(Hexamethylbenzene)Ru Complexes for the Aldehyde-Water Shift Reaction

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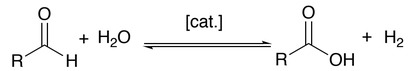
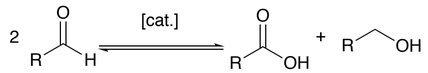
PURM Penn Undergraduate Research Mentoring Program

Introduction

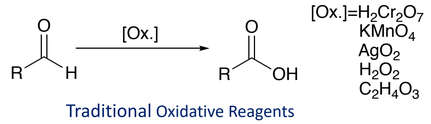
Aldehyde-Water Shift Reaction



Aldehyde Disproportionation



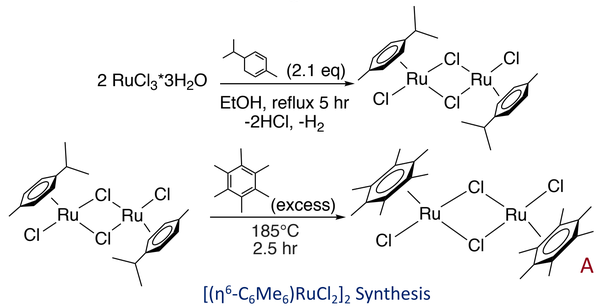
- Carboxylic acids are biologically and industrially useful
- Traditional oxidative techniques require stoichiometric amounts of toxic reagents
- The Aldehyde-Water Shift (AWS) is environmentally friendly, using H_2O as the oxidant[1, 2]
- H_2, industrially useful, is released
- Disproportionation is an unfavorable side reaction
- Previous work in the Goldberg group studied Ir, Rh, Ru complexes[3, 4]



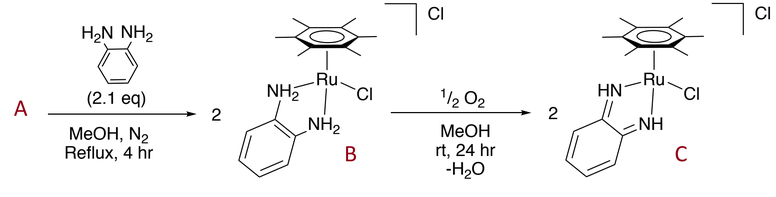
Traditional Oxidative Reagents

Precatalyst Syntheses

- Syntheses were performed under inert atmosphere using Schlenk techniques



$[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ Synthesis

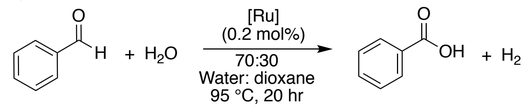


$[(\eta^6\text{-}C_6Me_6)Ru(o\text{-}pda)Cl]Cl$ Synthesis

$[(\eta^6\text{-}C_6Me_6)Ru(o\text{-}bdqi)Cl]Cl$ Synthesis

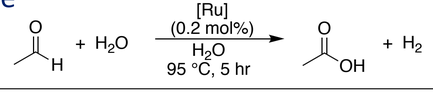
Precatalyst Performance

Benzaldehyde



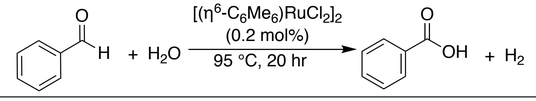
Precatalyst	Acid Yield (%)	Alcohol Yield (%)	Acid Selectivity (%)
A	24.4 ± 1.0	8.5 ± 0.5	74.3 ± 0.1
B	10.1 ± 0.2	1.1 ± 0	90.2 ± 0.3
C	4	-------	100

Acetaldehyde



Precatalyst	Acid Yield (%)	Alcohol Yield (%)	Acid Selectivity (%)
A	64.6 ± 1.5	6.5 ± 0.5	90.0 ± 0.5
B	58.9 ± 2.2	4.6 ± 1.0	92.9 ± 1.2
C	44.8 ± 1.6	4.4 ± 2.1	91.2 ± 3.5

Buffered Solution Performance

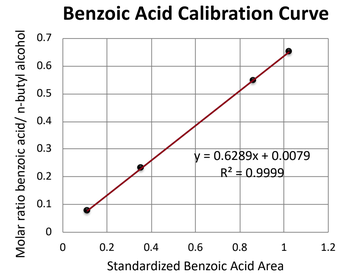


Phosphate Buffer pH	H_2O: 1,4-dioxane	Acid Yield (%)	Alcohol Yield (%)	Acid Selectivity (%)
7 (0.25 M)	70:30	30.0	8.5 ± 0.5	86.1
7 (0.25 M)	100:0	18.1	1.1	81.0
6 (0.25 M)	100:0	11.2 ± 0.9	6.2 ± 0.7	63.7 ± 4.2
6 (0.1 M)	100:0	10.7	3.1	72.5

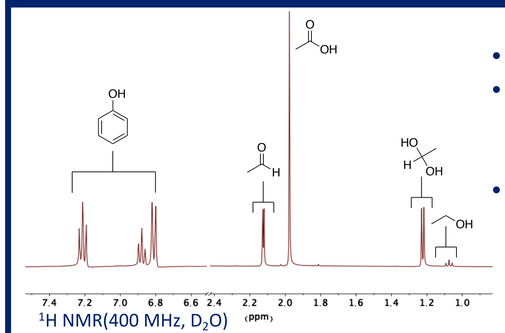
- In neutral solutions, the majority of benzoic acid exists as benzoate, requiring an acidic workup
- Solubility problems in 100% aqueous systems

Benzaldehyde Quantification Method

- Gas chromatography (GC-FID) calibration curve for substrate and each possible product gives relative concentrations
- *n*-butyl alcohol standard



Acetaldehyde Quantification Method

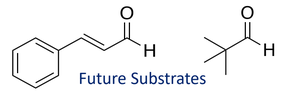


^{1}H NMR(400 MHz, D_2O)

- ^{1}H NMR
- 0.25 M phenol in D_2O standard added for quantification
- Integration of peaks gives ratio of products

Conclusion

- Precatalyst **A** was the most successful tested, so further testing with various aldehyde substrates will be done
- Preliminary work suggests a near neutral buffered system increases acid yield



Future Substrates

References

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2. Ou, W. C.; Cundari, T. R., DFT Modeling of the Aldehyde–Water Shift Reaction with a Cationic Cp*Ir Catalyst. *ACS Catal.* **2015**, *5*, 225-232.
3. Brewster, T. P.; Ou, W. C.; Tran, J. C.; Goldberg, K. I.; Hanson, S. K.; Cundari, T. R.; Heinekey, D. M., *ACS Catal.* **2014,** *4*, 3034-3038.
4. Brewster, T. P.; Goldberg, J. M.; Tran, J. C.; Heinekey, D. M.; Goldberg, K. I., High Catalytic Efficiency Combined with High Selectivity for the Aldehyde–Water Shift Reaction using (para-cymene)Ruthenium Precatalysts. *ACS Catal.* **2016**, 6302-6305.

Acknowledgements

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