	1639033	922611	0.000	V
3	1.093	1668768	100953	0.000	VE
4	1.169	409084	163667	0.000	SV
5	1.571	7416	4926	0.000	T
Total		6091931	3153821		



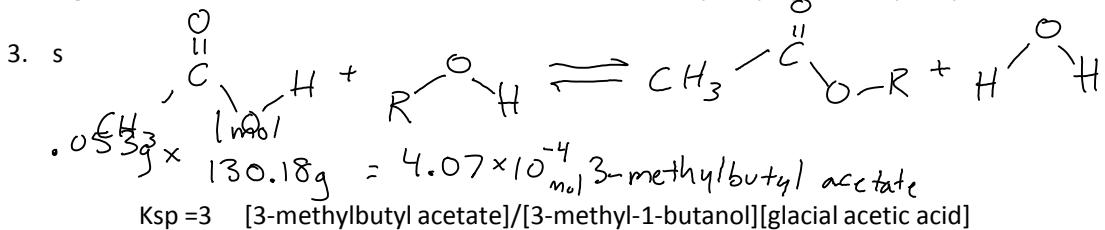
Peak Table - Channel 1					
Peak#	Ret.Time	Area	Height	Conc.	Unit
1	0.960	141365	122856	0.000	
2	0.998	46042	34491	0.000	V
3	1.111	3532840	1035862	0.000	VE
4	1.179	1221014	677706	0.000	SV
5	1.582	22425	15238	0.000	T
6	2.927	45132	24980	0.000	
Total		5008817	1911132		

Product weight after slurpie 0.9956g

Ratio: Area of 3-methylbutyl acetate/ area of 3-me-1-boh * .786

Post-Laboratory Questions:

1. Ratio = Area of 3-methylbutyl acetate / area of 3-methyl-1-butanol * .786 = 0.666
2. Figure 4 represents the eluent that had the strongest banana smell and Figure 5 represents the eluent that no longer had the banana smell. When comparing the GC to the controls (Figure 1 and 2), we can compare purity of our eluents. 3-methylbutyl acetate has two distinguished peaks at 1 minute and 3 minutes from our control. 3-methyl-1-butanol also has two peaks at 1 minute and 1.6 minutes. Our crude sample (Figure 3) clearly contains both substances with defined peaks at 1 minute, 1.6 minutes, and 3 minutes. The results of the 3rd and 6th eluent (figure 4 and 5 respectively), were not perfect. The third eluent has a large first peak, but we cannot determine which compound caused this since they both occur at 1 minute. The other two peaks are so infinitesimal that they are barely worth mentioning. Ideally, there would be a large peak at 3 minutes indicating presence of 3-methylbutyl, but this is not the case. In the sixth eluent, similar results are found, except the tiny peaks at 1.6 minutes and 3 minutes become larger. Because the peaks at 1.6 and 3 minutes are approximately at the same height in both Figure 4 and 5, I cannot conclude if we were successful in purifying 3-methylbutyl.



$$\frac{37 \text{ mol Group A}}{(6.57 \text{ mol yield})} = 3 \quad \frac{0.0625 \text{ mol glacial acetic acid}}{36 - 12x + x^2} = 3 \quad 60.05 \text{ g}$$

The yield is very low; however, we only slurped one small portion of eluent of the entire column. If a larger portion of the eluent from the column was slurped then we would obtain a higher percent yield.

Group	Mmole s 3- methyl- 1- butanol	Mmole s Glacial Acetic Acid	Class d Ratio	My calculated Ratio	$3x^2 - 37x + 108 = 0$	$= 4.74 \text{ or } 7.89$	larger than I
				Obtained Ratio			
				$[\text{3-methylbutyl acetate}] = 4.74$			
A	6.0	6.0	4.38	2.96	$3x^2 - 37x + 108 = 0$	$x = 7.89$	
B	6.0	12.0	19.4	14.5	$3x^2 - 37x + 108 = 0$	$x = 7.89$	
C	6.0	18.0	0.030	28.7	$3x^2 - 37x + 108 = 0$	$x = 7.89$	
D	12.0	6.0	0.666	.711	$3x^2 - 37x + 108 = 0$	$x = 7.89$	
Group B)		$\frac{x}{(6-x)(12-x)} = 3$	$\frac{x}{72-18x+x^2} = 3$				

$$216 - 54x + 3x^2 = x$$

$$3x^2 - 55x + 216 = 0$$

$$x = \frac{55 \pm \sqrt{433}}{6} = 5.70$$

$$\text{ratio: } \frac{5.70}{301} = 18.9 \times .786 = 14.9$$

$$\text{Group C) } x = 3 \quad x = 3$$

$$\begin{array}{c}
 \frac{(6-x)(18-x)}{324 - 72x + 3x^2} = \frac{108 - 24x + x^2}{3x^2 - 73x + 324} \\
 324 - 72x + 3x^2 = x \\
 3x^2 - 73x + 324 = 0 \\
 x = \frac{73 \pm \sqrt{1441}}{6} = 5.84
 \end{array}$$

ratio: $\frac{5.84}{160} = 36.5 \times .786 = 28.7$

Group D) $\frac{x}{(12-x)(6-x)} = 3$ see group B calculation for x

$$\begin{array}{c}
 x = 5.70 \\
 \frac{5.70}{6.30} = 0.905 \times .786 = 0.711
 \end{array}$$

Groups A, B, and D seem to have reasonable results based on my calculations. The K_{eq} used for calculations was given at 3, which is probably a very approximate K_{eq} . I also assumed that this reaction is a 1:1 ratio, and my calculations would be incorrect if it was not a 1:1 ratio. The calculations seem to be consistent with the majority of the results (exception with group C), so I believe it is a 1:1 ratio. See table above to see calculated ratio results.

By increasing the amount of 3-methyl-1-butanol, the ratio will be decreased. This makes sense because the ratio is 3-methylbutyl acetate divided by 3-methyl-1-butanol. By adding additional 3-methyl-1-butanol, the ratio will be smaller because it is being divided by a larger number.

By Le Chatlier's principle, when additional reactant is added, the equilibrium will shift toward the products. The results are consistent with Le Chatlier's principle, because when more reactant was used in a group, the ratio was higher because the product is in the numerator of the ratio. Group C's data did not follow this trend, so instead I used my calculated ratio using ICE and K_{eq} which followed the trend. The only anomaly was group D, in which it was divided by a very large 3-methyl-1-butanol, creating a very small ratio.

Conclusion:

Our ratio using GC area under the curve was .666 which compared nicely to a .711 calculation based on ICE and K_{eq} . The GC results were not optimal, which made it difficult to determine what was present in each eluent. There were also some issues with our column when the sand shifted from adding liquids to the top.