

**Title: Organometallic complexes:
synthesis, spectroscopy, and
electrochemistry.**

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CHM 240 (Research in Chemistry)
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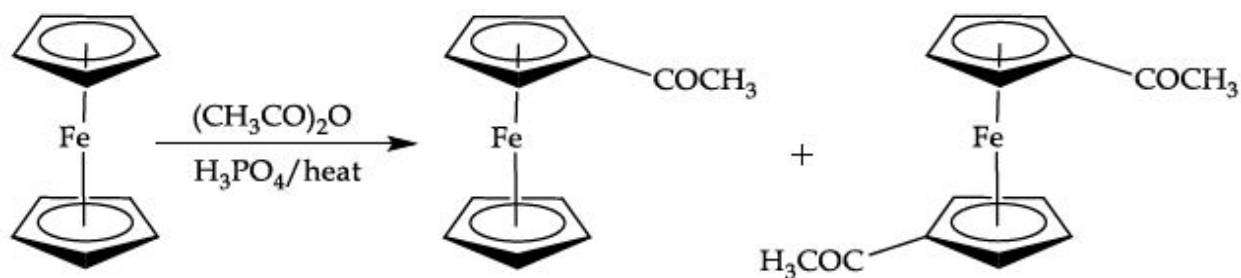
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Abstract: The synthesis of Mono acetylferrocene [$\text{Fe}(\text{C}_5\text{H}_4\text{COCH}_3)(\text{C}_5\text{H}_5)$] prepared by the refluxing of a mixture of Ferrocene [$\text{C}_{10}\text{H}_{10}\text{Fe}$], acetic anhydride [$\text{C}_4\text{H}_6\text{O}_3$], and 85% Phosphoric acid [H_3PO_4]. The collected product was worked up and separated from the water layer to obtain the organic layer. The product was later investigated to see if it contained acetylferrocene by TLC, UV-Vis, IR, and electrochemistry. Then this was refined to remove all impurities and collect pure acetylferrocene. Another result that was observed was the attempt to synthesize 1,1' Diacetylferrocene [$\text{Fe}(\text{C}_5\text{H}_4\text{COCH}_3)_2$] from ferrocene following the same steps but with the substitution of phosphoric acid for aluminum chloride [AlCl_3]. In the process multiple techniques were also learned to identify these compounds and differentiate them from each other.

Introduction: Synthesis of various organometallic compounds derived from the mother compound (ferrocene). Both professor Ernst Otto Fischer and Professor Geoffrey Wilkinson published their independent works in the 1950s, this lay way to a new interest to these compounds which before were thought to not be possible to make. Their pioneering works on transition metals and the development of the sandwich compound has started a new branch of chemistry, organometallics.

Experimental Section:

Synthesis process: In this reaction One of Ferrocenes' ring was acylated by acetic anhydride under moderate conditions using Phosphoric Acid as the catalyst. This is basically a Friedel-Crafts acylation reaction.



Ferrocene(98%)

**Mono
AcetylFerrocene**

1,1'-Di AcetylFerrocene

Sublimation: All available compounds were sublimed to get them to its purest form. As seen in the pictures, the technique that was used involved 2 Petri dishes and heating the compounds to their respected melting point. These were collected and tested for purity with melting point and TLC plate.



180° C



Procedure: This was followed as shown in the pictures a reflux of the mixture was done, later a workup to separate the water and organic layer (The separation consisted of 3 washes of 10 ml of ethyl acetate to the water layer.)

The unknown substance was then collected to be checked by TLC.

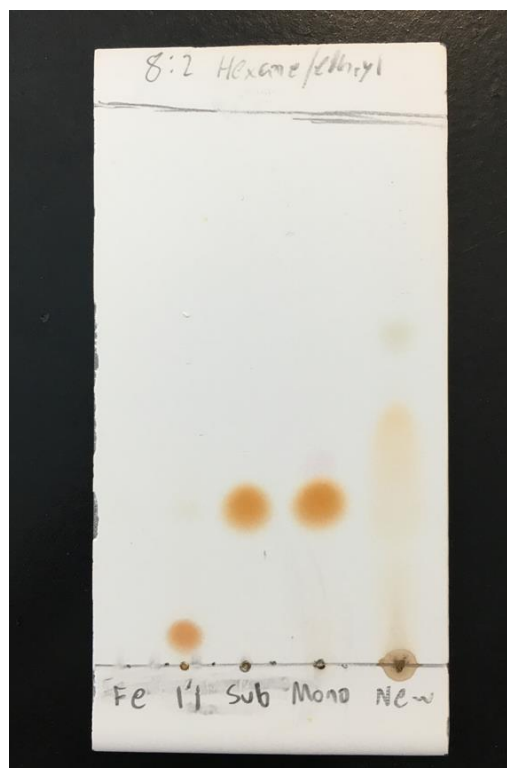
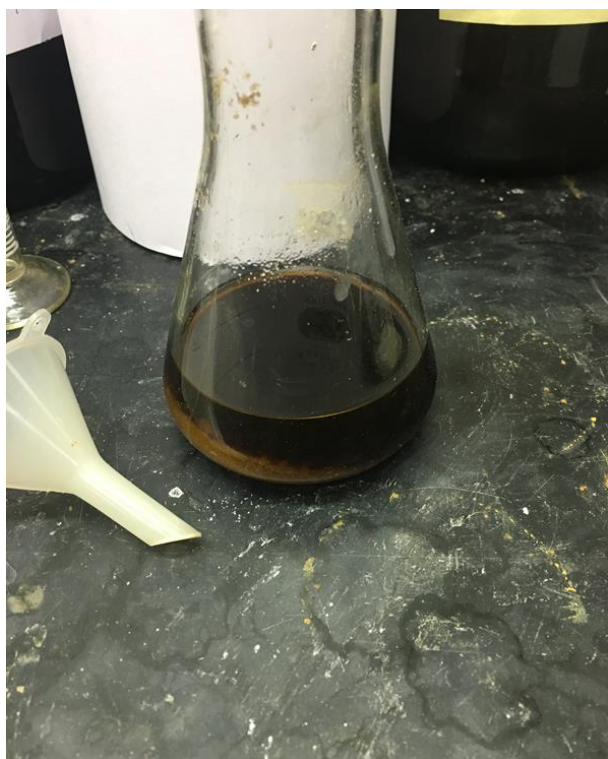
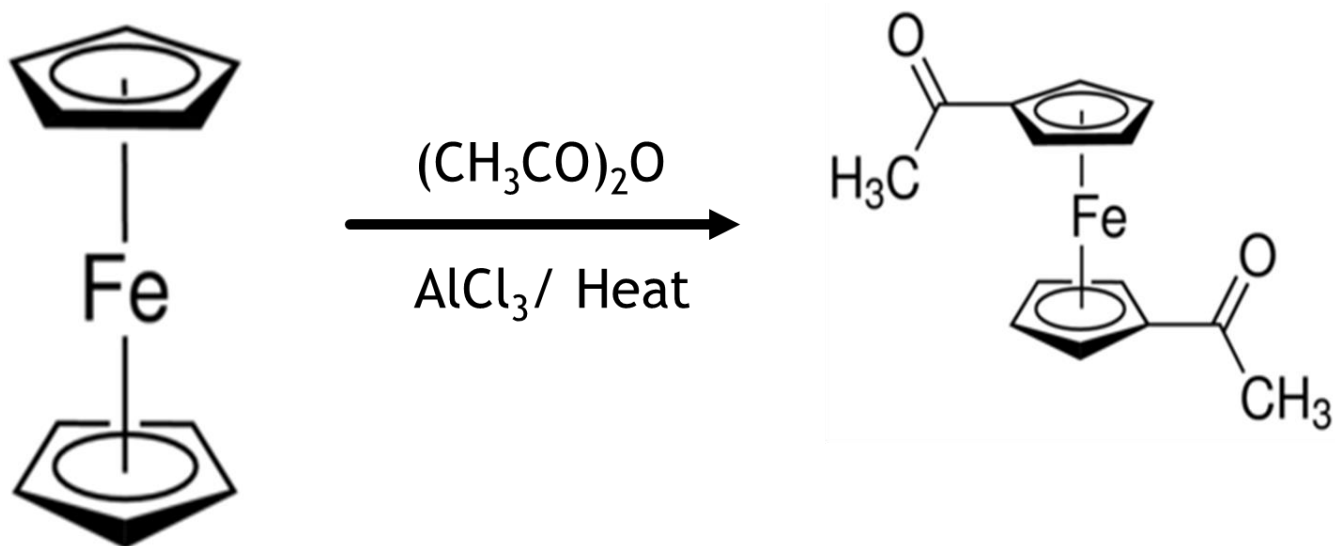
- Mixture included: 1.5mg of Ferrocene and 5mL of Acetic anhydride.
- To this mixture(drops) 1mL of 85% Phosphoric acid was added.
- Reflux the reaction mixture for 1 hour.
- Pour the heated mixture onto 10g of ice.
- When all the ice melts, it was neutralize with sodium bi carb(NaHCO_3) until CO_2 is no longer evolved.
- Work up is done to separate the organic layer from the water layer.*



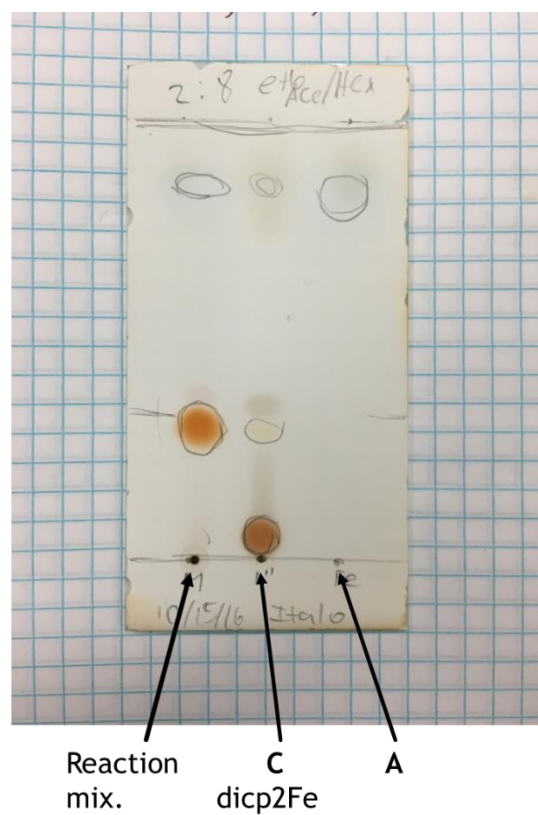
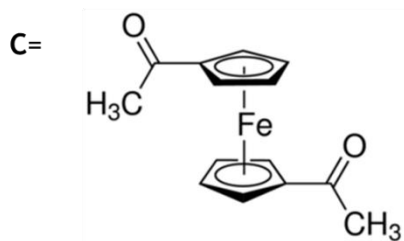
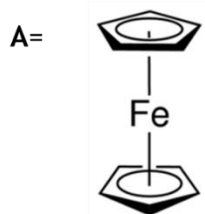
Procedure Results: theoretical yield was assumed to be 1.84g. but the actual yield after the main procedure was 1.40g.

Synthesis of 1,1'-diacetylferrocene: The Attempt to synthesize di compound using a newer method with the same starting material but aluminum chloride instead of phosphoric acid. As seen in the picture of the result, we see the compound actually oxidized and turned a dark color. This sample was still spotted on a TLC plate and as shown, did not seem to have any of the 1,1'diacetylferrocene, just unknown spotting.

The experiment was ruled out as not possible to be done or recreated in the lab with materials and hardware available.



TLC Observation: An unknown spot on Rf point 0.3 that does not match any of the other 2 compounds we have in lab was seen. This unknown shows some traces of Ferrocene which seems to be from unreacted starting material. This could have been avoided by letting the reaction run longer to fully react all the ferrocene. (TLC was done in 80% hexane and 20 % ethyl acetate).

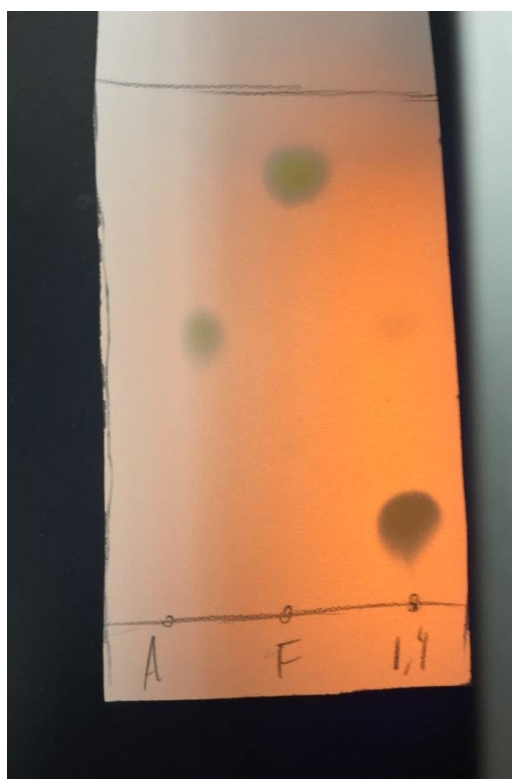


Column Chromatography: After the TLC plate was shown to have an unknown substance, the same TLC solvent system was used (80% hexane and 20% ethyl acetate), and silica to remove impurities and isolate the unknown compound.

A Total of 9 Fractions were collected from the column and impure fractions were discarded.



CC Conclusion: The collected pure unknown compound was put through TLC with the other derivatives to test the difference, its pure yield was 0.672g. from the original 1.40g.



Melting Point: Once an unknown substance was seen on the tlc plate and collected in purest form it was tested by melting point 3 times to verify it is monoacetylferrocene, Test 1: 80~83°C, Test 2: 80.5~83°C, and Test 3: 81 ~ 83°C.

Monoacetylferrocene MP= 81~83°C

After monoacetylferrocene was shown to be the unknown it and its derivatives were tested by multiple instruments to find the characteristics and differences of these organometallic compounds

Instrumentation: Ultraviolet-Visible Scanning Spectrophotometer and Ultraviolet-Visible fixed wavelength Spectrophotometer.

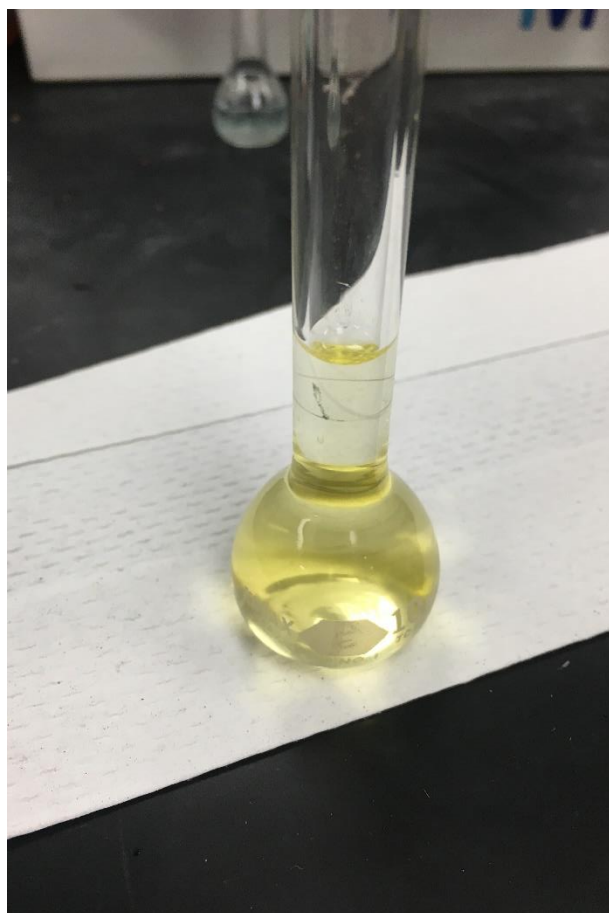
Preparation: 3 solutions were made of the ferrocene and its derivatives of 1×10^{-3} Molarity.

In addition, a solution containing 0.1M $\text{Ce}(\text{NH}_4)_2\text{SO}_4$ in water was made to observe the possible oxidation of the compound. Oxidation did not take place when 4 tests were done at different concentrations.

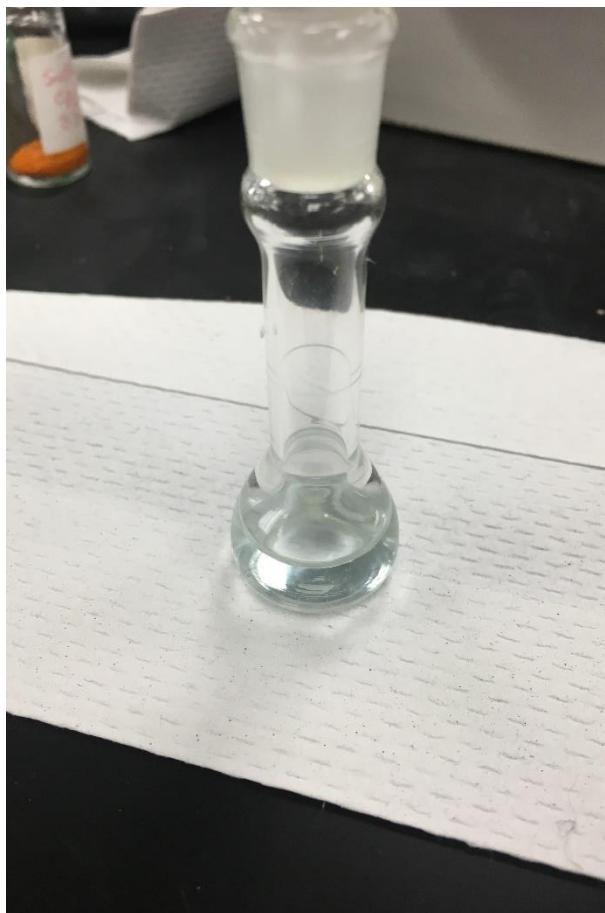
Tests	Concentration (0.1M : 1×10^{-3} M ferrocene sol.)	Results (visible oxidation)
#1	1:12	No change in color/ no oxidation
#2	4:10	No change in color/ no oxidation
#3	6:11	No change in color/ no oxidation
#4	13:21	No change in color/ no oxidation

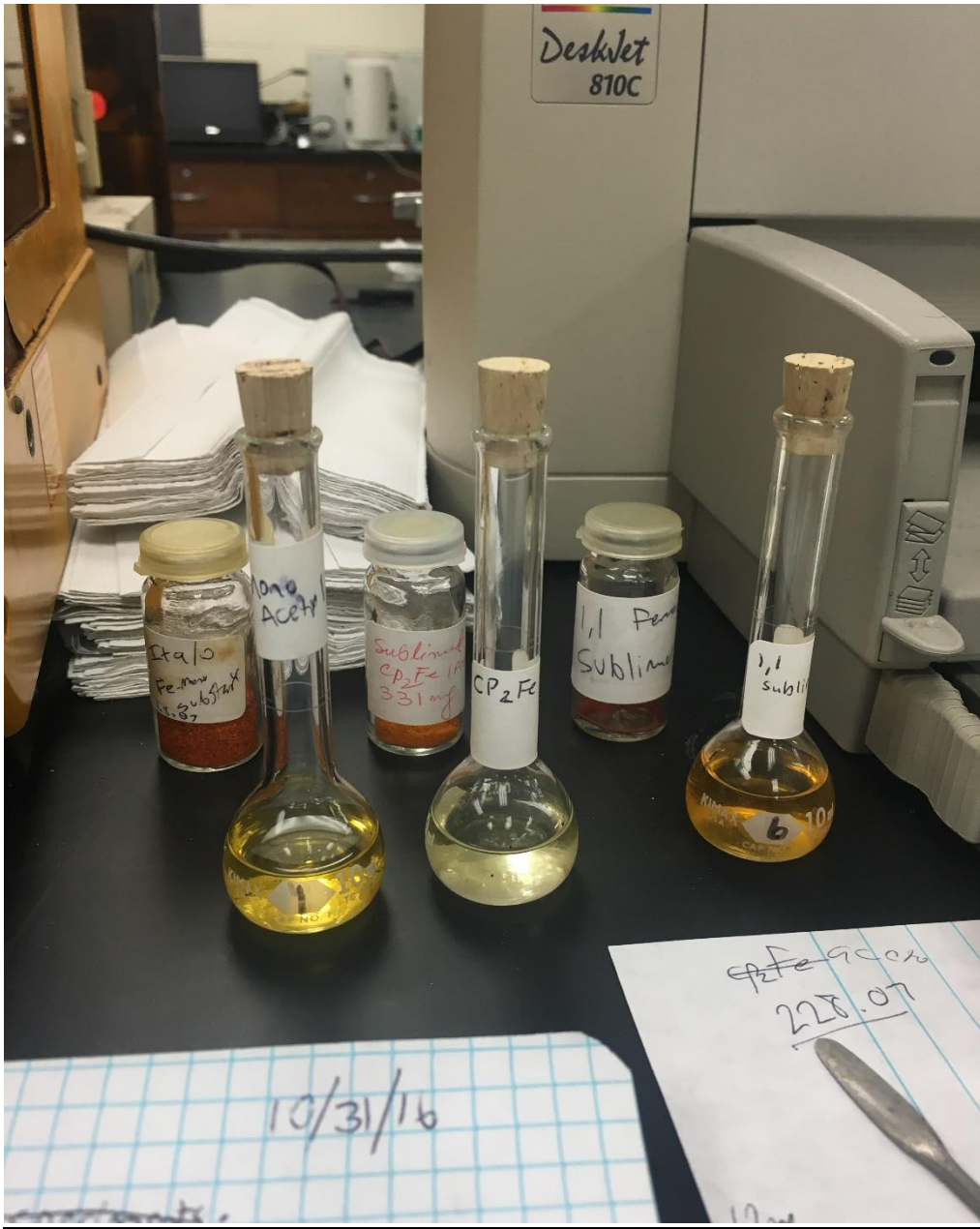
In conclusion, results show no oxidation with the 4 tests. A positive observation would have resulted into the blueish color (2) from the yellowish solution (1).

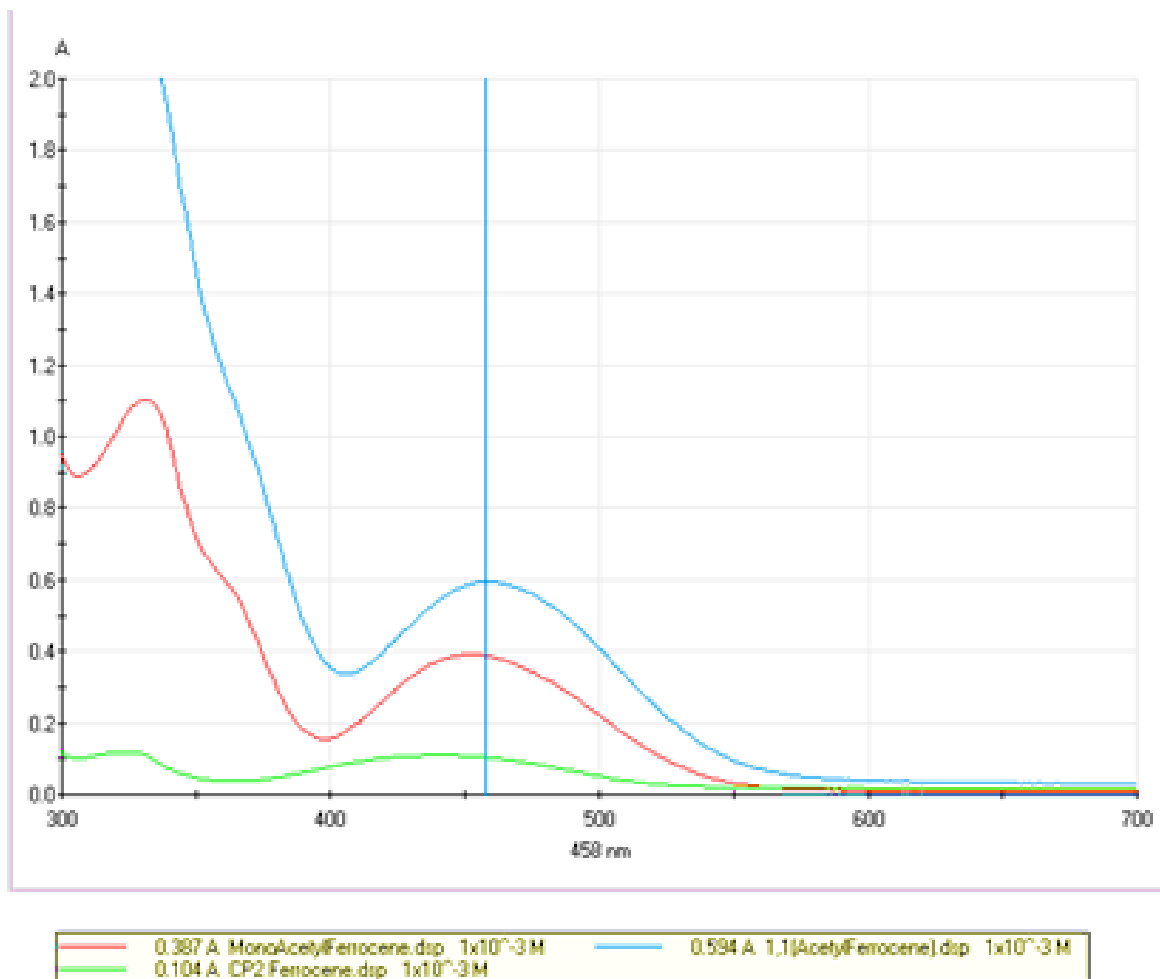
1



2







UV-Vis Results: The UV-visible spectrum graph shows the significant shifts. This is due to the electron withdrawing groups in the compounds and the lack of them in the ferrocene compound. In addition, a higher absorption is seen from mono acetylferrocene compared to ferrocene and smaller jump from mono to diacetylferrocene. The higher the epsilon value the greater the color intensity will be (as seen in the picture above).

Ferrocene, λ_{\max} : 440nm, ϵ : 110

Monoacetylferrocene, λ_{\max} : 455nm, ϵ : 391

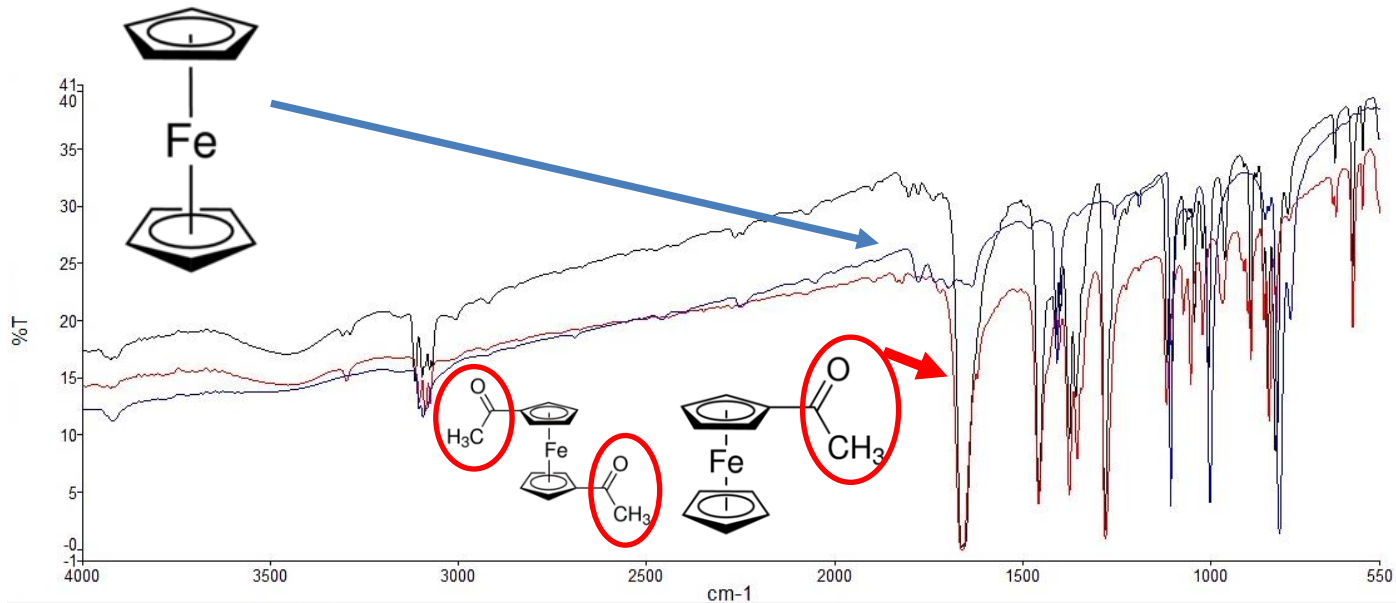
1,1'-Diacetylferrocene, λ_{\max} : 459nm, ϵ : 594

$$\epsilon = A / [\text{concentration}]$$

$$A = \epsilon cl$$

Infrared Characteristics: As shown in the graph below, ferrocene does not produce the same absorption stretch as 1,1'-diacetylferrocene and monoacetylferrocene.

It does not produce a stretch at the 1700 mark because of its lack of a carbonyl group unlike the others. Which is specific to this region.

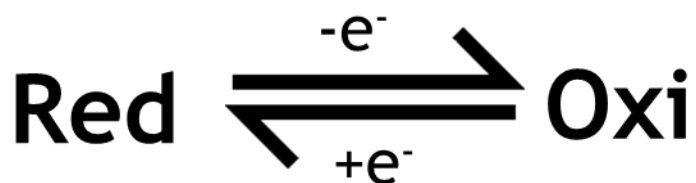


Name	Description
italo mono	Sample 191 By student Date Monday, Octo...
1'1 di	Sample 198 By student Date Monday, Octo...
ferrocene	Sample 197 By student Date Monday, Octo...

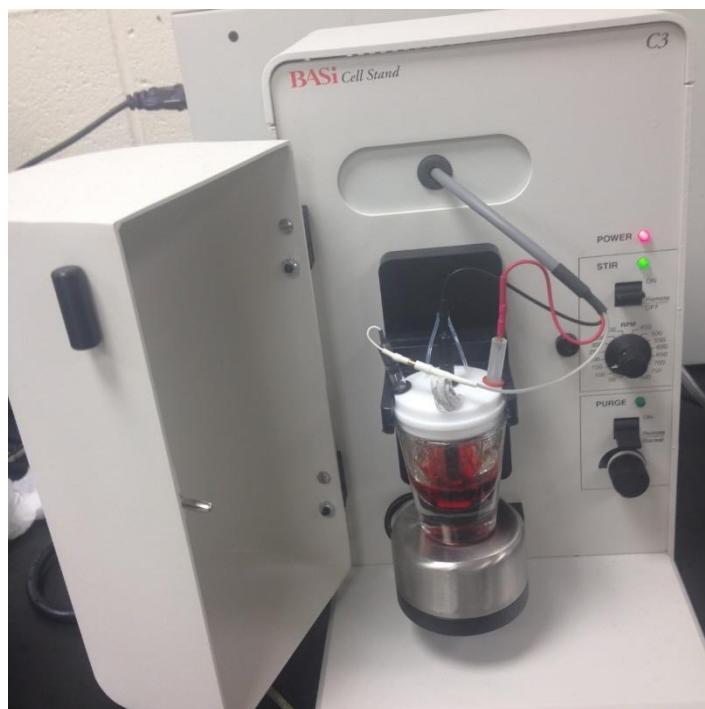
Electrochemistry (CV): Cyclic voltammetry is one of many techniques to measure redox potentials. CV is similar to a linear sweep, meaning when the current cycle begins the electrolysis product is either oxidized or reduced, now the scan doesn't stop but continues in reverse as we convert the electrolysis product back to the starting reactant. Only if REVERSIBLE.

The closer the peak current is to -1 (i_{pa}/i_{pc}) and the difference of the 2 peak potentials, ΔE , which in the ideal case should be 59mV, then the more fully thermodynamically reversible the reaction is.

In this case all work was done using a glossy carbon electrode and all scans were done in acetonitrile and 0.1M tetra butyl ammonium tetra fluoborate.



$$|E_{pc} - E_{pa}| = \Delta E = \frac{2.3RT}{nF} = 59\text{mV}$$

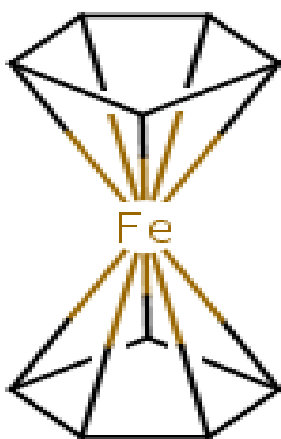


Determination of ΔE and $E_{1/2}$: ΔE is thermodynamically change. $E_{1/2}$ can be used to identify the unknown species while the height of the limiting current can determine the concentration

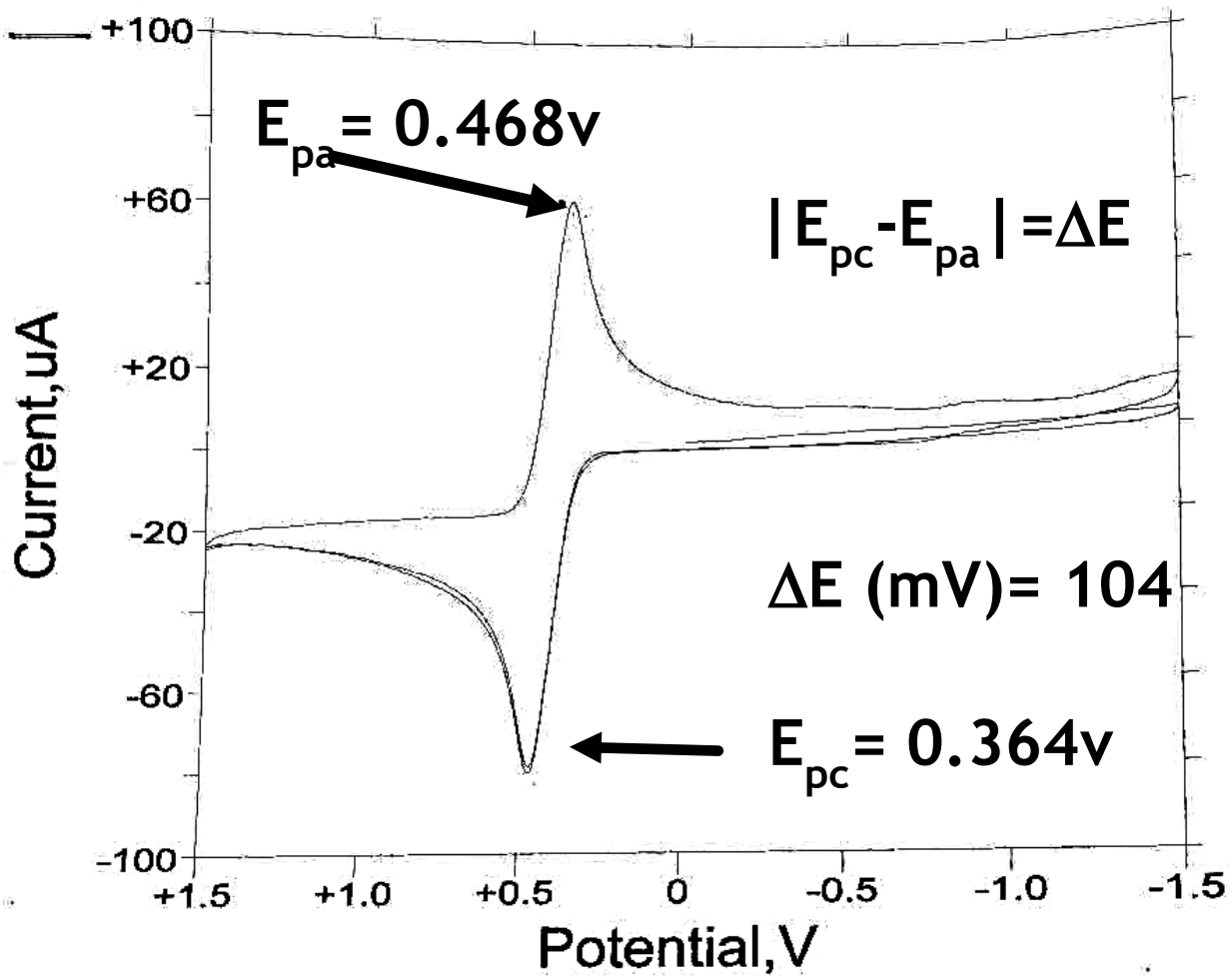
$$|E_{pc} - E_{pa}| = \Delta E$$

$$E_{1/2} = E_{pa} + E_{pc} / 2$$

Cyclic Voltammetry of ferrocene: The results on 100mV show a quasi-reversible system due to the $E_{1/2} = 0,416V$ and the $\Delta E = 104mV$ but it's not 56.



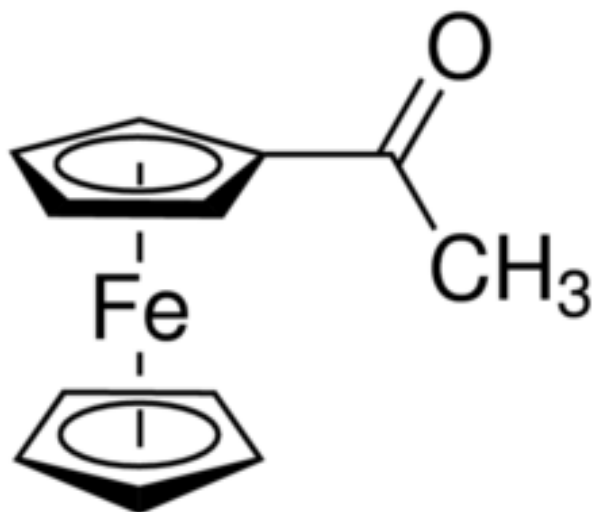
Scan Rate	$E_{pa}(V)$	$E_{pc}(V)$	$E_{1/2}(V)$	$\Delta E(mV)$	I_{pa}/I_{pc}	conclusion
100mV	0.468	0.364	0.416	104	-1.0	Quasi-reversible
200mV	0.478	0.356	0.417	122	-0.99	Quasi-reversible
400mV	0.492	0.340	0.416	152	-0.98	Quasi-reversible



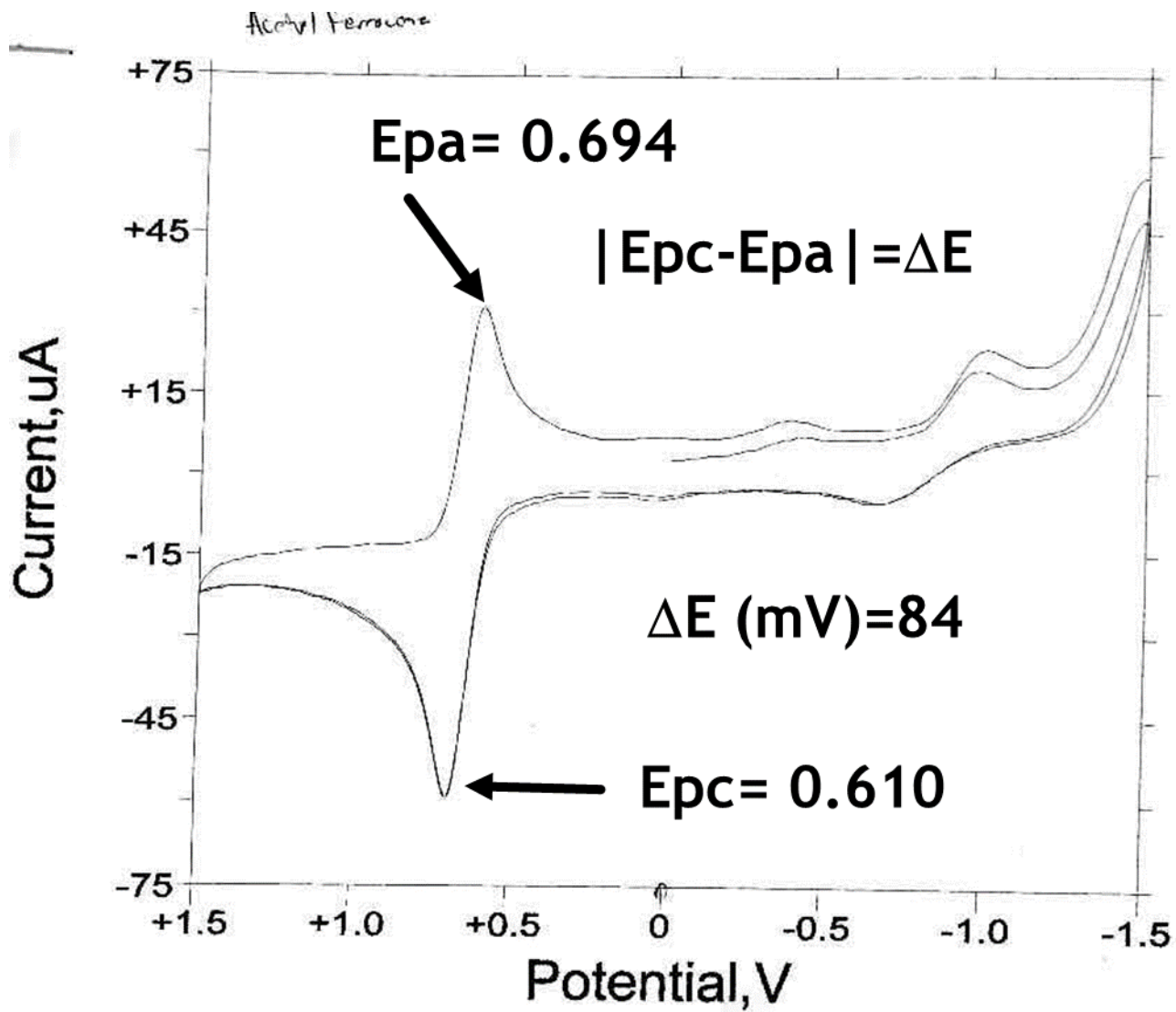
26-Oct-2016
 15:45:39
 Mode: CV
 Init E (mV) = 0
 High E (mV) = 1500
 Low E (mV) = -1500
 Init P/N = N
 V (mV/s) = 100
 Sweep Segments = 4
 Smpl Int (mV) = 2
 Quiet T (s) = 2
 Sens (A/V) = 1E-4

Segment 2:
 Ep (mV) = +468 - a
 ip (A) = -7.7350E-5
 Ah (A*V) = -5.7539E-6
 Segment 3:
 Ep (mV) = +364 - c
 ip (A) = +7.6722E-5
 Ah (A*V) = +5.8148E-6
 Segment 4:
 Ep (mV) = +470
 ip (A) = -7.7623E-5
 Ah (A*V) = -5.9606E-6

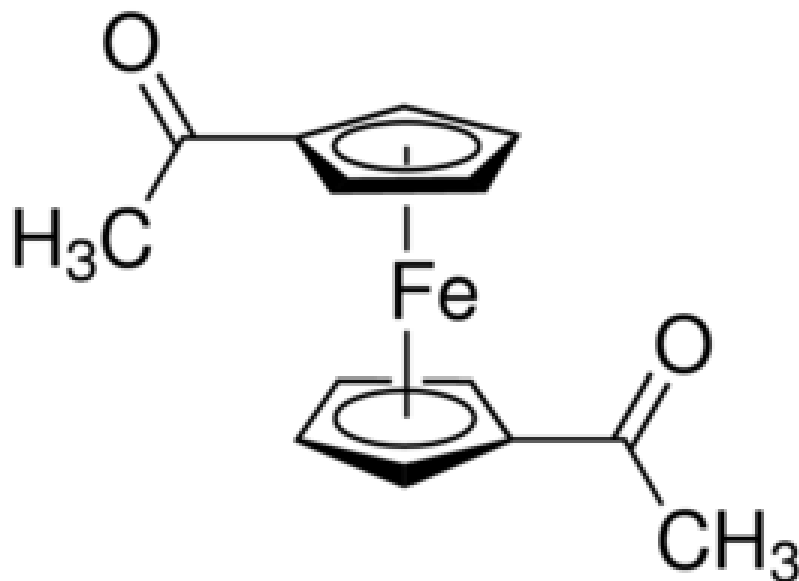
Cyclic Voltammetry of acetylferrocene: The results on 100mV show a quasi-reversible system due to the $E_{1/2} = 0,652V$ and the $\Delta E = 84mV$ but it's not 56.



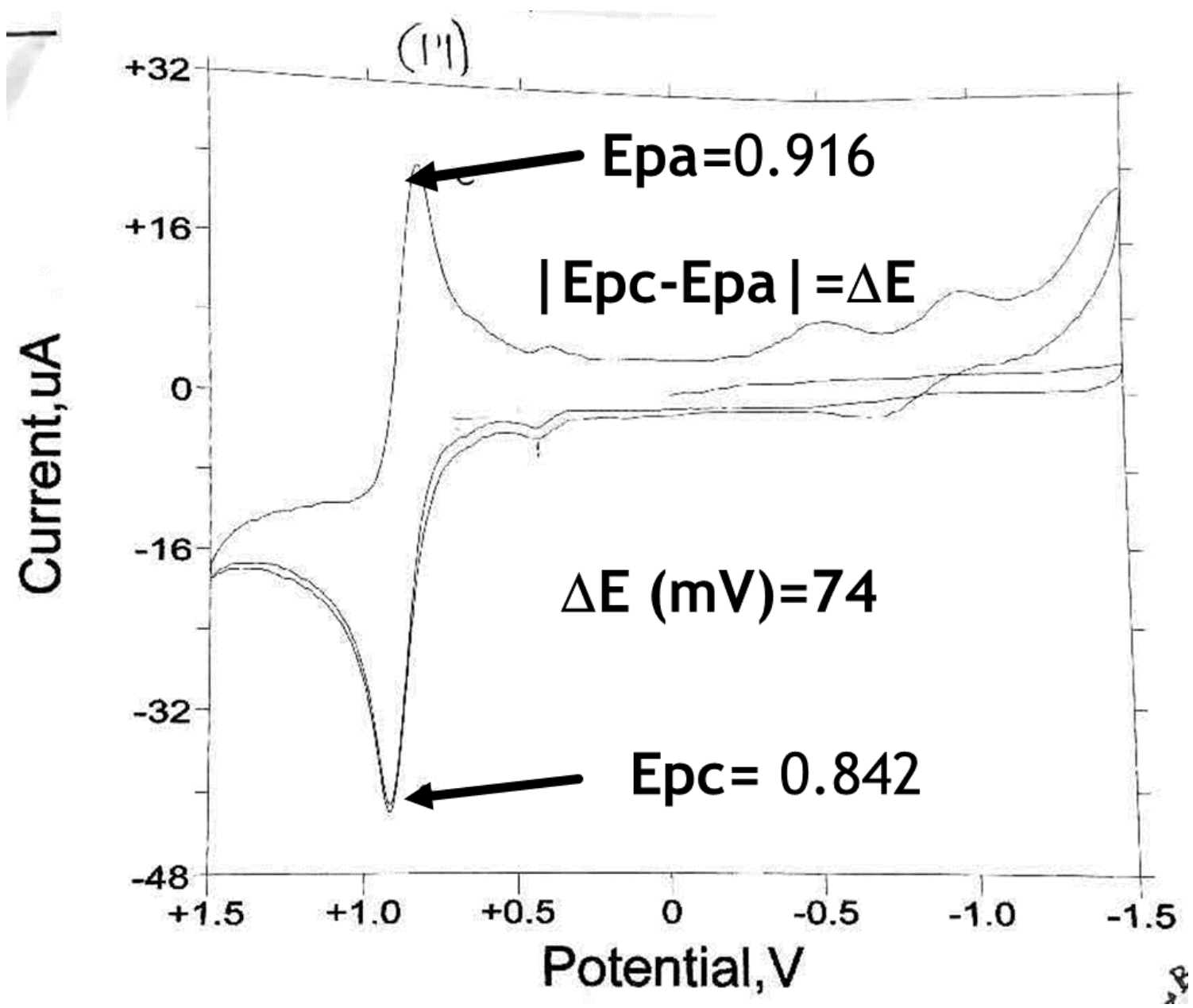
Scan Rate	E _{pa} (V)	E _{pc} (V)	E _{1/2} (V)	ΔE(mV)	I _{pa} /I _{pc}	conclusion
100mV	0.694	0.610	0.652	84	-1.18	Quasi-reversible
200mV	0.700	0.596	0.648	104	-1.11	Quasi-reversible
400mV	0.710	0.582	0.646	128	-1.04	Quasi-reversible



Cyclic Voltammetry of diacetylferrocene: The results on 100mV show a quasi-reversible system due to the $E_{1/2} = 0,652V$ and the $\Delta E = 84mV$ but it's not 56.



Scan Rate	E _{pa} (V)	E _{pc} (V)	E _{1/2} (V)	ΔE(mV)	I _{pa} /I _{pc}	conclusion
100mV	0.916	0.842	0.879	74	-0.95	Quasi-reversible
200mV	0.920	0.830	0.875	90	-1.04	Quasi-reversible
400mV	0.928	0.824	0.876	104	-1.03	Quasi-reversible



Results and Discussion: The synthesis of monoacetylferrocene was successful but the synthesis of 1,1' diacetylferrocene was not. This was believed to be because the aluminum chloride could not be completely free of water or it was impure. This could have been changed by either getting another aluminum chloride or doing this experiment in a vacuum box.

Scan Rate (100V)	$E_{1/2}$ (V)	Abs (I_{pa}/I_{pc})	ΔE (mV)
1,1'-diacetylferrocene	0.879	-0.95	74
Acetylferrocene	0.652	-1.18	84
Ferrocene	0.416	-1.0	104

As we see from the difference of the 3 compounds results of the cyclic voltammetry, it shows the clear addition of electron withdrawing group from ferrocene $0.416 + 0.236 = 0.652 =$ acetylferrocene $+ 0.227 = 0.879 =$ 1,1' diacetylferrocene.

Withdrawing group adds about $0.227 \sim 0.236$.

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References:

- ▶ **1. R.J. Graham, R. V. Lindsey, G.W. Parshall, M.L. Peterson, and G. M. Whitman, J. Am Chem soc.,79,3416 (1957).**
- ▶ **2. J. C. Gilbert and S. A. Monti, J. Chem. Edu., 50, 369(1973).**
- ▶ **3. Synthesis and characterization of inorganic compounds, Prentice-Hall, Inc. Englewood Cliffs, N.J.; William L. Jolly.**