



Hydrodefluorination of fluorobenzene catalyzed by rhodium metal prepared from $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ and supported on SiO_2 and Pd-SiO_2

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Received 14 May 2003; received in revised form 14 May 2003; accepted 17 June 2003

Abstract

The effects of solvent, pH, temperature, and hydrogen pressure were determined for the reaction of fluorobenzene (PhF) with hydrogen gas catalyzed by supported rhodium metal on silica. Non-polar and aprotic solvents, heptane and 1,2-dichloroethane (DCE), favor hydrogenation to fluorocyclohexane (CyF). Polar and protic solvents, heptane/methanol and heptane/water, favor hydrodefluorination to benzene (PhH) and subsequent hydrogenation to cyclohexane (CyH). The hydrodefluorination–hydrogenation of fluorobenzene to cyclohexane via benzene proceeds fastest in heptane/water under acidic conditions. For the hydrodefluorination of fluorobenzene in heptane/water, the hydrodefluorination product, benzene, inhibited further hydrodefluorination of fluorobenzene. In heptane or DCE, a side reaction between fluorocyclohexane and hydrogen fluoride, not catalyzed by rhodium, was discovered that provides an alternate pathway to cyclohexane. Reaction conditions can be modified to yield primarily fluorocyclohexane, benzene, or cyclohexane.

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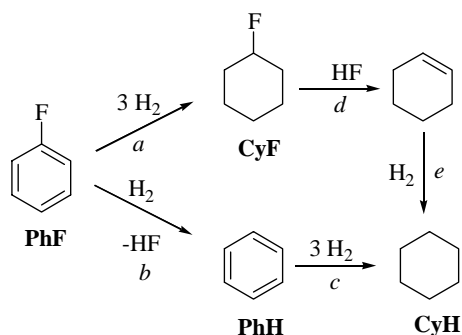
Keywords: Immobilized metal catalysts; Hydrodefluorination; Fluorobenzene; Rhodium; Silica; Palladium

1. Introduction

Carbon–fluorine (C–F) bonds are the strongest that carbon can form [1]. There are several examples of stoichiometric cleavage of C–F bonds by organometallic complexes, but few complexes have been reported that are capable of catalytic transformations of C–F bonds [2–11]. Even fewer systems are capable of catalytic hydrodefluorination to remove fluorine from non-activated monofluoroarenes [12–23]. Palladium on carbon (Pd/C), in the presence of NaOH at 82 °C, hydrodefluorinates fluorobenzene (PhF) to benzene (PhH) by hydrogen-transfer from isopropanol [14,15], but palladium was unable to catalyze the same reaction by hydrogen-transfer from HCOOK in ethanol/water (1:3) or under 4 atm of H_2 at 37 °C in methanol [15]. The first example of hydrodefluorination of a monofluoroarene by hydrogen gas over a heterogeneous metal was reported in 1920 by Swarts [16], who used Pt(black) in water to hydrodefluorinate PhF to cyclohexane (CyH) and *p*-fluorobenzoic acid to cyclohexanecarboxylic acid. Renoll utilized Swarts' con-

ditions to hydrodefluorinate 2-fluoro-4'-acetylbiphenyl to *p*-cyclohexylethylbenzene [17]. Pattison and Saunders [18] reported the hydrodefluorination of *p*-fluorophenylacetic acid to ethyl cyclohexylacetate with Raney Ni at 180–200 °C under 160–180 atm H_2 in ethanol. Tashiro et al. [19] used Raney Ni–Al and Raney Cu–Al alloys for the hydrodefluorination of *p*-fluoroacetophenone to 1-phenylethanol at 50 °C in 10% NaOH(aq). The first reported use of rhodium metal for the hydrodefluorination of a monofluoroarene was by Freedman et al. [20] who converted fluoroarylphosphonic acids to cyclohexylphosphonic acids under 4 atm of H_2 at room temperature in 95% ethanol. Young and Grushin [21] used $[(\text{C}_3\text{P})_2\text{Rh}(\text{H})\text{Cl}_2]$ to catalytically hydrodefluorinate 1-fluoronaphthalene to naphthalene under 80 psi hydrogen at 95 °C in the presence of 40% NaOH. However, $[(\text{C}_3\text{P})_2\text{Rh}(\text{H})\text{Cl}_2]$ was incapable of hydrodefluorinating PhF, 4-fluorotoluene, 3- or 4-fluoroanisole, or 4-fluoroaniline. Under identical conditions, metallic rhodium nanoparticles [21] catalyzed the hydrodefluorination of the C–F bond in 1-fluoronaphthalene, PhF, 4-fluorotoluene, 3- or 4-fluoroanisole, and 4-fluoroaniline while catalyzing only trace amounts of hydrogenation of the resulting arenes. Blum et al. [22] reports that

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Scheme 1. Reactions of PhF with H₂ catalyzed by Rh-SiO₂(A).

sol-gel encapsulated RhCl₃-Aliquat 336 catalyzes the hydrodefluorination and hydrogenation of fluorobenzene, 2- or 4-fluorotoluene, and 2-, 3-, or 4-fluoroanisole in 1,2-dichloroethane (DCE) at 80 °C under 16 atm of hydrogen to the corresponding dehalogenated, substituted cyclohexanes. Our initial hydrodefluorination studies showed that rhodium pyridylphosphine and bipyridyl complexes tethered to Pd-SiO₂ under 4 atm of hydrogen at 70 °C efficiently converted PhF to a mixture of CyH and CyF [23]. The relative amounts of these products were influenced by the solvent. In heptane, fluorocyclohexane (CyF) was the major product, but in heptane/ethanol, with added base (NaOAc being the best), benzene was formed initially but was subsequently hydrogenated to cyclohexane.

Our examination of supported bimetallic rhodium and palladium catalysts for arene hydrogenation [24] prompted us to explore their hydrodefluorination capabilities. These catalysts were prepared by adsorbing, various rhodium complexes including [Rh(COD)₂]⁺BF₄⁻ on SiO₂ or Pd-SiO₂ (10% Pd w/w) to give a ~2% Rh (w/w) loading. These materials were used as obtained or pretreated with H₂ for 24 h at 40 °C or for 4 h at 200 °C. The actual catalysts consisted of highly active rhodium(0) metal supported on SiO₂ formed by the reduction of the rhodium complex precursor by the hydrogen pretreatment or during the hydrogenation reaction (1 atm H₂ at 40 °C). Palladium, in the [Rh]-Pd-SiO₂ systems, served to facilitate the reduction of the Rh complex to active rhodium metal in situ. On SiO₂ without Pd, activities were improved by hydrogen pretreatments prior to reaction, but on Pd-SiO₂, the rhodium catalysts were less active when pretreated by hydrogen.

In the present paper, we describe the use of the Rh-SiO₂ catalysts in the hydrogenation of PhF to CyF, PhH, and/or CyH as shown in Scheme 1. The effects of solvent, pH, added base, temperature, and hydrogen pressure on product selectivity and reaction rates were determined. The relative amounts of the products can be controlled by choosing the proper conditions. The catalytic reactions described in this paper, when used with the proper solvent and pH, catalyze the hydrodefluorination of PhF under the mildest reported conditions (1 atm H₂ at 40 °C) while still providing rates that are faster than those of other hydrodefluorination systems.

2. Experimental

2.1. General considerations

Ethanol, 1,2-dichloroethane, NaH₂PO₄, Na₂HPO₄, Na₃PO₄, 85% phosphoric acid, sodium acetate (NaOAc), glacial acetic acid, heptane, fluorobenzene, fluorocyclohexane, and benzene were purchased from commercial sources and used as received. Methanol was distilled from Mg/I₂ under nitrogen [25]. The catalysts [Rh(COD)₂]⁺BF₄⁻-SiO₂/200 °C (Rh-SiO₂(A)), [Rh(COD)₂]⁺BF₄⁻-SiO₂/40 °C, Rh-SiO₂, [Rh(COD)₂]⁺BF₄⁻-Pd-SiO₂, [Rh(COD)₂]⁺BF₄⁻-Pd-SiO₂/40 °C, [Rh(COD)₂]⁺BF₄⁻-Pd-SiO₂/200 °C, and Pd-SiO₂ were prepared and characterized as described previously [24].¹ Briefly, the catalysts were prepared by adsorbing [Rh(COD)₂]⁺BF₄⁻ on SiO₂ or Pd-SiO₂ (10% Pd w/w) to give a ~2% Rh (w/w) loading. These materials were used as obtained or pretreated with H₂ for 24 h at 40 °C or for 4 h at 200 °C. The resulting catalysts consist of highly active rhodium(0) metal on supported SiO₂. Gas chromatographic (GC) analyses were performed on a Hewlett-Packard HP 6890 GC using a J&W 30 m alumina capillary column and a flame ionization detector (FID).

2.2. Preparation of buffer solutions

The 1.0M buffers were prepared [26] by dissolving 0.10 mmol of acid in 80 ml of water and then adding NaOH until the pH, monitored by a pH meter, had reached the desired value. This solution was rinsed into a 100 ml volumetric flask and diluted to volume. Other concentrations of the buffers were obtained by this same procedure modifying the amount of acid added as appropriate. Acetate buffers were prepared for pH = 4.8 solutions, and phosphate buffers were prepared for pH = 11.2, 7.1, and 2.2 solutions.

2.3. Hydrodefluorination reactions

The general experimental procedures for both atmospheric pressure and high pressure reactions are outlined below. A number of different solvent systems, pressures, and temperatures were examined. The specifics of the reaction conditions will be discussed in detail as required in the discussion of the results.

2.3.1. Hydrodefluorination reactions at 1 atmosphere pressure

A standard hydrogenation run consisted of placing 50.0 mg of catalyst (containing ~9.7 μmol of Rh) and base into the reaction vessel (described previously [24,27–30])

¹ The catalysts are designated by the notation [Rh]-Pd-SiO₂/T °C (where [Rh] is the rhodium precursor, Pd-SiO₂ indicates the presence of reduced Pd metal on the SiO₂ support, and T °C indicates the temperature of any hydrogen pretreatment). In the present paper, most of the studies used [Rh(COD)₂]⁺BF₄⁻-SiO₂/200 °C, which is abbreviated Rh-SiO₂(A).

and replacing the atmosphere with Ar using three vacuum/flush cycles. Next, the jacket of the vessel was attached to a constant temperature bath and the temperature was raised to reaction temperature, 40.0 (± 0.2) °C. While the temperature was being achieved, a hydrogen gas reservoir was filled by a series of three consecutive vacuum and hydrogen gas flush cycles so that the system could be held at 1 atm H₂ throughout the reaction. After the temperature had stabilized at 40.0 °C and the gas burette was full of hydrogen, the reaction vessel itself was evacuated and filled with hydrogen three times. Next, solvent (5.0 ml) was added via syringe; when the solvent mixture was heptane (3.0 ml) and water (2.0 ml), the heptane layer was on top. After the system had achieved the reaction temperature, fluorobenzene 0.10 ml (1.1 mmol) was added via syringe. The reaction was opened to the hydrogen gas reservoir, stirring was initiated, and hydrogen uptake was recorded. The reaction was monitored by periodic GC analyses of samples of the organic layer removed with a syringe.

2.3.2. Higher pressure hydrodefluorination reactions (15–58 psi of hydrogen)

The reagents, 30.0 mg (containing ~ 5.8 μmol of Rh) of catalyst, 0.36 g (4.4 mmol) of NaOAc, and 0.40 ml (4.3 mmol) of PhF, were added to a Fischer–Porter high-pressure tube containing a Teflon-coated stir bar. After the solvent (5.0 ml) was added, the atmosphere was replaced with hydrogen using three freeze-pump-thaw cycles. After purging the atmosphere with hydrogen, the hydrogen pressure was raised while being monitored by the regulator on the hydrogen gas cylinder. Upon reaching the desired reaction pressure, the system was closed and immersed in an oil bath at 70 (± 1) °C. After the reaction was stirred for 30 min, the tube was removed from the oil bath, cooled to room temperature in water, and vented. After the layers were separated, the organic layer was dried over sodium sulfate and filtered prior to GC analysis. GC analysis showed that PhF and products were present in the upper organic layer and drying with sodium sulfate had no effect on their concentrations. No corrections were made for pressure changes due to heating or reaction progress.

3. Results

3.1. Effects of solvent on the reaction of PhF with H₂

3.1.1. Heptane

In heptane solution, the reaction of fluorobenzene with 1 atm H₂ at 40 °C catalyzed by Rh-SiO₂(A) produces a mixture of fluorocyclohexane and cyclohexane (entry 1, Table 1). The ratio of CyF to CyH is constant throughout the course of the reaction (Fig. 1) indicating concurrent competing reaction pathways (paths a and bc, in Scheme 1). The reaction is essentially complete within 30 min. Fluorocyclohexane is not converted to CyH during the catalytic

Table 1
Effect of solvent on the rate and product selectivity of the reaction of PhF with H₂^a

| Entry | Solvent | 95% Completion time (min) | CyH (%) | CyF (%) |
|-------|-------------------------------|---------------------------|---------|---------|
| 1 | Heptane | 30 | 23.4 | 76.6 |
| 2 | DCE | 1880 (60%) ^b | 36.7 | 63.3 |
| 3 | Heptane/methanol ^c | 600 | 100 | 0 |
| 4 | Heptane/water ^d | 180 | 100 | 0 |

^a Reaction conditions: 50.0 mg (containing ~ 9.7 μmol Rh) of Rh-SiO₂(A) catalyst, 1.1 mmol PhF, 5.0 ml solvent, 40.0 (± 0.2) °C, 1 atm H₂.

^b Reaction was only 60% complete after 1880 min.

^c 3.0 ml of heptane over 2.0 ml of methanol.

^d 3.0 ml of heptane over 2.0 ml of water.

reaction as the ratio (3.3:1.0 for CyF: CyH) of these products remains constant at longer reaction times (Fig. 1). From a series of runs, the ratio of CyF: CyH produced by the reaction is temperature-dependent and the following ratios were observed for the following temperatures: 4.0:1.0 (0 °C), 4.4:1.0 (20 °C), 3.7:1.0 (40 °C), and 9.9:1.0 (70 °C).

3.1.2. 1,2-Dichloroethane (DCE)

In the more polar, aprotic solvent DCE, the reaction of PhF with 1 atm H₂ at 40 °C catalyzed by Rh-SiO₂(A) also produces a mixture of CyF and CyH (entry 2, Table 1). However, the reaction is much slower (60% complete after 1880 min) than in heptane, and the CyF: CyH ratio decreases from 6.6:1 in the initial stages, during the first 150 min, to a ratio of 1.7:1 at 1880 min (Fig. 1). At 70 °C with four times the normal amount of catalyst (200 mg), the ratio of CyF: CyH was 2.3:1 and did not significantly change until after the reaction was over 95% complete (270 min). After the conversion of PhF to CyF and CyH, a much slower reaction ($\sim 3\%$ h⁻¹) was observed that converted CyF to CyH. The changing ratios of CyF: CyH suggests that CyF is converted to CyH during the catalytic reaction. Further experiments (Section 3.6) show that the conversion of CyF to CyH in DCE is not catalyzed by rhodium, silica, or hydrogen gas but is due to a reaction between CyF and HF, produced during the hydrodefluorination reaction.

3.1.3. Heptane/methanol

In the polar, protic heptane/methanol (3 ml/2 ml) solvent system, where two phases are present, no CyF is produced (entry 3, Table 1), and CyH is the only final product observed (after 600 min) in the reaction (Fig. 1) of PhF with 1 atm H₂ at 40 °C catalyzed by Rh-SiO₂(A). However, under these conditions, the intermediate benzene is detected in small amounts (<2%) before it is hydrogenated to CyH (steps b and c, Scheme 1).

3.1.4. Heptane/water

The more polar, protic heptane/water (3 ml/2 ml) solvent system produces only CyH as the final product (entry 4,

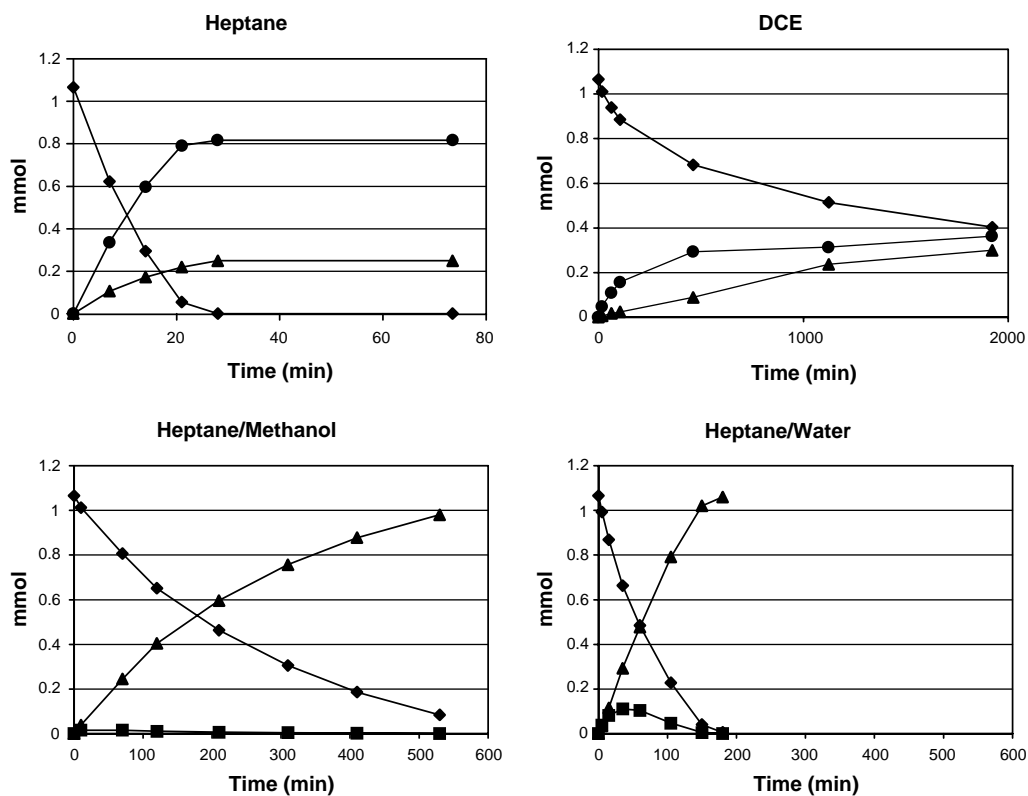


Fig. 1. Effect of solvent on the rate and selectivity of the reaction of PhF with H₂. (a) Reaction conditions are the same as those in Table 1. (◆) PhF, (●) CyF, (■) PhH, (▲) CyH.

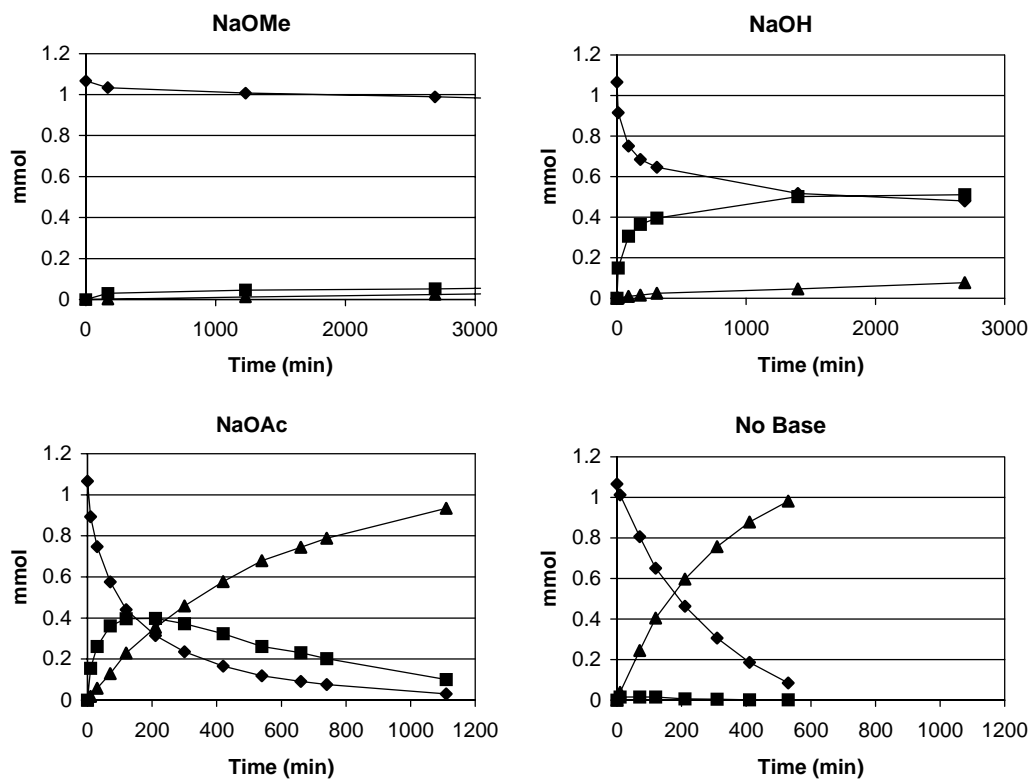


Fig. 2. Effect of base on the hydrodefluorination of PhF in heptane/methanol. Reaction conditions: 50.0 mg (containing $\sim 9.7 \mu\text{mol}$ Rh) of catalyst, Rh-SiO₂(A), 1.1 mmol PhF, 1.2 mmol base, 3.0 ml of heptane over 2.0 ml of methanol, 40 °C, 1 atm H₂. (◆) PhF, (●) CyF, (■) PhH, (▲) CyH.

Table 1) in the reaction of PhF with 1 atm H₂ at 40 °C catalyzed by Rh-SiO₂(A). As in heptane/methanol, PhH (steps b and c, Scheme 1) is observed (~10%) as an intermediate during the course of the reaction (Fig. 1). The reaction is faster in heptane/water, where it is essentially complete in 180 min, compared to heptane/methanol, where 600 min are required.

3.2. Effects of base and pH on the hydrodefluorination of PhF

3.2.1. Heptane/methanol

A number of different bases were used in the heptane/methanol solvent system for the reaction of PhF with 1 atm H₂ at 40 °C catalyzed by Rh-SiO₂(A) (Fig. 2). The rate of PhF hydrodefluorination (path bc, Scheme 1) decreased as the strength of the base increased: none > NaOAc ≫ NaOH ≫ NaOMe. For heptane/methanol without a base, the reaction is complete after 600 min and only small amounts (<2%) of the intermediate PhH are detected as it is hydrogenated to CyH (steps b and c, Scheme 1; Fig. 2). The reaction takes almost twice as long (1130 min) in the presence of NaOAc, and the intermediate PhH reaches a concentration of 36.4% during the course of the reaction (Fig. 2). With added NaOH, the first 310 min produce PhH (37%) with only trace hydrogenation to CyH (2%). After this point, conversion of PhF to PhH and PhH to CyH slows considerably and only 13% conversion of PhF occurs over the next 1100 min to provide PhH (47%) and CyH (5%). NaOMe deactivated the catalyst as only trace amounts of PhH (5%) and CyH (3%) were produced, even after 1500 min of reaction (Fig. 2).

3.2.2. Heptane/water

The rate of the Rh-SiO₂(A)-catalyzed reaction of PhF with 1 atm H₂ at 40 °C in buffered solutions depends on the pH of the aqueous phase (Table 2, Fig. 3). In general, slightly faster initial defluorination rates (step b, Scheme 1) were obtained in more basic media (Table 2). However, initial rates do not comprehensively describe the overall course of the reaction. In contrast to defluorination, the hydrogenation of benzene (step c, Scheme 1) is slower under more basic conditions (Table 2). The pH dependence of PhH hydrogenation accounts for the greater build-up of the PhH intermediate in the hydrodefluorination of PhF at higher pH (Fig. 3). The rate of benzene hydrogenation also affects the rate of hydrodefluorination of PhF, as the increase in PhH concentration decreases the rate of PhF reaction. This was shown in reactions of PhF in the presence of added PhH using the heptane/water (3 ml/2 ml) system buffered at pH = 2.2 under 1 atm H₂ at 40 °C catalyzed by Rh-SiO₂(A) (Table 3). As the concentration of PhH was increased, the rate of hydrodefluorination of PhF decreased. Thus, it appears that, because of inhibition by PhH, hydrodefluorination of PhF proceeds faster at lower pHs where PhH concentrations are low because of the rapid hydrogenation of PhH to CyH.

Table 2

Effect of pH on the hydrodefluorination of PhF^a and hydrogenation of PhH^b with H₂ in heptane/water solutions

| pH | Initial rate ^c | 95% completion time (min) ^a PhF hydrodefluorination | 95% completion time (min) ^b PhH hydrogenation |
|-------------------|---------------------------|--|--|
| 11.2 ^d | 54.5 | 1008 (68%) ^e | 293 |
| 7.1 ^d | 81.8 | 790 | 272 |
| 4.8 ^f | 28.7 | 600 | 226 |
| 2.2 ^d | 28.6 | 280 | 183 |

^a Reaction conditions: 50.0 mg (containing ~9.7 μmol Rh) of Rh-SiO₂(A) catalyst, 1.1 mmol PhF, 3.0 ml of heptane over 2.0 ml of 1.0 M aqueous buffer solution, 40.0 (±0.2) °C, 1 atm H₂.

^b Reaction conditions: 50.0 mg (containing ~9.7 μmol Rh) of Rh-SiO₂(A) catalyst, 0.36 mmol PhH, 3.0 ml of heptane over 2.0 ml of 1.0 M aqueous buffer solution, 40.0 (±0.2) °C, 1 atm H₂.

^c Initial rate calculated after 5 min of reaction according to [Δmole PhF/(mole Rh h)].

^d Phosphate buffer.

^e Reaction was only 68% complete after 1008 min.

^f Acetate buffer.

A series of hydrodefluorination reactions of PhF with 1 atm H₂ at 40 °C catalyzed by Rh-SiO₂(A) in heptane (3 ml) over aqueous buffered solutions of NaOAc/HOAc (2 ml, pH = 4.8) showed that the buffer concentration (1.0, 2.0, and 4.0 M) caused almost no variation in reaction rates or concentration of PhH intermediate (see Fig. 3, pH = 4.8 for a typical reaction profile). This indicates that the rate is independent of the acetate base concentration, but depends on the pH of the solution (Table 2, Fig. 3).

3.3. Re-use of Rh-SiO₂(A) in the hydrodefluorination of PhF

The catalyst, Rh-SiO₂(A), after use in the heptane/water reactions can be filtered in air, washed with water (5 × 10 ml/50 mg SiO₂), and re-used with no apparent loss of activity. This has been repeated two more times. Alternatively, the catalyst can be re-used by removal of solvent and

Table 3

Effect of added PhH on the rate of PhF hydrodefluorination in heptane/water buffered (pH = 2.2) solution^a

| PhH _i ^b (mmol) | Initial rate (ΔPhF) ^c | Initial rate (ΔPhH) ^d |
|--------------------------------------|----------------------------------|----------------------------------|
| 0 | 28.3 | – |
| 0.55 | 10.4 | 9.48 |
| 1.1 | 7.50 | 15.2 |
| 2.4 | 2.90 | 47.9 |

^a Reaction conditions: 50.0 mg (containing ~9.7 μmol Rh) of Rh-SiO₂(A) catalyst, 1.1 mmol PhF, 0–2.4 mmol PhH, 3.0 ml of heptane over 2.0 ml of 1.0 M aqueous acetate buffer solution at pH = 2.2, 40.0 (±0.2) °C, 1 atm H₂.

^b Initial amount of benzene (PhH_i).

^c Rate given as [Δmole PhF/(mole Rh h)] over the first 60 min of reaction.

^d Rate given as [Δmole PhH/(mole Rh h)] over the first 60 min of reaction.

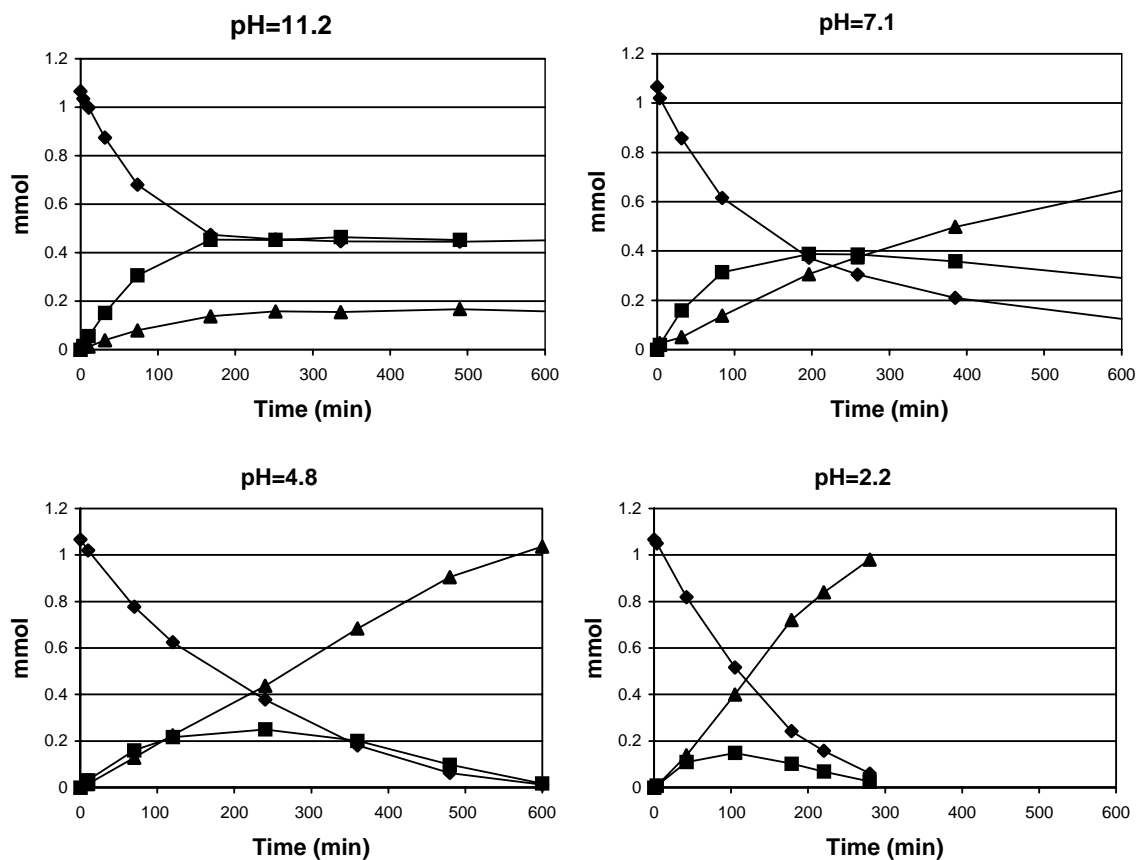


Fig. 3. Effect of pH on the hydrodefluorination of PhF in heptane/water solutions. Reaction conditions are the same as those in Table 2. Phosphate buffers were used for pH = 11.2, 7.1, and 2.2; an acetate buffer for pH = 4.8. (◆) PhF, (■) PhH, (▲) CyH.

substrate under vacuum followed by addition of fresh solvent and substrate without washing the catalyst. When this method of re-use was applied to the Rh-SiO₂(A)-catalyzed hydrodefluorination of PhF to CyH in heptane/water under 1 atm H₂ at 40 °C, three successive hydrodefluorinations were performed with no apparent catalyst deactivation. The unbuffered hydrodefluorination reactions in this example were more rapid (180 min to 95% completion) than the buffered reaction at pH = 2.2 (280 min to 95% completion) under the same conditions. The increased activity of the unbuffered reactions can easily be explained by the low pH (~1) of the solution at the end of the reaction; this low pH is presumably due to the HF produced during the reaction (see Scheme 1). Since lower pH values increase the rate of benzene hydrogenation (step c, Scheme 1) and the overall conversion of PhF (path bc, Scheme 1) (Section 3.2), the rate increase can be attributed to the more acidic conditions in the unbuffered reactions.

3.4. Effect of hydrogen pressure on the hydrodefluorination of PhF

The effect of hydrogen pressure on the reaction was examined for a heptane/ethanol/water (3/1.2/0.6 ml) solvent system with added NaOAc (0.36 g, 4.4 mmol) using the

high-pressure tube (Section 2.3.2) using Rh-SiO₂(A) with hydrogen pressures ranging from 15 to 58 psi at 70 °C. The following rates² were observed under the following pressures: 451 h⁻¹ (58 psi), 410 h⁻¹ (44 psi), 381 h⁻¹ (40 psi), 399 h⁻¹ (36 psi), 350 h⁻¹ (29 psi), 348 h⁻¹ (22 psi), 295 h⁻¹ (18 psi), 276 h⁻¹ (15 psi). The rate of reaction increases with increasing hydrogen pressure, and over the range of 15–58 psi (~1–4 atm) of H₂, the rates vary by a power of 1/3, i.e. rate ∝ P_{H₂}^{1/3} (Fig. 4).

The effect of hydrogen pressure on the ratio of CyF to CyH was examined for heptane (5 ml) using Rh-SiO₂(A) with hydrogen pressures ranging from 15 to 58 psi at 70 °C. All reactions were complete within 30 min and the following ratios of CyF: CyH were observed under the following pressures: 9.9:1.0 (15 psi), 12.0:1.0 (29 psi), and 8.2:1.0 (58 psi). Thus, it was observed that variations in hydrogen pressure over 1–4 atm caused very little change in the ratio of CyF to CyH. However, the resulting solution contains HF, which is capable of promoting the conversion of CyF to CyH; this will decrease the CyF: CyH ratio at longer times (see Section 3.6).

² Rate given as [Δ mole PhF/(mole Rh)] over the first 30 min of reaction.

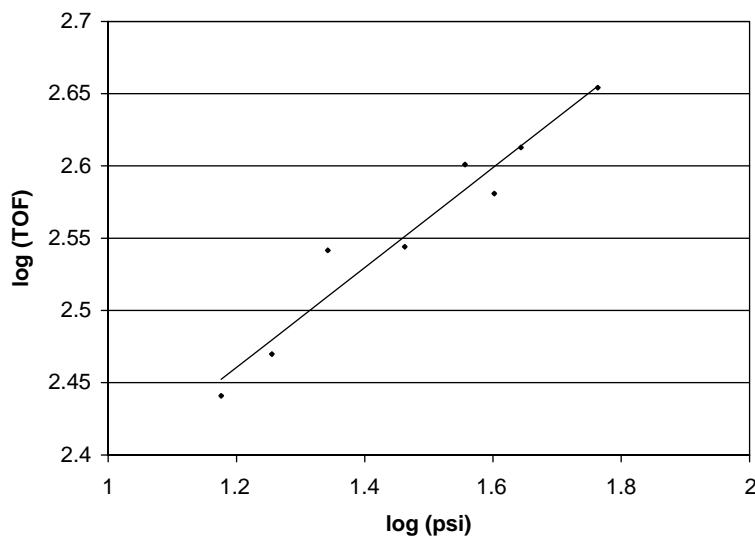


Fig. 4. Effect of hydrogen pressure on the hydrodefluorination of PhF. Reaction conditions: 30.0 mg (containing $\sim 5.8 \mu\text{mol}$ Rh) of Rh-SiO₂(A) catalyst, 4.3 mmol PhF, 0.36 g (4.4 mmol) NaOAc, 3.0 ml of heptane over 1.2 ml ethanol and 0.8 ml water, 70 °C, 30 min reaction time, $P_{\text{H}_2} = 15 - 58$ psi, Fischer–Porter reaction vessel. The equation for the best-fit line is $y = 0.35x + 2.05$. Thus, over the range 1–4 atm, rate $\propto P_{\text{H}_2}^{1/3}$.

3.5. Other catalysts for the hydrodefluorination of PhF

The [Rh(COD)₂]⁺BF₄⁻-SiO₂/40 °C, Rh-SiO₂, [Rh(COD)₂]⁺BF₄⁻-Pd-SiO₂, [Rh(COD)₂]⁺BF₄⁻-Pd-SiO₂/40 °C, [Rh(COD)₂]⁺BF₄⁻-Pd-SiO₂/200 °C, and Pd-SiO₂ catalysts were examined for their PhF hydrodefluorination activity under 29 psi H₂ at 70 °C with NaOAc base in the heptane/ethanol/water solvent system (Table 4). The activities of the various rhodium and rhodium/palladium

Table 4
Rates of hydrodefluorination of PhF^a and hydrogenation of toluene^b using various catalysts

| Catalyst | Rate (PhF) ^c | Rate (PhMe) ^d |
|--|-------------------------|--------------------------|
| Rh-SiO ₂ (A) | 350 | 246 |
| [Rh(COD) ₂] ⁺ BF ₄ ⁻ -SiO ₂ /40 °C | 244 | 95 |
| Rh-SiO ₂ | 280 | 151 |
| [Rh(COD) ₂] ⁺ BF ₄ ⁻ -Pd-SiO ₂ | 371 | 230 |
| [Rh(COD) ₂] ⁺ BF ₄ ⁻ -Pd-SiO ₂ /40 °C | 369 | 210 |
| [Rh(COD) ₂] ⁺ BF ₄ ⁻ -Pd-SiO ₂ /200 °C | 135 | 46 |
| Pd-SiO ₂ | 12.1 ^e | ~ 1.4 ^e |

^a Reaction conditions: 30.0 mg (containing $\sim 5.8 \mu\text{mol}$ Rh) of the catalyst indicated, 4.3 mmol PhF, 0.36 g (4.4 mmol) NaOAc, 3.0 ml of heptane over 1.2 ml ethanol and 0.8 ml water, 70 °C, $P_{\text{H}_2} = 29$ psi, 30 min reaction time, Fischer–Porter reaction vessel.

^b Reaction conditions: 50 mg of solid catalyst, 5 ml of toluene, 40.0 °C, 1 atm of H₂ from [24].

^c Rate given as [Δ mole PhF/(mole Rh h)] over 30 min of reaction.

^d Rate given as [Δ mole PhH/(mole Rh h)] over the first hour of reaction [24].

^e To facilitate comparison, the rate for the Pd-SiO₂ catalyst is reported in terms of an effective rate. Since, it does not contain rhodium, a rate based on rhodium cannot be calculated. The rate value here is calculated by assuming the Pd-SiO₂ catalyst contains the standard rhodium loading (5.8 μmol /30.0 mg).

catalysts in the hydrodefluorination of PhF to PhH and CyH approximately parallels their toluene hydrogenation activities [24]. Detailed characterization (DRIFTS, TEM, XPS, and mercury poisoning experiments) of the rhodium containing catalysts showed that they all consist of rhodium metal on silica, which is responsible for their toluene hydrogenation activity [24]. The effect of the palladium in the [Rh]-Pd-SiO₂ systems is to facilitate the reduction of the Rh complex to active rhodium metal. The catalytic activity of supported rhodium catalysts is structure sensitive and depends on particle size with metal clusters of $\sim 10 \text{ \AA}$ or larger needed for arene hydrogenation [31–37]. For catalysts prepared from the rhodium precursor [Rh(COD)₂]⁺BF₄⁻ on silica, toluene hydrogenation activities are improved by hydrogen pretreatments prior to reaction. The activity increases with the temperature of the hydrogen pretreatment, 200 °C (Rh-SiO₂(A), rate = 246 h⁻¹) being greater than 40 °C ([Rh(COD)₂]⁺BF₄⁻-SiO₂/40 °C, rate = 95 h⁻¹). For [Rh(COD)₂]⁺BF₄⁻ on Pd-SiO₂, a different trend is observed as the catalysts are more active when they are not pretreated. The untreated catalyst ([Rh(COD)₂]⁺BF₄⁻-Pd-SiO₂, rate = 230 h⁻¹) is the most active of the series. A 40 °C H₂-pretreatment produces no appreciable change in rate ([Rh(COD)₂]⁺BF₄⁻-Pd-SiO₂/40 °C, rate = 210 h⁻¹). A 200 °C, hydrogen pretreatment severely reduces the catalytic activity by almost five-fold ([Rh(COD)₂]⁺BF₄⁻-Pd-SiO₂/200 °C, rate = 46 h⁻¹). This treatment apparently changes the structure of the catalyst to a form that is substantially less active for arene hydrogenation than just rhodium on the same support. This lower activity was attributed either to the formation of a rhodium–palladium alloy or to the formation of rhodium clusters that are smaller than the 10 \AA size required for

arene hydrogenation activity [24,31,32]. Since the most active hydrogenation catalysts are also the most active hydrodefluorination catalysts (Table 4) and benzene is observed to inhibit the hydrodefluorination reaction, the same catalytic sites on rhodium metal are probably used for both toluene hydrogenation and fluorobenzene hydrodefluorination.

3.6. Attempted hydrodefluorination of CyF

Hydrodefluorination of CyF was attempted using Rh-SiO₂(A) as a catalyst under all of the reaction conditions (heptane, DCE, heptane/water; pH = 11.2–2.2; 1–4 atm H₂; 40–70 °C) examined in this study, but CyF remained unreacted even after 24 h of treatment. However, Blum et al. [22] reported that thermal defluorination of fluorocyclohexane to cyclohexane occurs in DCE at 80 °C under 16 atm H₂. Also, during the hydrodefluorination of PhF, CyF was converted to CyH in DCE under 1 atm H₂ at 70 °C over Rh-SiO₂(A) (see Section 3.1.2). We observe that the addition of 0.1 ml of HF (49% aqueous solution) to CyF in DCE under 1 atm H₂ at 70 °C over Rh-SiO₂(A) causes a rapid conversion (<40 min) of CyF to CyH. The slower conversion of CyF to CyH (~3% h⁻¹) observed during the hydrodefluorination of PhF in DCE indicates that the rate of conversion of CyF depends on the amount of HF added. However, changing the amount of Rh-SiO₂(A) did not change the rate of CyF conversion. Moreover, in the absence of Rh-SiO₂(A), but in the presence of 0.1 ml of aqueous HF, CyF is quantitatively converted to cyclohexene in DCE at 70 °C within 30 min. Thus, the conversion of CyF to CyH is a two-step process consisting of the conversion of CyF to cyclohexene in the presence of HF (step d, Scheme 1) followed by the Rh-catalyzed hydrogenation of cyclohexene to CyH (step e, Scheme 1). This HF-promoted conversion of CyF to CyH (path de, Scheme 1) also occurs in heptane, but is more rapid in DCE.

4. Discussion

4.1. Effect of solvent on the Rh-SiO₂(A)-catalyzed reaction of PhF with H₂

For the Rh-SiO₂(A)-catalyzed reaction of fluorobenzene with hydrogen, the solvent system affects the product distribution (path a or path bc, Scheme 1). The non-polar solvent heptane produces mixtures of CyF and CyH with a CyF: CyH ratio of 3.3:1.0 at 40 °C and 9.9:1.0 at 70 °C. DCE, an aprotic but more polar solvent than heptane, still favors initial arene hydrogenation over hydrodefluorination, but the ratio of CyF to CyH is lower because the HF-promoted conversion of CyF to CyH (path de, Scheme 1) occurs at a rate similar to the rate of the rhodium-catalyzed reaction of PhF and H₂ (paths a and bc, Scheme 1). In contrast, reactions in polar protic solvent systems, heptane/methanol and heptane/water, proceed only by path bc, Scheme 1. The reaction is faster in heptane/water than in heptane/methanol.

Prior to this work, there were only a limited number of reports of the catalytic hydrodefluorination of monofluoroarenes [12–23] and fewer by rhodium metal [20–23]. No studies of solvents on these reactions have been reported. The effects of solvent on the reaction of hydrogen with PhF catalyzed by Rh-SiO₂(A) are complex. The ratio of CyF: CyH decreases as the solvent polarity increases: heptane (3.3:1) > DCE (2.3:1) > heptane/methanol (0:1) = heptane/water (0:1). The rate of reaction also varies with solvent but is complicated by the existence of two reaction pathways (path a and path bc, Scheme 1). For the solvents examined, the trend in the rate of reaction of PhF is heptane > heptane/water > heptane/methanol > DCE. Furthermore, the ability of our system to catalyze the formation of CyF from PhF in heptane is notable because studies in other systems show that metal catalyzed reactions of arylfluorides with hydrogen give only hydrodefluorinated products and no fluorocyclohexanes are formed [12–22,37–41].

4.2. Effect of pH on the hydrodefluorination of PhF in heptane/water

The Rh-SiO₂(A)-catalyzed hydrodefluorination of PhF in heptane/water follows path bc in Scheme 1. The hydrodefluorination step b is slightly faster when the solution is basic (initial rate = 54.5 h⁻¹ at pH = 11.2 compared to an initial rate of 28.6 h⁻¹ at pH = 2.2, Table 2), but the overall reaction (path bc, Scheme 1), including arene hydrogenation to CyH (step c, Scheme 1), is faster under acidic conditions (Table 2 and Fig. 3). This is because benzene inhibits hydrodefluorination (step b), confirmed by competition reactions between PhF and PhH using the heptane/water system buffered at pH = 2.2 (Table 3), and can slow the overall process to the point where PhH hydrogenation determines the rate of PhF hydrodefluorination (see pH = 7.1 and 11.2, Fig. 3). Therefore, the conversion of PhF to CyH is fastest under acidic conditions (Fig. 3) because PhH hydrogenation is fastest under these conditions (Table 2).

At first glance, this result seems to contradict previous studies of hydrodehalogenation (F, Cl, Br, I) reactions over supported metals (Pd, Rh, Pt, Ni), where base has often been used to neutralize the hydrogen halide product as it is formed [38,41]. However, previous studies of arene hydrogenation catalyzed by rhodium metal have found inhibition by strong bases [37–41] (especially strong nitrogen bases such as amines and pyridines), while acids have been observed to both promote and inhibit the reaction [37–41]. For example, Stocker observed that acetic acid in methanol increased the rate of hydrogenation of certain aromatics over rhodium on alumina [38,42]; but the hydrogenation of toluene or benzoic acid in methanol over 5% rhodium on carbon was neither promoted nor inhibited by the addition

of several weak or strong acids, except HCl which was a strong inhibitor [37–41,43].

For the hydrodefluorination of PhF by Rh-SiO₂(A) in heptane/water solvent, the hydrodefluorination product interacts strongly enough with the catalyst to inhibit further hydrodefluorination of PhF. This inhibition is particularly important when the concentration of PhH is highest, which occurs at high pH where the rate of PhH hydrogenation to CyH is slowed. This leads to a situation where conventional hydrodefluorination conditions, i.e. use of strong bases to neutralize the hydrogen halide acid as it is formed, becomes detrimental to rhodium-catalyzed hydrodefluorination. The inhibition of hydrodefluorination by PhH and low rate of PhH hydrogenation under basic conditions may explain the much lower rates of fluorobenzene hydrodefluorination observed by Young and Grushin [21] who used a rhodium nanoparticle catalyst in a very basic 40% NaOH aqueous solvent under 40 psi H₂ at 95 °C; these conditions yielded only 88 turnovers in 1 day with minimal hydrogenation of the resulting benzene.

5. Conclusions

In these studies of the Rh-SiO₂(A)-catalyzed reactions of PhF with H₂, non-polar, aprotic solvents (heptane and DCE) favor arene hydrogenation (path a, Scheme 1), while polar, protic solvents (heptane/methanol and heptane/water) favor hydrodefluorination (path bc, Scheme 1). A benzene intermediate, on the way to CyH, was detected in the heptane/methanol and heptane/water reactions confirming the pathways shown in Scheme 1. The complete hydrodefluorination of fluorobenzene to cyclohexane was found to proceed best in heptane/water under acidic conditions. This is because PhH inhibits the hydrodefluorination of fluorobenzene to benzene (step b), and the hydrogenation of benzene to cyclohexane is fastest under acidic conditions. Since the supported rhodium catalysts most active for toluene hydrogenation are also the most active hydrodefluorination catalysts (Table 4) and benzene is observed to inhibit the hydrodefluorination reaction, the same catalytic sites on rhodium metal are probably used for both arene hydrogenation and fluorobenzene hydrodefluorination. To the best of our knowledge, the systems described in this paper, when used in heptane/water at low pH, catalyze the hydrodefluorination of PhF under the mildest reported conditions, 1 atm H₂ at 40 °C, while still providing rates that are faster than those of other hydrodefluorination systems which utilize more strenuous conditions.

Acknowledgements

This research was supported at Ames Laboratory by the US Department of Energy, Office of Science, Office

of Basic Energy Sciences, Division of Chemical Sciences, under Contract W-7405-Eng-82 with Iowa State University.

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