

## Rh-Catalyzed Oxidative Carbonylation of Toluene to *p*-Toluic acid

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### Introduction

Pd- and Rh-based catalysts are known to activate C-H bonds for the oxidative carbonylation of arenes to the corresponding aromatic acids in the presence of carbon monoxide [1-2]. The reaction is thought to proceed through an electrophilic mechanism [3] and utilizes an oxidant, such as Cu, Fe, Mn, V compounds, to regenerate the active noble metal center [4-6]. Systems with vanadium in the presence of oxygen are particularly interesting because they improve significantly the rate of noble metal re-oxidation compared to systems simply using oxygen. The present study was undertaken to investigate systems the oxidative carbonylation of toluene to toluic acid catalyzed by Rh. The principal objective was to identify the steps in the reaction mechanism that are involved in the formation of toluic acid and the reoxidation of Rh.

### Materials and Methods

Reactions were conducted in a stirred, 50 mL Parr autoclave made of Hastelloy C. During typical reactions, anhydrous toluene, trifluoroacetic acid and its anhydride, Rh(acac)<sub>3</sub>, NH<sub>4</sub>VO<sub>3</sub> were placed into the autoclave, which was sealed and purged with nitrogen or helium. After purging, the reactor was pressurized at with O<sub>2</sub> and CO and heated to 353K for four hours. Upon completion of the reaction, the reactor was quenched with ice water to 308K and vented. Deionized water was added to work-up the reactor contents and extract the trifluoroacetic acid from the organic phase. The concentration of toluic acid in the organic phase was determined by gas chromatography. GC-MS was used to identify unknown products and UV-Visible spectroscopy used to characterize the oxidation states of the vanadium species.

### Results and Discussion

The Rhodium-vanadium system was investigated to determine the influence of reaction conditions on the rate *p*-toluic acid synthesis. The effects of temperature, O<sub>2</sub> and CO partial pressure, anhydride concentration, oxidants, catalysts, and time on catalytic activity and selectivity were investigated. The results of this work lead to the mechanism shown in Figure 1. Two cycles are identified. In the first Rh(III) activates toluene to form a aryl intermediate into which CO then inserts. The mixed anhydride of toluic and trifluoroacetic acids is formed and concurrently Rh(III) is reduced to Rh(I). Rh(I) is reoxidized to Rh(III) by VO<sub>2</sub>(TFA). The VO(TFA)<sub>2</sub> formed in this process is then oxidized by O<sub>2</sub>. The water content in vanadium-rhodium systems strongly influences the catalytic activity; excess water severely reduces catalytic activity, but insufficient water prevents vanadium re-oxidation by oxygen. The water content in the system is controlled by the concentration of anhydride present. Increased vanadium content increases the rhodium activity; however, the moles of toluic acid formed per mol of vanadium remains constant. A maximum in the yield of toluic acid occurs with increasing CO partial pressure, but yield increases monotonically with O<sub>2</sub> partial pressure. The yield of toluic acid increases with time but the selectivity to the *para* isomer decreases because of isomerization to the *ortho* and *meta* isomers. Conversion to toluic acid increases with

increasing temperature but the *p/m* and *p/o* isomer ratios decrease. Turnover numbers based on Rh of 700 were observed for a reactions occurring over a 4 h period.

### Significance

A detailed understanding of the elementary processes by which toluene undergoes oxidative carbonylation to toluic acid has been established. The results of this study show that high yields of *p*-toluic acid require the use of moderate temperature, and CO partial pressures, and a high O<sub>2</sub> partial pressure. This work also shows that the management of water concentration is critical.

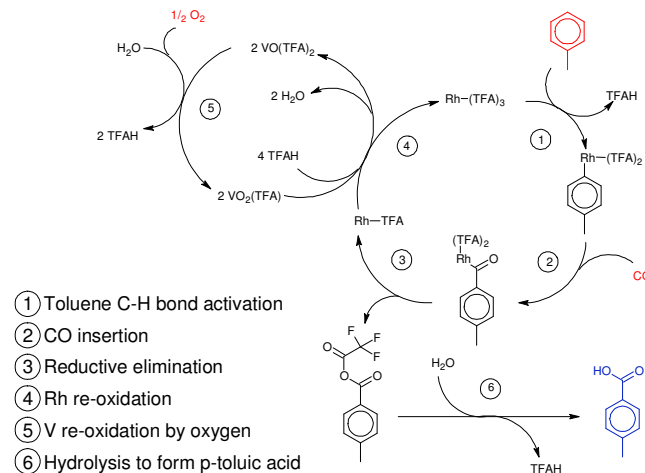


Figure 1. Proposed mechanism for oxidative carbonylation of toluene to *p*-toluic acid.

### References

1. Fujiwara, Y., Kawata, I., Sugimoto, H., Taniguchi, H. *J. Organometal. Chem.* 256 C35-C36 (1983).
2. Sugimoto, H., Kawata, I., Taniguchi, H., Fujiwara, Y. *J. Organometal. Chem.* 266 C44-C46 (1984).
3. Jintoku, T. Fujiwara, Y., Kawata, I., Kawauchi, T., Taniguchi, H. *J. Organometal. Chem.* 385 297-306 (1990).
4. Kalinovskii, I., Lescheva, A., Kuteinikova, M., Gel'bshtein, A. Translated from *Zhurnal Obshchei Khimii*, Vol. 60, No. 1, 123-130 (1990).
5. Kalinovskii, I., Pogorelov, V., Gelbshtein, A., Akhmetov, N. *Russ. J. Gen. Chem.* Vol. 71, No. 9, 1457-1462 (2001).
6. Kalinovskii, I., Gel'bshtein, A., Pogorelov, V. *Russ. J. Gen. Chem.* Vol. 71, No. 9, 1463-1466 (2001).