

Hydrogenolysis of Benzylic Alcohols on Rhodium Catalysts

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Abstract: Alumina-supported catalysts from various sources and with different rhodium dispersions predominantly yield the hydrogenation product perhydro-1-indanol in the liquid-phase hydrogenation of 1-indanol, while carbon-supported catalysts mainly give the C–O bond scission–hydrogenation product perhydroindane. Addition of organic or inorganic bases to the reaction mixture suppresses C–O bond scission. To distinguish between the two possible pathways for C–O bond scission of direct hydrogenolysis or dehy-

dratation followed by hydrogenation, deuteration studies have been carried out with carbon-supported catalysts. Not only 1-indanol but also indane and indene (the two possible mechanistic intermediates in the C–O bond scission routes) were deuterated. Information about the actual pathway has been obtained by determining the degree of

deuteration and the positions at which deuterium is incorporated in the resulting perhydroindane product by means of mass spectrometry and ¹³C NMR spectroscopy. The results prove that C–O bond scission takes place primarily through the direct hydrogenolysis pathway on the carbon-supported catalysts. Direct hydrogenolysis occurs on the carbon support because of the formation of a better leaving group (OH₂⁺) from the benzylic hydroxy group and its subsequent substitution by spillover hydrogen.

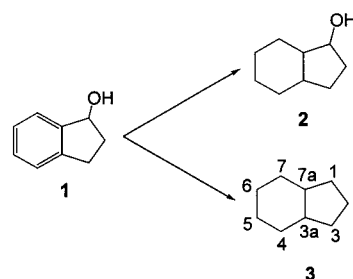
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Introduction

Aromatic substrates with a benzylic hydroxy or a benzylic alkoxy group are prone to scission of the C–O bond^[1] during hydrogenation on noble metal catalysts.^[2] The extent of bond scission depends on the nature of the noble metal used as the catalyst,^[3] and thus the choice of catalyst therefore depends on whether C–O bond scission is desired. In order to achieve C–O cleavage, palladium is employed because, in addition to being a superior hydrogenolysis catalyst, it lowers the risk of hydrogenation of the aromatic ring compared with rhodium or platinum catalysts.^[3, 4] If C–O bond scission is not desired, the choice of metal catalyst depends on the functional group of the substrate that is to be hydrogenated. Rhodium is often employed for aromatic ring hydrogenation because it is active at moderate temperature and pressure. Platinum is also a good catalyst for aromatic hydrogenation, but it requires higher temperature and pressure than rhodium to achieve comparable activity.^[3, 5] Although rhodium hydrogenates all the other reducible functional groups of the substrate along with the aromatic ring, it very often leaves the nonreducible functional groups intact.^[6]

While studying the influence of the nature of the support on diastereoselective induction in the liquid-phase hydrogenation

of 1-indanol (**1**, Scheme 1) over rhodium catalysts, we found a large difference in the chemoselectivity of the carbon-supported and alumina-supported agents.^[7] Various commercially produced carbon-supported catalysts predominantly yielded perhydroindane (**3**), while alumina-supported catalysts mostly gave perhydro-1-indanol (**2**, Scheme 1). Similar



Scheme 1. Hydrogenation and hydrogenolysis of 1-indanol.

results were obtained for 1-tetralol and 1-phenylethanol. To the best of our knowledge, such a big difference in the chemoselectivity of rhodium catalysts on these two common supports has never been described. Furthermore, the high C–O bond scission capability of carbon-supported rhodium was surprising. We, therefore, conducted experiments to study the mechanism of C–O bond scission in 1-indanol on carbon-supported rhodium catalysts, focussing for the most part on deuteration experiments. The average extent of incorporation of deuterium in the C–O bond scission product, perhydro-

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indane, was measured by mass spectrometry. This value exceeded the expected values when the incorporation took place exclusively by saturation of the C=C double bonds and C–O bond scission, and thus it was necessary to determine the isotopic composition at each carbon atom in the product. ^2H coupled ^{13}C NMR spectroscopy was used for this purpose, because ^2H NMR spectroscopy has insufficient resolution.

Experimental Section

Rh/C (Fluka, Aldrich, PCC), Rh/Al₂O₃ (Fluka) and Rh black (Johnson Matthey, >99.9% pure, based on the metal) catalysts were used. The PCC catalyst contained 54% water and was not dried before use. Activated carbon-supported (Fluka) and graphite-supported (Lonza) catalysts were made by impregnating the respective supports with an aqueous rhodium nitrate solution. After being dried (120 °C) overnight in air these catalysts were then calcined (350 °C for 3 h) in nitrogen. A series of Rh/Al₂O₃ catalysts was prepared by impregnation of solutions of different rhodium salt precursors on Al₂O₃ (Condea). Rh/Al₂O₃ I was made from a solution of rhodium tris(acetylacetonate) in acetone, and two separate Rh/Al₂O₃ II catalysts were made from the incipient wetness of the alumina with an aqueous Rh(NO₃)₃ · 2H₂O solution. The alumina catalysts were treated like the carbon and graphite catalysts, with the exception that the final calcination was done in air. The salt precursors were supplied by Johnson Matthey. All the catalysts except for 1.25 Rh/Al₂O₃ II had a metal loading of 5 wt% rhodium. The metal loading of the 1.25 Rh/Al₂O₃ II catalyst was 1.25 wt%. A list of all the catalysts used is given in Table 1. The metal surface area of some of the catalysts was quantified by hydrogen chemisorption measurements. Details of these measurements can be found elsewhere.^[8] Zeolite beta was used as an additive in the protonated form, obtained by pretreating the supplied material (CU Chemie Uetikon, Si/Al = 9.1, Na form) with ammonium nitrate followed by calcination.

Hydrogenation experiments were conducted at room temperature in a stainless steel autoclave (60 mL), with stirring provided by a gas-inducing impeller. In a typical experiment, 1-indanol (0.5 g, Fluka) was dissolved in the solvent (15 mL) in the autoclave and then the supported catalyst (50 mg and additives, if used) was added to this solution. The autoclave was closed, flushed with nitrogen and hydrogen, and pressurized (\approx 50 bar) with

Abstract in German: Bei der katalytischen Flüssigphasenhydrierung von 1-Indanol liefern Rhodium/Aluminiumoxidkatalysatoren unterschiedlicher Dispersion Hexahydro-1-indanol als Hauptprodukt. Wird Aktivkohle als Trägermaterial benutzt, entsteht unter C–O Bindungsspaltung vorwiegend Hexahydroindan. Die Zugabe organischer oder anorganischer Basen zur Reaktionsmischung verhindert die C–O Bindungsspaltung. Als mögliche Reaktionswege bei der Bildung von Hexahydroindan kommen die direkte Hydrogenolyse oder eine Wasserabspaltung mit nachfolgender Hydrierung in Frage. Zur Aufklärung des Mechanismus wurden mit den Aktivkohlekatalysatoren Markierungsversuche mit Deuterium durchgeführt. Sowohl 1-Indanol als auch Indan und Inden waren deuteriert. Das Deuterium-tragende Kohlenstoffatom sowie der Grad der Deuterierung des Reaktionsproduktes Hexahydroindan wurde mit ^{13}C -NMR Spektroskopie sowie mittels Massenspektrometrie bestimmt. Die Ergebnisse lassen den Schluss zu, dass vorwiegend die direkte Hydrogenolyse zu der C–O Bindungsspaltung führt. Dieser Mechanismus wird auf dem Aktivkohleträger wegen der Bildung einer guten Abgangsgruppe (OH₂⁺) aus der Benzylhydroxylgruppe favorisiert.

Table 1. Various catalysts.

Catalyst	Source	Precursor ^[a]	Dispersion (H/M)
Rh black	Johnson Matthey	n. a.	not applicable
Rh/Al ₂ O ₃ I	Condea alumina	Rh(acac) ₃	0.27
Rh/Al ₂ O ₃ II	Condea alumina	Rh(NO ₃) ₃ · 2H ₂ O	0.74
1.25 Rh/Al ₂ O ₃ II	Condea alumina	Rh(NO ₃) ₃ · 2H ₂ O	1.22
Rh/Al ₂ O ₃ (F)	Fluka	n. a.	
Rh/C (A)	Aldrich	n. a.	0.29
Rh/C (F)	Fluka	n. a.	
Rh/C (P)	PCC	n. a.	
Rh/C	Fluka carbon	Rh(NO ₃) ₃ · 2H ₂ O	
Rh/G	Lonza graphite	Rh(NO ₃) ₃ · 2H ₂ O	

[a] n. a. = not available.

hydrogen. Samples were taken through a sample tube to determine the extent of the reaction (reaction time was usually less than 4 h), but thorough kinetic measurements were not made. Samples were analyzed on an HP-5890 GC equipped with an HP-1 capillary column and a FID detector.

Deuteration experiments^[9] were conducted with the Rh/C (A) catalyst under the same process conditions as the hydrogenation experiments. In addition to the deuteration of 1-indanol, the deuteration of indane and indene (both from Aldrich) was studied to help us understand the mechanism of C–O bond cleavage. To compare the performance of carbon-supported and alumina-supported catalysts, indane deuteration was carried out in cyclohexane on the Rh/Al₂O₃ (F) catalyst. The substrate/catalyst molar ratio and the reaction conditions were kept constant in all the deuterium experiments. The isotopic purity of the deuterium (Sauerstoffwerke Lenzburg) was 99.8%. C₂H₅OD (Fluka, isotopic purity >99.5%) was used as the solvent instead of ethanol in the deuterium experiments, while cyclohexane was used in its undeuterated form. Mass spectra of the gas phase in the autoclave (measured on a quadrupole Balzer QME Prisma 200 instrument) after the deuteration experiments with 1-indanol in C₂H₅OD and cyclohexane indicated that the concentration of deuterium in the gas phase was higher than 85%, the main impurities being HD and H₂. This indicates that deuterium rather than hydrogen was predominantly added to the substrate during the deuteration experiments. GC-MS analysis was used to quantify the total deuterium incorporation in the perhydroindane product. The reaction mixture was analyzed directly by injecting a sample at the end of the reaction, that is, at 100% conversion of 1-indanol. Injection of the gas phase in equilibrium with the liquid sample allowed us to measure the mass spectrum of the solvent. More than 95% of the molecules of C₂H₅OD and cyclohexane did not incorporate a deuterium atom during the reaction. MS analyses were done in the EI mode on an HP-6890 GC coupled to an HP-5973 MS at an ionization energy of 70 eV. Deuterium incorporation was calculated on the basis of molecular peaks of perhydroindane isotopomers in the mass spectrum. Since the mass spectrum varied according to the point on the perhydroindane peak at which it was measured, the average mass spectrum of the entire peak was used for calculations. In calculating the percentage of each isotopomer of perhydroindane, the isotopomers with concentrations lower than 5% of the main isotopomer (as calculated from the molecular peak intensities) were omitted. For the NMR analyses, the perhydroindane product was removed from the other products and from the solvent after separating the reaction mixture by filtering the solid catalyst.^[10] ^{13}C NMR spectra and ^{13}C NMR DEPT spectra^[11] were then measured on the isolated samples with a Bruker AVANCE DPX 300 instrument in order to determine the degree of deuteration at individual carbon atoms.^[12] The resonance frequency of the instrument was 75 MHz.

Results

Hydrogenation of 1-indanol led to the formation of the C–O bond scission–hydrogenation product perhydroindane and the hydrogenation product perhydro-1-indanol (Scheme 1). Although the *cis* as well as the *trans* isomers of both **2** and **3**

were obtained, the *cis:trans* ratio was very high (usually above 20). Both the *cis,cis* and *cis,trans* products of **2** were obtained. The *cis,cis* isomer was always obtained in excess, and the magnitude of the diastereoselectivity depended on the catalyst employed.^[7] The yield of the products varied with the catalyst used. The C–O bond scission product indane, an intermediate between **1** and **3**, was found with some catalysts, and small amounts (up to 5%) of partly hydrogenated cyclohexene intermediates between **1** and **2** were found with all catalysts. Table 2 lists the selectivity for the C–O bond

Table 2. Selectivity to the C–O bond scission–hydrogenation products and hydrogenation products at 100% conversion of **1** with various solvents and catalysts.

Catalyst ^[a]	Solvent	Selectivity to 3 [%]	Selectivity to 2 [%]
Rh black	EtOH	3	96
Rh/Al ₂ O ₃ I	EtOH	9	91
Rh/Al ₂ O ₃ II	EtOH	4	95
1.25Rh/Al ₂ O ₃ II	EtOH	10	89
Rh/Al ₂ O ₃ (F)	hexane	3	96
Rh/Al ₂ O ₃ (F)	EtOH	7	93
Rh/C (A)	hexane	32	60
Rh/C (A)	EtOH	77	19
Rh/C (F)	EtOH	74	19
Rh/C (P)	EtOH	79	18
Rh/C	EtOH	100	0
Rh/G	EtOH	95	3

[a] 200 mg of 1.25 Rh/Al₂O₃ II, 25 mg of Rh black and 50 mg of all other rhodium catalysts were used.

scission–hydrogenation products (*cis*- and *trans*-perhydroindane) and the hydrogenation products (*cis,cis*- and *cis,trans*-perhydro-1-indanol) obtained with various catalysts (Table 1) at 100% conversion of **1** and all the intermediates. The data in Table 2 show that carbon-supported catalysts cause extensive C–O bond breaking. The selectivity for perhydroindane on alumina-supported catalysts varied with the catalyst used but was never above 10%. Rhodium black has a small but significant selectivity for perhydroindane. With hexane as the solvent, the extent of C–O bond scission was reduced for both the alumina-supported and the carbon-supported catalysts. The reaction of **1** was faster over carbon-supported catalysts than over the alumina-supported catalysts. The rate of reaction depended on the solvent and was higher in hexane than in ethanol. In the case of ethanol, the reaction was slowed down considerably towards the end. It was verified that **2** does not undergo hydrogenolysis to **3** under the reaction conditions employed by running the reaction over all the catalysts for a few more hours after the complete conversion of **1** and the intermediates. Figure 1 shows the consumption of **1** and the formation of **2** and **3** as a function of time in a reaction over the Rh/C (A) catalyst in hexane. It is clear that the pathway from **2** to **3** can not be followed under the present reaction conditions since their concentrations remain unaltered with time after complete consumption of **1**. The formation and the consumption of the intermediate **5** (Scheme 2) is also shown in Figure 1. (The cyclohexene intermediates between **1** and **2** are not shown for clarity.)

The selectivity for perhydroindane of the water-saturated Rh/C (P) catalyst was comparable with that of Rh/C (A)

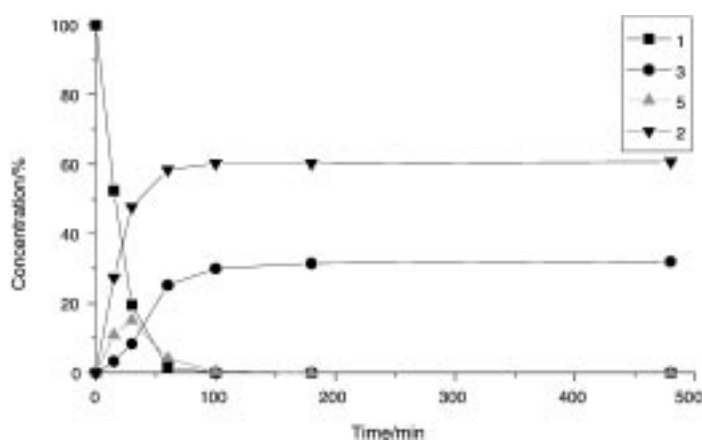
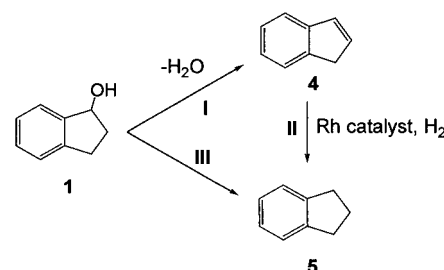


Figure 1. Kinetics of hydrogenation of **1** on the Rh/C (A) catalyst in hexane.



Scheme 2. Pathways to C–O bond cleavage in 1-indanol.

(Table 2). A separate experiment was conducted with the Rh/C (A) catalyst in which water (0.3 mL) was added to the reaction mixture. The selectivity for perhydroindane in this experiment was 79%, comparable with that obtained with Rh/C (A) in ethanol. In an experiment with the Rh/Al₂O₃ II catalyst, extra alumina support (150 mg) was added to the reaction mixture; the selectivity for perhydroindane remained unchanged at 4%. In another experiment, activated carbon (50 mg) was added to the reaction mixture in an experiment with the Rh/Al₂O₃ (F) catalyst in ethanol. The selectivity for perhydroindane was 33%. In a *reverse* experiment, alumina support (50 mg) was added to the reaction mixture in an experiment with Rh/C (A), but the catalytic performance remained the same. Addition of zeolite beta (50 mg) to the mixture in a reaction with the Rh/Al₂O₃ (F) catalyst in ethanol resulted in 24% selectivity for perhydroindane. Use of a small amount of concentrated hydrochloric acid (0.1 mL) instead of the zeolite beta gave a 96% selectivity for perhydroindane. Conducting the reaction in acetic acid instead of in ethanol with the Rh/Al₂O₃ (F) catalyst yielded 82% selectivity for perhydroindane.

Table 3 lists the selectivity for the fully hydrogenated products of C–O bond scission obtained from other benzylic alcohols hydrogenated in ethanol under the same reaction conditions as for 1-indanol. The carbon-supported catalyst shows a substantially higher activity in C–O bond scission than the alumina-supported catalyst with all the substrates. The difference in the selectivity for C–O bond scission products between the carbon-supported and the alumina-supported catalyst is lowest in the case of benzyl alcohol.

Table 3. Selectivity to the fully hydrogenated C–O bond scission products at 100% conversion of various benzylic alcohols.

Substrate	Substrate to rhodium molar ratio	Selectivity to fully hydrogenated C–O bond scission product(s) [%]	
		Rh/Al ₂ O ₃ (F)	Rh/C (A)
1-tetralol	139	12 ^[a]	82 ^[a]
1-phenylethanol	169	8	68
benzyl alcohol	191	49 ^[b]	92

[a] Selectivity to *cis*+*trans* decalin. [b] Selectivity to methylcyclohexane+toluene (the catalyst was deactivated before complete conversion of toluene to methylcyclohexane).

We also added bases to the reaction mixture for hydrogenation with Rh/C (A), because they are known to suppress C–O bond scission.^[13, 14] When an aqueous solution (0.3 mL, 0.5 N) of the inorganic bases LiOH, KOH, NaOH or Na₂CO₃ was added to the reaction mixture C–O bond scission was suppressed completely. This was accompanied by a decrease in the activity for hydrogenation of 1-indanol to perhydro-1-indanol by an order of magnitude. Adding the organic base triethylamine to the reaction mixture also suppressed this scission, and only 2% perhydroindane was obtained with an amine/rhodium molar ratio of 10:1. As in the case of the inorganic bases, there was a simultaneous reduction in activity.

Mass spectrometric analyses of the perhydroindane product of the deuteration of 1-indanol in C₂H₅OD and cyclohexane gave a distribution of deuterium incorporation. Figure 2 illustrates the percentage of each isotopomer of perhydroindane corresponding to the number of deuterium atoms

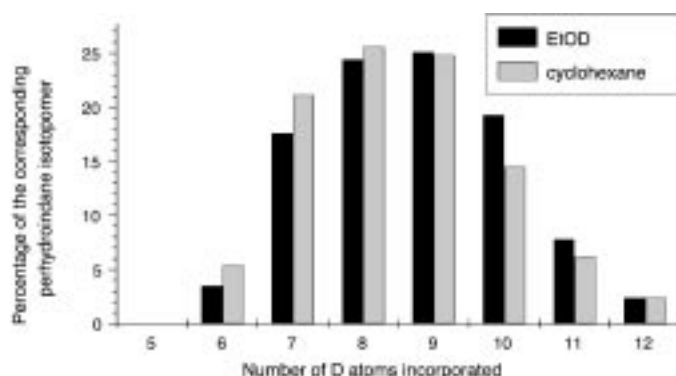


Figure 2. Deuterium incorporation in the perhydroindane product of the deuteration of 1-indanol on the Rh/C (A) catalyst in C₂H₅OD and cyclohexane.

incorporated, as obtained with the Rh/C (A) catalyst. The incorporation of deuterium in perhydroindane in the C₂H₅OD and cyclohexane experiments was very similar. The number of deuterium atoms included in the majority of the isotopomers exceeds the number required for complete saturation of the aromatic ring and direct cleavage of the C–O bond (that is, 6 + 1 = 7).

Figure 3 shows the normal ¹³C NMR spectrum (A) of the reaction product perhydroindane obtained in the deuteration of 1-indanol in C₂H₅OD. In addition, its corresponding ¹³C NMR DEPT spectrum (B) and a ¹³C NMR DEPT spectrum (C) of an undeuterated perhydroindane sample are

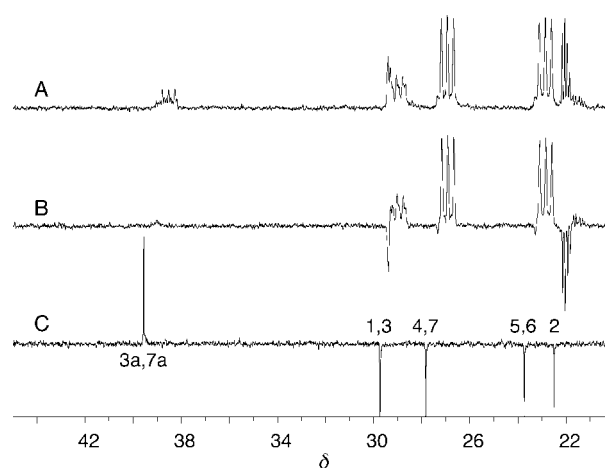


Figure 3. ¹³C NMR spectra: A) ²H-coupled spectrum (solvent, C₆H₆/C₆D₆ mixture) of the perhydroindane product obtained in the deuteration of 1-indanol on the Rh/C (A) catalyst in C₂H₅OD; B) ²H-coupled DEPT spectrum (solvent, C₆H₆/C₆D₆ mixture) of the perhydroindane product obtained in the deuteration of 1-indanol on the Rh/C (A) catalyst in C₂H₅OD; C) DEPT spectrum of undeuterated perhydroindane (Solvent, C₆D₆).

shown. The peaks in spectrum C have been numbered according to their position on the ring in perhydroindane (3). The assignment of the ¹³C NMR peaks to the carbon atoms in perhydroindane was confirmed by a 2D-INADEQUATE NMR experiment^[11] with an undeuterated sample of perhydroindane. The peaks of the carbon atoms in spectra A and B are shifted to high field compared with the peaks in spectrum C because of the replacement of protons by deuterium atoms.^[15] The order of the peaks, however, remains unchanged. Spectrum B in Figure 3 shows that all the carbon atoms in the six-membered ring have mostly taken on one deuterium atom. The peaks corresponding to carbon atoms 4–7 are of the CHD type, because they are triplets in the normal as well as in the DEPT spectrum, while those corresponding to atoms 3a and 7a are of the CD type since they do not appear in the DEPT spectrum. Spectrum B also shows that the carbon atoms at positions 1 and 3 are partly deuterated. The carbon atom at position 2 is predominantly undeuterated and is of the CH₂ type. Several CH₂ peaks are observed because of the difference in the chemical shift of the isotopomers of perhydroindane. These isotopomers differ in deuterium substitution patterns on the carbon atoms at positions 1 and 3. The higher the degree of deuteration at carbon atoms 1 and 3, the greater the magnitude of the high-field shift of the CH₂ peak of carbon atom 2.^[15] It is clear from spectrum B that the carbon atoms at positions 1 and 3 are both CH₂ and CHD types; as expected, the CHD peak is shifted to high field compared with the CH₂ peak. The NMR spectra of the reaction product perhydroindane obtained in the deuteration of 1-indanol in cyclohexane (not presented) were similar to those obtained in the deuteration of 1-indanol in C₂H₅OD.

Figure 4 shows deuterium incorporation in experiments with indane in C₂H₅OD and cyclohexane. The number of deuterium atoms incorporated exceeds the number required for complete saturation of the aromatic ring (that is, 6) in the majority of the isotopomers. The pattern of deuterium

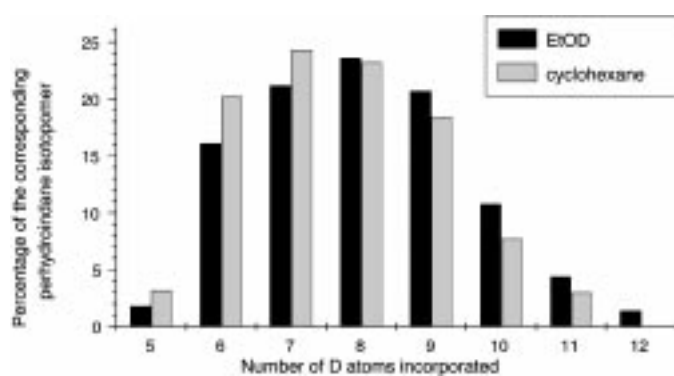


Figure 4. Deuterium incorporation in the perhydroindane product of the deuteration of indane on the Rh/C (A) catalyst in C_2H_5OD and cyclohexane.

inclusion in the perhydroindane products obtained in the 1-indanol and indane deuteration experiments is similar, but has shifted to lower deuterium incorporation in the case of indane. The NMR spectra of these samples (not presented) are also comparable with those obtained in the 1-indanol deuteration experiments. NMR analyses of these samples show that the carbon atoms at positions 1 and 3 are partly deuterated, while carbon atom 2 is largely undeuterated. The ratio of intensities of peaks corresponding to the CH_2 and the CHD type of carbon atoms at positions 1 and 3 is higher in perhydroindane obtained from indane deuteration than the ratio obtained for deuteration of 1-indanol. The carbon atoms in the six-membered ring generally bear one deuterium atom. Figure 5 compares the incorporation of deuterium in the deuteration of indane in cyclohexane on Rh/C (A) and Rh/ Al_2O_3 (F). The concentrations of different isotopomers of perhydroindane obtained with both catalysts are similar. This result was also confirmed by the ^{13}C NMR spectra of the product perhydroindane in both experiments.

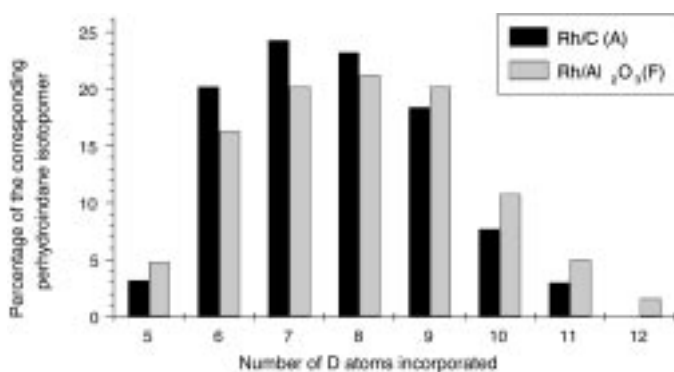


Figure 5. Deuterium incorporation in the perhydroindane product of the deuteration of indane on the Rh/C (A) and Rh/ Al_2O_3 (F) catalysts in cyclohexane.

Deuterium incorporation in perhydroindane in the deuteration of indene in C_2H_5OD is shown in Figure 6. The distribution of deuterium is narrower and shifted towards higher deuterium incorporation than that obtained with 1-indanol and indane, as would be expected from a parent substrate with a higher degree of unsaturation. Figure 7 depicts the normal ^{13}C NMR spectrum (A) and the ^{13}C NMR

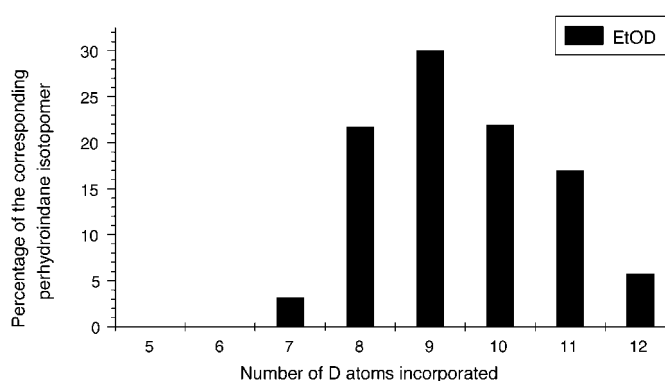


Figure 6. Deuterium incorporation in the perhydroindane product of the deuteration of indene in C_2H_5OD .

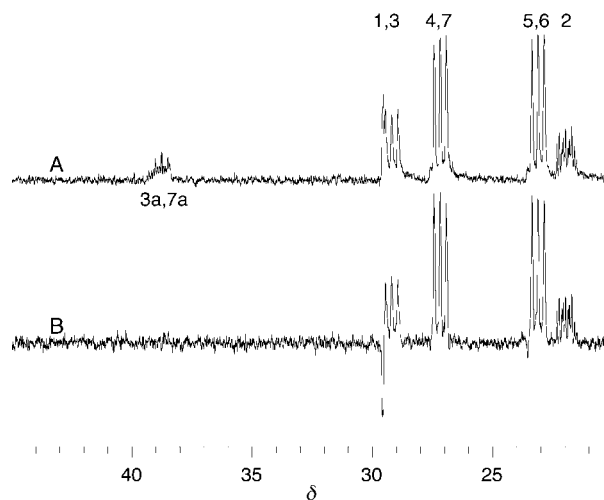


Figure 7. ^{13}C NMR spectra of the perhydroindane product of the deuteration of indene on the Rh/C (A) catalyst in C_2H_5OD . A) 2H coupled spectrum (solvent, C_6H_6/C_6D_6 mixture); B) 2H coupled DEPT spectrum (solvent, C_6H_6/C_6D_6 mixture).

DEPT spectrum (B) of the isolated sample obtained in this experiment. After deuteration, all the carbon atoms in the six-membered indene ring have one deuterium atom, as in the case of 1-indanol and indane. The spectra indicate deuterium incorporation at carbon atoms 1, 2 and 3. The average incorporation of deuterium in perhydroindane and the theoretical incorporation expected in these experiments are shown in Figure 8. The degree of inclusion of deuterium in

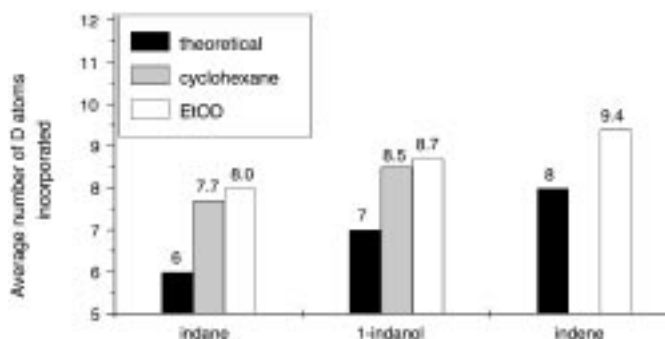


Figure 8. Average incorporation of deuterium in the deuteration of indane and 1-indanol on the Rh/C (A) catalyst in C_2H_5OD and cyclohexane, and the deuteration of indene on the Rh/C (A) catalyst in C_2H_5OD , as well as the theoretical predicted incorporation based on saturation of $C=C$ bonds by deuterium and replacement of OH by D.

1-indanol and indane is slightly higher in C_2H_5OD than in cyclohexane. The theoretical value of deuterium incorporation was calculated by assuming that the incorporation in perhydroindane occurs only when deuterium is added to the aromatic ring and to the C=C double bond. As shown in Figure 8, the theoretical values of deuterium incorporation are 6 and 8 for indane and indene, respectively. The actual incorporation of deuterium in indane and indene always exceeds the theoretical value by 1.5–2. In the case of 1-indanol, the average incorporation of deuterium is between that for indene and indane. The theoretical value of deuterium incorporation in perhydroindane during deuteration of 1-indanol is 7 or 8, depending on the mechanism by which C–O bond scission takes place (vide infra). However, only a value of 7 has been considered in Figure 8.

Discussion

The data presented in Table 3 show that the big difference in the chemoselectivity of the carbon-supported and the alumina-supported catalysts is not restricted to 1-indanol only, but is also observed for other benzylic alcohols. The data in Table 2 indicate that the carbon-supported catalysts (obtained from different sources) exhibit a higher activity of C–O bond scission than the alumina-supported catalysts, which have widely different dispersions, a different salt precursor and are obtained from different sources. Thus, differences in salt precursors and dispersion cannot explain the higher C–O bond scission capability of carbon-supported catalysts. Such C–O cleavage can proceed by two routes (Scheme 2): either dehydration followed by hydrogenation of the resulting olefin on rhodium (**I** followed by **II**) or the direct hydrogenolysis of the C–O bond (**III**). The former route involves protonation of the hydroxy group, elimination of water, and formation of indene, followed by hydrogenation to indane. The latter route involves direct scission of the C–O bond. Hydrogenation in steps **II** and **III** requires hydrogen from the metal (either on the metal or spillover hydrogen). The dehydration step **I** needs acidic sites, which, in a reducing atmosphere, are present only on the support. The carbon support can have acidic sites, depending on the preparation procedure.^[16] Different carbon supports have been reported to catalyze etherification, albeit at a higher temperature of 150 °C,^[17] and etherification is known to be catalyzed by acids. Manninger et al.^[18] have shown that a charcoal-type carbon support catalyzed the dehydration of cyclohexanol to cyclohexene at 300 °C. Alumina is also known to be a good dehydration catalyst at higher temperature. However, very little C–O bond scission is observed on the alumina catalysts under the conditions employed in the current hydrogenation. An experiment in which extra alumina was added to the reaction mixture with the Rh/Al₂O₃ II catalyst provides proof that alumina is not involved in the overall C–O bond scission reaction. In addition, Rh black is also active in C–O bond cleavage, though to a very small extent.

Two questions must now be addressed. Does C–O bond scission on the carbon-supported catalysts proceed by paths **I**

and **II** or by path **III**? If it proceeds simultaneously by both routes, which of the two routes is faster? The most obvious answer is that acidic sites on the carbon catalyze the dehydration and that the subsequent hydrogenation takes place on the rhodium catalyst. In that case, indene would not be observed, because the activated double bond would be rapidly hydrogenated. This agrees with the facts that C–O bond scission is completely suppressed when inorganic and organic bases (which neutralize the acidic sites) are added and that cleavage occurs to a lower extent in apolar solvents such as hexane. However, bases have been added to suppress hydrogenolysis catalysed by palladium and rhodium catalysts.^[19, 20] Moreover, it is well known that alkali and alkaline earth metal additives prevent hydrogenolysis in the hydrogenation of carbon monoxide to methanol on palladium and rhodium catalysts.^[21] Acidity of the carbon support cannot, therefore, be deemed responsible for the observed C–O bond scission solely on the basis of the results of experiments in which a base was added.

Deuterium experiments offer a possibility to distinguish between the two pathways of C–O bond scission. If C–O bond cleavage proceeds through step **I** followed by step **II**, then deuterium incorporation should be observed at carbon 2. If the pathway is direct hydrogenolysis then no deuterium is expected on this carbon. Thus, in the absence of proton–deuterium exchange, eight deuterium atoms should be incorporated into the product perhydroindane if **I** followed by **II** is the main pathway, and seven deuterium atoms if **III** is the principal route. Figure 2 shows that on deuteration of 1-indanol a relatively wide distribution of deuterium incorporation in perhydroindane is obtained. The distribution is similar for the solvents C_2H_5OD and cyclohexane, although it is slightly shifted to higher deuterium incorporation for C_2H_5OD (as also seen in the average degree of deuterium inclusion in Figure 8). Moreover, the average deuterium incorporation exceeds the theoretically expected values (Figure 8), which implies that some proton–deuterium exchange occurs. The exchange is not restricted to the deuteration of 1-indanol and it also occurs in the deuteration of indane and indene (Figures 4, 6). Furthermore, the exchange must take place before the saturation of the aromatic ring, since it was observed that further exchange does not take place once the completely hydrogenated products are formed.

There are three types of carbon atoms at which proton–deuterium exchange can take place. The aromatic carbons (4–7), the benzylic carbons (1 and 3), and the carbon at position 2. The ²H-coupled ¹³C NMR DEPT spectrum allowed us to identify the carbon atoms to which deuterium is bonded. From spectra A and B in Figure 3, we conclude that deuterium exchange occurs at carbon atoms 1 and 3, but not at position 2. Each carbon atom in the six-membered ring bears a single deuterium atom, indicating that the aromatic protons do not undergo exchange under the reaction conditions employed. This is also clear from the spectra in Figure 7, in which the carbon atoms in the six-membered ring of deuterated indene bear one deuterium each after deuteration. Only the benzylic C–H bond undergoes scission during the hydrogenation of 1-indanol, indane and indene because of its lower strength compared with the other C–H bonds.

In the light of the above results, the theoretical values for incorporation of deuterium can be modified to include proton–deuterium exchange at the benzylic position. Thus, depending on the extent of exchange in the deuteration of indane, indanol and indene, the theoretical values for the incorporation of deuterium should lie between 6 and 10, 7 and 10 (or 11), and 8 and 11, respectively for these substrates. The results in Figures 2, 4 and 6 indicate deuterium incorporation to be broader than the theoretical range for the three substrates. Deuterium incorporation values lower than those predicted by theory indicate that, in some perhydroindane isotopomers, hydrogen rather than deuterium has been added during deuteration. The source of the hydrogen may be the catalyst support, the substrate, or the solvent. Deuterium incorporation values higher than the theoretical range of values in some perhydroindane isotopomers are possible because of the inclusion of two deuterium atoms at carbon atoms 4 to 7 and the incorporation of one or even two deuterium atoms at carbon atom 2. In the spectra shown in Figures 2 and 6, it appears that none of the carbon atoms, including those at positions 1 and 3, is of the CD₂ type. From the distribution of deuterium shown in Figures 2, 4, 5 and 6, it is clear that the perhydroindane isotopomers, doubly deuterated at positions 1 and 3, are present in significant concentrations. The absence of the CD₂ type of carbon atoms at positions 1 and 3 in the NMR spectra is attributed to the longer relaxation time of a carbon nucleus coupled with a deuterium nucleus. It is even more difficult to detect the CD₂ type of carbon atoms at the other positions in the perhydroindane molecule, because the concentrations of such perhydroindane isotopomers are very low.

Fortunately, the total number of deuterium atoms on the neighbouring carbon atoms can be determined from the chemical shifts of a carbon peak in the ¹³C NMR spectrum.^[15] In this way, the presence of CD₂ type carbon atoms at positions 1 and 3 could be verified by the chemical shifts induced in the peaks of carbon atoms at positions 2, 3a and 7a. Furthermore, the chemical shifts of carbon atoms 1 and 3 enabled us to confirm that a CD₂ type carbon atom was not present at position 2.

The absence of deuterium at position 2 in spectra A and B (Figure 3) indicates that direct hydrogenolysis (III) is the dominant pathway. This is confirmed by the deuteration experiments with indene under similar conditions. In Figure 7, spectra A and B indicate that the carbon atom at position 2 is predominantly of the CHD type. Further proof of C–O bond scission by pathway III is provided by the average values of deuterium incorporation presented in Figure 8. Path III is the only one to allow an average deuterium incorporation value in perhydroindane (obtained in the deuteration of 1-indanol) between those found in the indane and indene deuteration experiments.

Although the pathway of C–O bond scission is, without a doubt, direct hydrogenolysis, a fundamental question still remains to be answered: why is carbon-supported rhodium much more active for hydrogenolysis than alumina-supported rhodium? There are two possible explanations of the high hydrogenolysis capability of the carbon-supported rhodium

catalysts. One is that the rhodium particles on carbon and alumina supports differ in morphology and/or oxidation state, and the other is that carbon facilitates the formation of a better leaving group (that is, water) from the alcohol functional group and that the resulting OH₂⁺ group is replaced by spillover hydrogen (or deuterium). From the deuterium distribution in the perhydroindane product obtained in the deuteration experiments with indane in cyclohexane on carbon-supported and alumina-supported rhodium catalysts (Figure 5), it is concluded that the proton–deuterium exchange is similar for both catalysts. This implies that the rhodium particles on both supports have similar capabilities of scission of the benzylic C–H bond. In the experiment in which activated carbon was added to a reaction mixture with a Rh/Al₂O₃ catalyst, considerably more hydrogenolysis is obtained when carbon is added to the reaction mixture. A similar increase in selectivity for perhydroindane is observed in the experiment with the zeolite beta additive. This suggests that the hydrogenolysis step occurs on the extra support with the help of spillover hydrogen that is transferred from the supported catalyst.^[22] The proton on the carbon or on the zeolite thus facilitates the formation of a better leaving group. Although alumina has Lewis acidic sites, they are covered with water and are unable to protonate the hydroxy group unless catalytic amounts of a protic acid are present. Accordingly, extensive hydrogenolysis was observed in the experiments in which acetic acid was used as the solvent instead of ethanol or in which concentrated hydrochloric acid was added. Thus, hydrogenolysis proceeds readily under the present reaction conditions on the carbon-supported catalysts but not on the alumina-supported catalysts.

Conclusion

Carbon-supported rhodium catalysts are much more active in C–O bond scission than their alumina-supported counterparts. C–O bond scission on the carbon-supported catalysts can be suppressed by adding organic and inorganic bases during the reaction. Different isotopomers (with varying degrees of deuterium incorporation) of the C–O bond scission–hydrogenation product perhydroindane were obtained in deuteration experiments with 1-indanol, indane and indene. ²H-coupled ¹³C NMR experiments revealed the degree of deuteration at each carbon atom in the perhydroindane product. Under the present experimental conditions, proton–deuterium exchange occurs only at the benzylic carbon atoms. In addition, the absence of deuterium at carbon 2 enabled us to distinguish between the two pathways for cleavage. C–O bond scission occurs through the direct hydrogenolysis route and not through the dehydration route. The greater hydrogenolysis activity of the carbon-supported catalysts is due to the formation of a better leaving group from the benzyl hydroxy group on the carbon support followed by the cleavage of the C–O bond with spillover hydrogen on these catalysts.

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- [1] Although both routes to C–O bond cleavage (Scheme 2), namely, dehydration–hydrogenation (**I**+**II**) and direct hydrogenolysis (**III**), are empirically referred to as hydrogenolysis, we have used the term hydrogenolysis in its strictest sense, that is, cleavage of the C–O bond accompanied by the addition of hydrogen. Thus, only path **III** involves hydrogenolysis, while routes **I** followed by **II** and route **III** are collectively referred to as C–O bond scission paths.
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- [12] The degree of deuteration at a carbon atom is determined by the multiplicity of the carbon peak in a normal ¹³C NMR spectrum and a ¹³C NMR DEPT spectrum and by its direction in the ¹³C NMR DEPT spectrum. Carbon atoms with no deuterium bonded to them appear as

singlets in the normal as well as the DEPT spectrum because the carbon nucleus is decoupled from the hydrogen nucleus. Multiplicity arises because of the coupling of a carbon nucleus with a deuterium attached to it. Thus, a monodeuterated carbon appears as a triplet, while a bideuterated carbon appears as a quintuplet in the normal spectrum. In the DEPT spectrum, peaks corresponding to carbon atoms with no proton attached to them (CD and CD₂ type carbon atoms in the case of perhydroindane) disappear. In this spectrum the peaks corresponding to the CHD type carbon atoms point upwards, while those corresponding to the CH₂ type carbon atoms point downwards.

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Table 4.

Substituent(s)	α shift (ppm)	β shift (ppm)	γ shift (ppm)
D	–0.4	–0.12	–0.02
D ₂	–0.7	–0.24	–0.08
D ₃	–0.9	–0.36	–0.16

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