

# Hydrogenation of substituted aromatic compounds over a ruthenium catalyst

Petr Kluson, Libor Cerveny \*

*Institute of Chemical Technology – ICT Prague Technická 5, 166 28 Prague 6, Czech Republic*

Received 27 September 1995; accepted 13 November 1995

## Abstract

Selected aromatic compounds were hydrogenated over a ruthenium catalyst to evaluate the effect of a substituting group on the reactivity of an aromatic ring or a carbonyl function. In case of the aromatic aldehydes preferential hydrogenation of a carbonyl group was observed. When carbonyl group was not present, reactivity of the aromatic ring depended on the type of substituent.

*Keywords:* Ruthenium; Hydrogenation; Aromatic substrates; Selectivity; Carbonyl group

## 1. Introduction

Ruthenium is well known as a suitable catalyst for selective hydrogenation of an aromatic ring to cyclohexene and its derivatives [1–24]. It has also been successfully used for selective hydrogenation of a carbonyl group in the vicinity of conjugated or isolated double bonds or an aromatic ring [5,24–33]. Aromatic or unsaturated alcohols prepared in this way are compounds of great commercial importance. According to literature data acetophenone [5,34], citral [35–37], cinnamaldehyde [35–38], crotonaldehyde [32], etc., have already been used for such research.

For our study we chose a group of aromatics substituted with hydroxy, methoxy or carbonyl

functions. The group included phenol, anisole (methoxybenzene), benzaldehyde, 4-hydroxybenzaldehyde, 4-methoxybenzaldehyde and vanillin (4-hydroxy-3-methoxybenzaldehyde). In this paper we report on the role of the type of substituent on the reactivity of the aromatic ring or the carbonyl group.

## 2. Experimental

### 2.1. Chemicals

Phenol, p.a. (Reactivul); anisole, p.a. (Fluka); benzaldehyde, p.a. (Fluka); 4-hydroxybenzaldehyde, p.a. (Hoechst); 4-methoxybenzaldehyde, p.a. (Aroco); vanillin, p.a. (Eurovanillin); methanol, p.a. (Lachema). Hydrogen and nitrogen were grades 3.0 and 4.0, respectively (Linde-Technoplyn).

\* Corresponding author.

## 2.2. Catalyst

5% Ru/act. charcoal type Ru-97 (Batch No. 118097003) catalyst supplied by Johnson Matthey was used in all experiments. The total surface area of the catalyst was  $1\,033\text{ m}^2/\text{g}_{\text{cat}}$  (BET) and the specific surface of ruthenium attained  $130\text{ m}^2/\text{g}_{\text{Ru}}$  (titration method [39]). The catalyst (both the metal and the support) was X-ray amorphous with elemental crystallites of ruthenium less than 1 nm. The diffractograms revealed not very diffused bands typical for  $\alpha\text{-SiO}_2$  (quartz) crystallographic phase [40]. Quantitative analysis showed that the amount of quartz was in a range 1.5–1.7 wt%. Also considerable amount of sodium ions (0.20 wt%) was detected in the catalyst (AAS).

## 2.3. Experiments

All the experiments were carried out in a semi-batch, isothermal, stirred reactor connected to gasometric burettes at 303 K and atmospheric pressure. Detail description of a system is given elsewhere [41,42]. Typically the catalyst (fine powder, 0.1–0.3 g) was activated at 403 K for 1.5 h in a stream of hydrogen (50 ml/min), then covered with a solvent (methanol) and transferred to the reactor, where it was subjected to a final activation (303 K, 10 min, 50 ml/min,  $\text{H}_2$ ). The reaction was started by injection of a substrate to the reactor.

## 2.4. Analyses

Samples of a reaction mixture were analyzed on a H&P 5890 Series II Plus gas chromatograph (Hewlett and Packard, USA) with FID detector using HP-20M capillary column (50 m/0.32 mm/0.32  $\mu\text{m}$ ),  $T_1\text{--}T_2 = 333\text{--}353\text{ K}$ ,  $P(\text{N}_2) = 23\text{ kPa}$ , split ratio 1:35 and on a GC-MS analytical system JEOL DX 303 (JEOL, Japan) supplemented with a quartz capillary column SPB 5 (60 m).

## 3. Results and discussion

Experimental data obtained in the hydrogenation of selected substrates were described in terms of Langmuir–Hinshelwood differential rate equations based on the following assumptions: there was only one type of surface active site, each molecule of reactant is adsorbed on a single active site, the surface reaction is the rate determining step and the total number of active sites is incorporated into a rate constant. The adsorption terms of the equations were further rearranged by using relative adsorption coefficients. Kinetic and adsorption parameters were evaluated by the random walk method.

Although all the reactions proceeded with total conversion of the initial compound, decrease in catalytic activity was not observed, only in the hydrogenation of anisole. Thus, when an initial substrate disappeared from the reaction mixture, the reactions slowed down significantly and stopped soon after. As confirmed by addition of fresh substrates to a reaction mixture such behavior was caused by deactivation of the catalyst. In view of the above it is reasonable to define selectivity of a reaction to an intermediate in two different ways. The first definition,  $S_B = \%B / (\%A + \%B + \%C\dots)$ , for a maximum concentration of an intermediate in a reaction mixture, is suggested for reactions when no deactivation occurs (in our experiments only in the hydrogenation of anisole). The second definition of selectivity,  $S_B^* = \%B / (\%B + \%C\dots)$  reflects composition of a reaction mixture when hydrogenation stops owing to loss of activity of the catalyst.

### 3.1. Hydrogenation of phenol and anisole

In the hydrogenation of phenol (A) primarily cyclohexanol (B) was formed which partly further converted into cyclohexene by dehydration. The consecutive reaction is very slow and the amount of cyclohexane (C) formed from cyclohexene by hydrogenation did not usually exceed

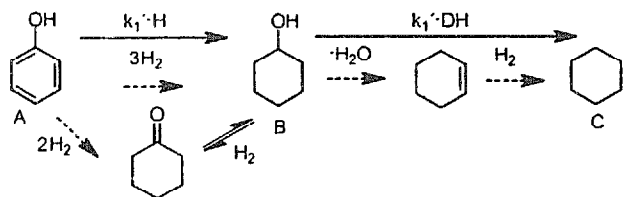


Fig. 1. Reaction scheme of the transformations proceeding under the conditions for hydrogenation of phenol.

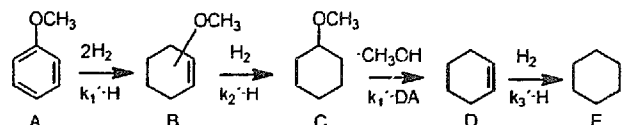


Fig. 2. Reaction scheme of the transformations proceeding under the conditions of hydrogenation of anisole.

10 mol%. Traces of cyclohexanone (less than 5 mol%) were also detected in the reaction mixture. If cyclohexanone is assumed to be a keto-form of cyclohexenol (tautomeric isomers) the reaction might be assumed to be selective to a derivative of cyclohexene. The simplified reaction scheme (neglecting the marginal formation of cyclohexanone and cyclohexene) is given in Fig. 1.

The reactivity of anisole was very high and no deactivation of the catalyst occurred. The main product of the reaction was methoxycyclohexane (Fig. 2), which was formed in a stepwise manner through an intermediary, methoxycyclohexene ( $S_B = 0.20$ ). Further transformation of methoxycyclohexane to cyclohexene by splitting off methanol was very slow and rather limited due to low activity of the catalyst for this reaction under the conditions studied. A typical course of the reaction is given in Fig. 3, where the maximum in the concentration of

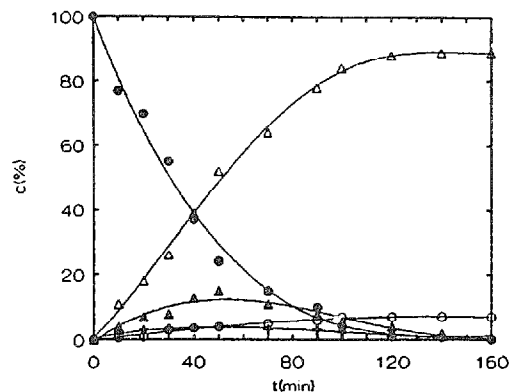


Fig. 3. A typical course of the transformations of anisole under the conditions for its hydrogenation: (●) anisole, (△) methoxycyclohexene, (△) methoxycyclohexane, (+) cyclohexene, (○) cyclohexane.

methoxycyclohexene vs. time curve is clearly seen.

Kinetic and adsorption parameters evaluated on a basis of experimental data coming from hydrogenations of phenol and anisole are given in Table 1. Because catalyst deactivates in the hydrogenation of phenol, comparison of the reactivities of both the substrates is somewhat questionable. Nevertheless, it is obvious that the reactivity of anisole was significantly higher than that of phenol. In both cases values of the relative adsorption coefficients show that the reactants with an aromatic ring or the derivatives of cyclohexene were more strongly adsorbed on the surface of ruthenium than corresponding derivatives of cyclohexane.

### 3.2. Hydrogenation of substrates with a carbonyl group

Hydrogenations of benzaldehyde, 4-hydroxybenzaldehyde, 4-methoxybenzaldehyde and of

Table 1

Kinetic and adsorption parameters of transformations proceeding under conditions for the hydrogenation of phenol and anisole

| Phenol  | $k_1'-H$ | $k_1'-DH$ | $k_1'-H/k_1'-DH$ | $K_A/K_B$ | $K_C/K_B$ | $S_B^*$   |           |           |       |       |       |
|---------|----------|-----------|------------------|-----------|-----------|-----------|-----------|-----------|-------|-------|-------|
|         | 4.24     | 0.51      | 8.31             | 2.99      | 0.25      | 0.90      |           |           |       |       |       |
| Anisole | $k_1'-H$ | $k_2'-H$  | $k_3'-H$         | $k_1'-DA$ | $K_A/K_C$ | $K_B/K_C$ | $K_D/K_C$ | $K_E/K_C$ | $S_B$ | $S_C$ | $S_D$ |
|         | 21.1     | 6.38      | 0.65             | 1.15      | 1.94      | 1.65      | 0.54      | 0.16      | 0.18  | 0.89  | 0.05  |

$k_1'-H$ ,  $k_2'-H$ ,  $k_3'-H$ ,  $k_1'-DA$ ,  $k_1'-DH$ , all in mmol/g<sub>cat</sub> min.

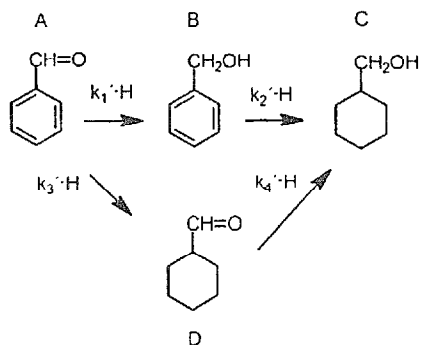


Fig. 4. Reaction scheme of the hydrogenation of benzaldehyde.

vanillin (4-hydroxy-3-methoxybenzaldehyde) proceeded with total conversion of the initial substrate. However, after disappearance of the substrate from the reaction mixture, the rate of hydrogenation of the aromatic ring of the corresponding alcohol slowed down and depending on the type of molecule the reaction stopped. This was due to the considerable loss of activity of the catalyst.

In the hydrogenation of benzaldehyde primarily formation of benzyl alcohol was observed. In addition a small portion of this was further transformed to cyclohexylmethanol, which was formed in parallel from hexahydrobenzaldehyde – a side intermediate of the reaction (Fig. 4). In experiments not described in this paper [30], it was shown that in the hydrogenation of benzyl alcohol, the initial substrate, there was almost no decrease in activity of the catalyst. It seems reasonable that under the conditions studied, the activity of the ruthenium active sites was 'exhausted' in the hydrogenation of a carbonyl group.

Reactions of 4-hydroxybenzaldehyde and 4-methoxybenzaldehyde proceeded similarly (Fig. 5). While the reactivities of benzaldehyde and 4-methoxybenzaldehyde were comparable, the reactivity of 4-hydroxybenzaldehyde was much lower. On the other hand a positive role of the

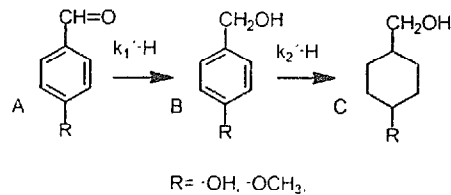


Fig. 5. Reaction scheme of the hydrogenation of 4-hydroxybenzaldehyde and 4-methoxybenzaldehyde.

alkoxy group in a consecutive hydrogenation of the aromatic ring was not observed. Although such an effect was already described by comparing reactions with phenol and anisole, its absence in this case was most likely due to the activity lost of the catalyst. Besides the reaction pathways indicated in Fig. 5, dehydration of 4-hydroxycyclohexylmethanol and demethanolation of 4-methoxycyclohexylmethanol also participated on the reaction scheme. However, the amount of products of these transformations did not exceed a limit of 3 mol% in a reaction mixture and their formation was not included to the rate model.

The last substrate used – vanillin (4-hydroxy-3-methoxybenzaldehyde) – contains two electron-donor functional groups in positions 3, 4 and an electron-acceptor group in position 1. 4-Hydroxy-3-methoxybenzyl alcohol was the principal product of its hydrogenation. Low reactivity and no consecutive hydrogenation of the aromatic ring were the typical features of the reaction under the conditions studied. Besides the principal product some other species were also formed, however, their total amount in a reaction mixture did not exceed 13 mol%. To simplify the model it was considered these compounds to be expressed as one hypothetical side product of the reaction. The reaction scheme reflecting the above facts is given in Fig. 6.

Kinetic and adsorption parameters of the dis-

Table 2  
Kinetic and adsorption parameters of hydrogenations of benzaldehyde

| $k_1\text{-H}$ | $k_2\text{-H}$ | $k_3\text{-H}$ | $k_4\text{-H}$ | $K_A/K_B$ | $K_C/K_B$ | $K_D/K_B$ | $S_B^*$ | $S_D^*$ |
|----------------|----------------|----------------|----------------|-----------|-----------|-----------|---------|---------|
| 2.31           | 0.79           | 0.41           | 0.38           | 1.17      | 0.36      | 0.08      | 0.76    | 0.06    |

[ $k_1\text{-H}$  to  $k_4\text{-H}$ ] in mmol/g<sub>cat</sub> min.

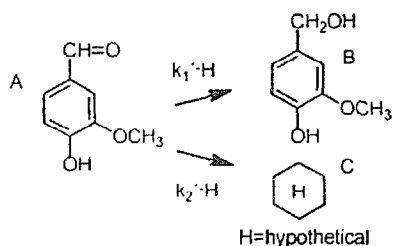


Fig. 6. Reaction scheme of the hydrogenation of vanillin.

Table 3  
Kinetic and adsorption parameters of hydrogenations of 4-hydroxybenzaldehyde, 4-methoxybenzaldehyde and vanillin

|                       | $k_1\text{-H}$ | $k_2\text{-H}$ | $K_A/K_B$ | $K_C/K_B$ | $S_B^*$ |
|-----------------------|----------------|----------------|-----------|-----------|---------|
| 4-hydroxybenzaldehyde | 0.98           | 0.34           | 0.66      | 0.26      | 0.95    |
| 4-methoxybenzaldehyde | 1.99           | 0.64           | 1.41      | 0.53      | 0.69    |
| vanillin              | 0.86           | 0.71           | 0.73      | 0.62      | 0.89    |

$[k_1\text{-H}, k_2\text{-H}]$  in mmol/g<sub>cat</sub> min.

cussed reactions are given in Tables 2 and 3. Values of rate constants were previously used for discussion of the reactivities of the substrates. In this case  $S_B^*$  defines the selectivity because of the loss of the activity of the catalyst. In some cases (4-hydroxybenzaldehyde, vanillin) the relative adsorption coefficients of an initial compound were less than one. Regarding the types of the molecules it does not seem reasonable that the adsorptivities of the products and intermediates would be higher than those of the substrates. It is most likely that the loss of activity was also reflected in the values of the adsorption coefficients.

#### 4. Conclusion

A group of six aromatic substrates with hydroxy, methoxy or carbonyl functions were hydrogenated over ruthenium catalyst. In reactions with phenol and anisole a positive effect of the alkoxy group on hydrogenation of an aromatic ring was shown. Formation of methoxycyclohexene was also observed. With aromatic carbonyl compounds there was considerable loss of activity of the catalyst when the substrate disappeared from the reaction mixture. The main

products of the hydrogenations of benzaldehyde and its derivatives were benzyl alcohol and its corresponding derivatives. A positive effect of the alkoxy group in position 4 to the carbonyl function on its reactivity was also observed.

#### Acknowledgements

This work was supported by the Grant Agency of the Czech Republic, Grant No. GACR 203/93/0013. Special thanks are also due to Johnson Matthey, Chemicals, for their kind assistance with the search for a suitable catalyst.

#### References

- [1] P. Kluson and L. Cervený, Chem. Listy, 88 (1994) 34.
- [2] M.M. Johnson and G.P. Nowack, J. Catal. 38 (1975) 518.
- [3] S. Niwa, F. Mizukami, S. Isoyama, T. Tsuchiya, K. Shimizu, S. Imai and J. Imamura, J. Chem. Technol. Biotechnol. 36 (1986) 236.
- [4] C.U.I. Odenbrand and S.L.T. Andersson, J. Chem. Technol. Biotechnol. 32 (1981) 691.
- [5] P. Kluson and L. Cervený, Catal. Lett. 23 (1994) 299.
- [6] C.U.I. Odenbrand and S.L.T. Andersson, J. Chem. Technol. Biotechnol. 33 (1982) 365.
- [7] S. Niwa, E.L. Salinas, F. Mizukami and M. Toba, Yukagaku, 38/11 (1989) 24.
- [8] M.C. Schoenmaker-Stolk, J.W. Verwijs, J.A. Don and J.J.F. Scholten, Appl. Catal. 29 (1987) 73.
- [9] S. Niwa, F. Mizukami, M. Kuno, K. Takeshita, H. Nakamura, T. Tsuchiya, K. Shimizu and J. Imamura, J. Mol. Catal. 34 (1986) 247.
- [10] J. Struijk, M. d'Angremond, W.J.M. Lucas-de-Regt and J.J.F. Scholten, Appl. Catal. 83 (1992) 263.
- [11] C.U.I. Odenbrand and S.T. Lundin, J. Chem. Technol. Biotechnol. 30 (1980) 677.
- [12] C.U.I. Odenbrand and S.T. Lundin, J. Chem. Technol. Biotechnol. 31 (1981) 660.
- [13] C.U.I. Odenbrand and S.L.T. Andersson, J. Chem. Technol. Biotechnol. 32 (1982) 691.
- [14] C.U.I. Odenbrand and S.L.T. Anderson, J. Chem. Technol. Biotechnol. 33 (1983) 151.
- [15] J. Struijk, R. Moene, T. van der Kamp and J.J.F. Schoelten, Appl. Catal. 89 (1992) 77.
- [16] P.J. van der Steen and J.J.F. Scholten, Appl. Catal. 58 (1990) 29i.
- [17] J. Struijk and J.J.F. Scholten, Appl. Catal. 82 (1992) 277.
- [18] F. Mizukami, S. Niwa, M. Toba, T. Tsuchiya, K. Shimizu, S. Imai and J. Imamura, Stud. Surf. Sci. Catal., 31 (1987) 45.
- [19] T. Walton and P.A. Sermon, Stud. Surf. Sci. Catal., 75 (1993) 1776.

- [20] S. Niwa, F. Mizukami, J. Imamura and K. Itabashi, *Sekiyu Gakkaishi*, 32/6 (1989) 299.
- [21] T. Lopez, P. Bosch, M. Asomoza and R. Gomez, *J. Catal.* 133 (1992) 247.
- [22] T. Lopez, P. Bosch and R. Gomez, *React. Kinet. Catal. Lett.* 41/1 (1990) 217.
- [23] S. Niwa, F. Mizukami, M. Toba, T. Tsuchiya, K. Shimizu and J. Imamura, 64th CATSJ Meeting Abstracts No. 1B05, 31/6 (1989) 421.
- [24] P. Kluson and L. Cerveny, *Appl. Catal. A*, 128 (1995) 13.
- [25] D.G. Blackmond, R. Oukaci, B. Blanc and P. Gallezot, *J. Catal.* 131 (1991) 131.
- [26] D. Richard, P. Fouilloux and P. Gallezot, in M.J. Phillips et al. (Eds.), *Proc. 9th Int. Congr. Catalysis*, Calgary, 1988, Chem. Inst. Can., Ottawa, 1988, p. 1074.
- [27] A. Giroir-Fendler, D. Richard and P. Gallezot, *Stud. Surf. Sci. Catal.*, 41 (1988) 171.
- [28] D. Richard, J. Ockelford, A. Giroir-Fendler and P. Gallezot, *Catal. Lett.* 3/1 (1989) 53.
- [29] A. Waghray, R. Oukaci and D.G. Blackmond, *Stud. Surf. Sci. Catal.*, 75 (1993) 2480.
- [30] P. Kluson, PhD Thesis, Inst. Chem. Technol., Prague, 1994.
- [31] M.A. Vannice and B. Sen, *J. Catal.* 115 (1989) 65.
- [32] J. Kaspar, M. Graziani, G.P. Escobar and A. Trovarelli, *J. Mol. Catal.* 72 (1992) 243.
- [33] S. Galvagno, A. Donato, G. Neri and R. Pietropaolo, *Catal. Lett.* 8 (1991) 9.
- [34] A.A. Wismeijer, A.P.G. Kieboom and H. van Bekkum, *React. Kinet. Catal. Lett.* 29/2 (1985) 311.
- [35] S. Galvagno, C. Milone, A. Donato, G. Neri and R. Pietropaolo, *Catal. Lett.* 18 (1993) 349.
- [36] S. Galvagno, G. Capammeli, G. Neri, A. Donato and R. Pietropaolo, *J. Mol. Catal.* 64 (1991) 237.
- [37] S. Galvagno, C. Milone, A. Donato, G. Neri and R. Pietropaolo, *Catal. Lett.* 17 (1993) 55.
- [38] A. Donato, G. Neri, R. Pietropaolo and G. Capannelli, *J. Mol. Catal.* 78 (1993) 227.
- [39] I. Paseka, L. Cerveny and P. Kluson, *Appl. Catal. B*, 128 (1995) 33.
- [40] Powder Diffraction File of the JCPDS – International Center for Diffraction Data, Swathmore, PA, 1993.
- [41] V.W. Weekman, *AIChE J.*, 20/5 (1974) 833.
- [42] L. Cerveny, V. Heral, A. Marhoul, V. Ruzicka, *Chem. Listy*, 68 (1977) 1286.