# Catalytic Transfer Hydrogenation of Benzaldehyde in a Microwave Oven

Edward M. Gordon,* Daniel C. Gaba, Kimberly A. Jebber, and
Dawne M. Zacharias

*Department of Chemistry, Baldwin-Wallace College, Berea, Ohio 44017*

*Received July 19, 1993*

*Summary: The catalytic transfer hydrogenation of benzaldehyde catalyzed by (carbonyl)chlorohydridotris-(triphenylphosphine)ruthenium(II) was carried out in a sealed Teflon vessel using a household microwave oven as the heat source. Carrying out the reaction in the microwave oven produced an improvement in the average catalytic turnover rate from 280 to 6700 turnovers/h in comparison with traditional reflux heating.*

## Introduction

The past decade has witnessed the introduction of the microwave oven to the chemical laboratory. The early uses of the microwave oven focused on the area of analytical chemistry where the microwave oven is primarily used to rapidly prepare samples for further analysis.[1] More recently, studies of the effect of a microwave oven on reaction chemistry such as the recent report by Landry and Barron of the solid state synthesis of $CuInS_2$ have received increasing attention.[2] This note describes the examination of an organic reaction that is catalyzed by a transition metal compound. In this study, we examined the effect of using microwave radiation as a heat source upon the catalysis of the reaction.

The specific reaction described herein is the catalytic transfer hydrogenation of benzaldehyde. This note compares the catalytic activity of $RuHCl(CO)(PPh_3)_3$ for the transfer hydrogenation of benzaldehyde under three heating conditions. The three heating methods examined were traditional heating to reflux with a heating mantle, intermittent heating in a microwave oven, and persistent heating in the microwave oven. The specific transfer hydrogenation reaction studied was originally reported by Watanabe and co-workers and is shown in Scheme I.[3] The catalyst promotes the transfer of two hydrogen atoms from formic acid to benzaldehyde to give benzyl alcohol. Because formic acid is still present as the benzyl alcohol is formed, a secondary esterification occurs, giving benzyl formate. The microwave oven reactions were carried out in a sealed microwave digestion vessel setup like the one
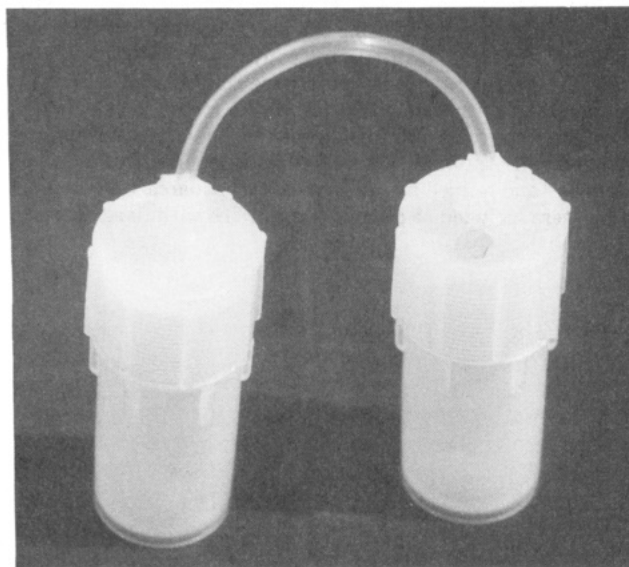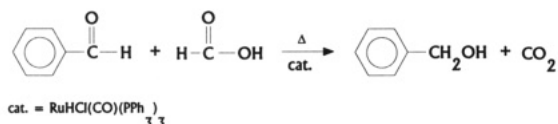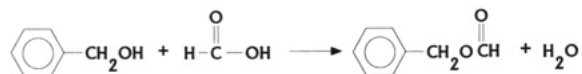


**Figure 1.** Photograph of the Teflon digestion vessel setup used in the microwave oven reactions.

**Scheme I**

PRIMARY REACTION

$$\text{PhCHO} + \text{HCO}_2\text{H} \xrightarrow[\text{cat.}]{\Delta} \text{PhCH}_2\text{OH} + \text{CO}_2$$

cat. = $RuHCl(CO)(PPh_3)_3$

SECONDARY REACTION

$$\text{PhCH}_2\text{OH} + \text{HCO}_2\text{H} \longrightarrow \text{PhCH}_2\text{OCH(O)} + \text{H}_2\text{O}$$

shown in Figure 1. The setup shown in Figure 1 includes a 140-mL vessel with a pressure release valve connected to a relief vessel.

## Experimental Section

All the reactions compared here were run in the absence of solvent with the same relative mole ratios of formic acid:$RuHCl(CO)(PPh_3)_3 = 1.76 \times 10^3$, benzaldehyde:$RuHCl(CO)(PPh_3)_3 = 781$, and formic acid:benzaldehyde = 2.25.

**Reagents.** The $RuHCl(CO)(PPh_3)_3$ catalyst was prepared according to the published procedure.[4] Benzaldehyde and formic acid (96%) were purchased from Aldrich Chemical Co. and used without further purification.

* Present address: Wilberforce University Research Scientist, Mail Stop 302-1, NASA Lewis Research Center, Cleveland, OH 44135.

⊗ Abstract published in *Advance ACS Abstracts*, November 1, 1993.

(1) (a) Kingston, H. M., Jassie, L. B., Eds. *Introduction to Microwave Sample Preparation: Theory and Practice*; American Chemical Society: Washington, DC, 1988. (b) Andrews, J. *J. Chem. Educ.* **1984**, *61* (2), 177. (c) Barrett, P.; Davidowski, L. J., Jr.; Penaro, K. W.; Copleland, T. R. *Anal. Chem.* **1978**, *50* (7), 1021. (d) Hesek, J. A.; Wilson, R. C. *Anal. Chem.* **1975**, *47* (8), 1160.

(2) (a) Mingos, D. M. P.; Baghurst, D. R. *Chem. Soc. Rev.* **1991**, *20*, 1. (b) Landry, C. C.; Barron, A. R. *Science* **1993**, *260*, 1653. (c) Adamek, F.; Hajek, M. *Tetrahedron Lett.* **1992**, *33*, 2039. (d) Bose, A. K.; Manhas, M. S.; Ghosh, M.; Shah, M.; Raju, V. S.; Bari, S. S.; Newaz, S. N.; Banih, B. K.; Chaudhary, A. C.; Barahat, K. J. *Org. Chem.* **1991**, *56*, 6968. (e) Bram, G.; Loupy, A.; Villemin, D. In *Solid supports and catalysts in organic synthesis*; Smith, K., Ed.; Ellis Horwood and Prentice Hall: Englewood Cliffs, NJ, 1992; Chapter 12, pp 302–326.

(3) Watanabe, Y.; Ohta, T.; Tsuji, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2441.

(4) Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 45.

**Conventional Heating.** In a typical reaction, 7.40 mL of formic acid and 8.50 mL of benzaldehyde were added to 0.1006 g of RuHCl(CO)(PPh₃)₃ under nitrogen. The reaction mixture was mantle heated at reflux for 3 h. Periodically, aliquots were removed by syringe for analysis by NMR.

**Microwave Heating.** All microwave heating was carried out in a Samsung MW5510 microwave oven producing microwave radiation with a frequency of 2450 MHz. This microwave oven is a 600-W oven with power settings of 0–10. The power setting 10 uses the full 60 W of power while a setting of 5 would correspond to an average powder of 300 W. A 250-mL beaker half full of water was kept in the microwave oven to ensure the presence of sufficient microwave absorbing material to avoid damaging the magnitron tube. It was determined by heating samples of benzaldehyde and formic acid separately that both of these materials absorb microwave radiation at 2450 MHz, resulting in a rapid temperature rise.

**Intermittent Microwave Heating.** Here, 0.0510 g of catalyst, 3.70 mL of formic acid, and 4.25 mL of benzaldehyde made up a typical reaction mixture. The reaction mixture was sealed in a Teflon digestion vessel under a nitrogen atmosphere. The mixture was heated in the microwave oven at power level 5 (on a scale of 0–10) for 2.00 min. The vessel was removed and cooled in an ice bath to reduce the internal pressure before opening to remove an aliquot for analysis. The vessel was then resealed under N₂ and the heating, cooling, and aliquot removal cycle repeated.

**Continuous Microwave Heating.** The reaction mixture was prepared in the same way as for the intermittent heating. The key difference is that a single longer sustained microwave heating period was used. The effect of variations in the power level was examined by using power levels of 2, 4, 6, and 8. The effect of volume was determined by preparing a sample with the mole ratios listed above and placing sample volumes ranging from 4 to 16 mL in the reaction vessel.

**Control Reactions.** Control reactions were run in which the reaction was carried out with the catalyst but without heat and in the absence of catalyst but with heat (both with conventional heating and in the microwave oven). These reactions demonstrated that the primary reaction in Scheme I will only occur in the presence of both heating and a catalyst while the secondary esterification requires neither.

**NMR Analysis.** The aliquots from the reactions were analyzed by dissolving them in acetone-$d_6$ and recording a spectrum on a Varian EM360A NMR spectrometer. The key resonances used for the analysis were the aldehyde resonance of benzaldehyde at 9.95 ppm, the methylene resonance of benzyl alcohol at 4.51 ppm, and the methylene resonance of benzyl formate at 5.15 ppm. By integrating these key resonances, the percentage of benzaldehyde that had been hydrogenated was determined.

## Results and Discussion

Both of the microwave heating methods catalyzed the transfer hydrogenation reaction more rapidly than conventional reflux heating. For example, after 10 min of refluxing, 6% of the benzaldehyde was hydrogenated. After 10 min of microwave heating in 2-min intervals, 19% of the benzaldehyde was hydrogenated. After 10 min of continuous microwave heating, 100% of the benzaldehyde was hydrogenated. The data from the analyses of the aliquots from the conventional and intermittent microwave heating methods are shown in Tables I and II, respectively. Repeated runs of the continuous microwave heating method (using several catalyst batches) showed that 7 min of irradiation produces complete hydrogenation of the benzaldehyde. These data produce average catalyst turnover rates of 280/h for the conventional heating

**Table I. Percent of Primary and Secondary Benzaldehyde Hydrogenation Products from a Refluxing Reaction Mixture Containing 7.40 mL of Formic Acid, 8.50 mL of Benzaldehyde, and 0.1006 g of RuHCl(CO)(PPh₃)**

| time (min) | benzyl formate (%) based on benzaldehyde | benzyl alcohol (%) based on benzaldehyde |
|---|---|---|
| 10 | 6 | 0 |
| 20 | 12 | a |
| 30 | 13 | a |
| 45 | 17 | a |
| 60 | 22 | a |
| 90 | 36 | 3 |
| 120 | 55 | 9 |
| 180 | 51 | 47 |

*a* Too small to quantify.

**Table II. Percent of Primary and Secondary Benzaldehyde Hydrogenation Products Produced by Intermittent Microwave Heating of a Reaction Containing 3.70 mL of Formic Acid, 4.25 mL of Benzaldehyde, and 0.0510 g of RuHCl(CO)(PPh₃)₃**

| time (min) | benzyl formate (%) based on benzaldehyde | benzyl alcohol (%) based on benzaldehyde |
|---|---|---|
| 2 | 4 | 0 |
| 4 | 10 | a |
| 6 | 13 | a |
| 8 | 15 | a |
| 10 | 16 | 3 |
| 12 | 18 | 3 |
| 14 | 21 | 4 |
| 16 | 23 | 4 |

*a* Too small to be quantified.

method, 890/h for the intermittent microwave heating method, and 6700/h for the continuous microwave heating method.

In addition to the comparison between conventional and microwave heating methods, an evaluation of factors affecting the rate of the microwave reaction was undertaken. The factors considered were catalyst batch, microwave power setting, and volume.

The first of these factors, the catalyst batch, applies to both conventional and microwave heating although the effect is more noticeable with microwave heating. Significant differences were observed for the same reactions carried out with different catalyst batches, presumably due to small differences in the purity of the samples. As a result, except where noted, the comparisons made here are based on experiments which used samples from a single catalyst batch.

The microwave power setting controls the time averaged microwave intensity. Thus, increasing the power setting increases the average microwave radiation striking an area per unit time. For a given reaction mixture and microwaving time, increasing the power setting dramatically increases the percent hydrogenation of the benzaldehyde. For example, microwaving a reaction mixture for 5.00 min at power level 2 produced 7% hydrogenation of the benzaldehyde. An identical reaction microwaved for 5.00 min at power level 8 resulted in 95% hydrogenation of the benzaldehyde. This clearly shows a strong dependence of the catalytic activity on the microwave intensity.

The final factor examined was the dependence of the catalytic activity on the volume of reaction mixture irradiated in the microwave oven. Here, an inverse relationship was observed. While the mole ratios of the reaction mixture, the reaction time, and the power level were kept constant, the volume was varied from 4 to 16 mL. The percent of hydrogenation products dropped from

75% with 4 mL to 19% with 16 mL, showing the inverse relationship between the volume and catalytic activity.

## Conclusion

This note describes the effect of microwave heating on the catalytic activity of the $RuHCl(CO)(PPh_3)_3$ catalyzed transfer hydrogenation of benzaldehyde in which formic acid serves as the hydrogen donor. The results demonstrate that carrying out the reaction in a microwave oven increases the rate at which this reaction is catalyzed considerably. Under the conditions used in this study, reaction times were reduced to around 7 min in a household microwave oven as compared with 3 h under traditional reflux conditions. This corresponds to an improvement in the average catalytic activity from 280 to 6700 turnovers/ h. Further results indicate that the degree of improvement decreases as the volume is increased, since there is an inverse relationship between volume and catalytic activity. This decrease in activity can be counteracted by increasing the microwave intensity, which shows a positive correlation with catalytic rate.

OM930491E