

Hydrogenation and dehalogenation of aryl chlorides and fluorides by the sol–gel entrapped RhCl_3 –Aliquat 336 ion pair catalyst

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Abstract

The SiO_2 sol–gel entrapped ion pair $[(\text{C}_8\text{H}_{17})_3\text{NMe}]^+[\text{RhCl}_4n\text{H}_2\text{O}]^-$, generated from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, Aliquat 336[®] and $\text{Si}(\text{OMe})_4$ catalyzes at 80°C and 16 atm. H_2 , the hydrogenation of aryl fluorides and chlorides to give halogen-free hydroaromatics. Fluorobenzenes initially yield fluorocyclohexanes which eliminate HF, in a non-catalytic process, followed by hydrogenation of the cyclohexenes. In contrast, chlorobenzenes are first dehalogenated to the corresponding benzene derivatives, that in a second step are hydrogenated to cyclohexanes. Aryl bromides undergo dehalogenation and hydrogenation as well, but only in the presence of a free radical scavenger. The catalyst in these reactions is leach-proof and recyclable with little or no loss in activity. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The ion pair generated from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and methyltrioctylammonium chloride (Aliquat 336[®]) [1] was shown to be under phase transfer conditions an efficient catalyst for a variety of hydrogen transfer [2], alkyne oligomerization [3], cyclorearrangement [4] and addition pro-

cesses [5]. In some of these catalyses [1,2,6,7], the rhodium catalyst could be recovered in part (though not entirely) as water soluble recyclable rhodium compounds, by treatment of the reaction mixtures with lipophilic salts (NaClO_4 , NaBPh_4), while in other cases the ion pair was transferred to non-recyclable complexes and occasionally even to metallic rhodium. Among the latter processes of particular interest is the hydrogenation of aromatic C–C bonds [8–11]. Lately, Finke and his group have demonstrated by detailed studies that in their laboratory the RhCl_3 –Aliquat 336 catalyst is converted into nanoclusters of rhodium during the hydrogenation

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tion of benzene. These metallic particles proved to catalyze, even in trace amounts, the transformation of benzene to cyclohexane [12]. Since the physical entrapment of RhCl_3 together with Aliquat 336 in a sol–gel matrix forms a highly stable, recyclable and efficient double bond migration, dihydroarene isomerization and olefin hydroformylation catalyst [13,14], we have investigated the activity of the ceramic catalyst also in some arene hydrogenation processes [13]. Intensive activity in the preparation of sol–gel catalysts in other laboratories focused on the covalent attachment of the catalytic moiety [15,16] to the ceramic backbone. Most of our activity in this field focused on the *direct physical entrapment* of the catalyst which provides the advantages of not needing special synthetic steps to enable the anchoring of the catalyst, and of not altering the molecular structure of the catalyst by its derivatization. In this study, we report on the hydrogenation and dehalogenation of aryl fluorides, chlorides and bromides (the latter only in the presence of a free radical scavenger), many of which are known environmental hazards [17], by silica sol–gel encapsulated RhCl_3 –Aliquat 336 catalyst.

2. Experimental

2.1. General

^1H and ^{13}C NMR spectra were recorded on Bruker AMX-300 and AMX-400 instruments. MS measurements were performed on a Hewlett-Packard model 4989A mass spectrometer equipped with an HP gas chromatograph model 5890 series II. XPS experiments were performed on a PHI AES-XPS model 555 spectrometer with a background pressure of 2×10^{-10} Torr using $\text{Al K}\alpha$ radiation. Gas chromatographic separations and analyses were carried out with the aid of a Hewlett-Packard GC model 417. Electronic spectra were recorded on a Hewlett-Packard spectrophotometer model 2454A. Atomic absorption spectrometry was carried out on a Perkin-Elmer spectrophotometer model 403 using a Juniper rhodium cathode lamp. The hydrogenation experiments were performed either in a Parr bench top micro reactor Series 4591 with a temperature controller No. 4841 equipped with a mechanical stirrer and a sampler, or in a 45 ml Parr pressure vessel model 4712 with a gage block No. 4316.

Table 1

Hydrogenation–dehalogenation of aryl fluorides and chlorides in the presence of the sol–gel entrapped RhCl_3 –Aliquat 336 catalyst under comparable conditions^a

Experiment	Substrate	Products (yield in the first run, %) ^b
1	fluorobenzene	cyclohexane (100)
2	2-fluorotoluene	methylcyclohexane (100)
3	4-fluorotoluene	methylcyclohexane (100)
4	2-fluoroanisole	1-fluoro-2-methoxycyclohexane (12), fluorocyclohexane (12), cyclohexane (17), cyclohexanol (19), cyclohexanone (8)
5	3-fluoroanisole	cyclohexane (13), cyclohexanol (21), cyclohexanone (10)
6	4-fluoroanisole	cyclohexane (9), cyclohexanol (25), cyclohexanone (20)
7	chlorobenzene	cyclohexane (100)
8	1-chloronaphthalene	tetralin (20)
9	2-chlorotoluene	methylcyclohexane (14)
10	3-chlorotoluene	methylcyclohexane (60)
11	4-chlorotoluene	methylcyclohexane (32)
12	1,4-dichlorobenzene	cyclohexane (60)
13	3-chloroanisole	cyclohexane (19)
14	4-chloroanisole	cyclohexane (23)
15	4-chlorophenol	cyclohexane (14), cyclohexanone (17)

^aReaction conditions: 2 mmol substrate, catalyst containing 4.1×10^{-2} mmol, Rh, 16 atm. H_2 , 3 ml 1,2-dichloroethane, 80°C, 18 h.

^bThe missing percentage reflects on the unreacted starting material.

2.2. Entrapment of the ion pairs

Sol–gel encapsulated RhCl_3 –Aliquat 336, RhCl_3 –methyltrioctylammonium bromide, and RhCl_3 –tetraheptylammonium bromide (SG-1, SG-2 and SG-3, respectively) were prepared and analyzed essentially as described previously for SG-1 [14].

2.3. General procedure for the hydrogenation of aryl chlorides and fluorides

A mixture of 2 mmol of substrate, the sol–gel entrapped catalyst (from 4.1×10^{-2} mmol of each of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and the quaternary ammonium salt) and 3 ml of $(\text{CH}_2\text{Cl})_2$ was placed in a pressure vessel. After purging with either N_2 or Ar, the autoclave was filled with H_2 at the desired pressure and heated at $80 \pm 0.2^\circ\text{C}$ for the desired length of time. After cooling to room temperature, the catalyst was filtered off and the products in the filtrate were analyzed in the crude state as well as after chromatography (column or GC), either by direct comparison with authentic samples or by comparison of their spectral data (^1H , ^{13}C NMR or GC-MS) with those reported in the literature. Typical results are summarized in Table 1. The filtrate was analyzed for leached rhodium by atomic absorption spectrometry. The recovered catalyst was refluxed in 20 ml CH_2Cl_2 for 30 min, sonicated for 30 min in the same solvent, washed with water at 80°C and dried at 0.1 mm for at least 3 h before recycling in a subsequent run.

3. Results and discussion

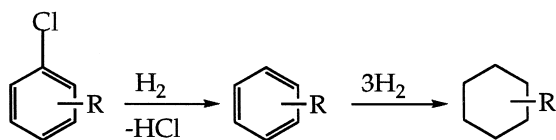
The addition of equimolar quantities of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and Aliquat 336 to tetra-methoxysilane in aqueous methanol, during its polycondensation forms a sol–gel encapsulated ion pair, SG-1, whose electronic spectrum resembles that of the non-immobilized $[(\text{C}_8\text{H}_{17})_3\text{NMe}]^+[\text{RhCl}_4 \cdot n\text{H}_2\text{O}]^-$ [14]. In analogy to the soluble complex, the hybrid material was

found to catalyze the hydrogenation of benzene and other aromatics to give cyclohexane derivatives. No significant change in the orange color of the entrapped ion pair was observed during the catalytic process. The X-ray photoelectron spectrum of the used SG-1 catalyst that was taken using 25 eV pass energy (calibrated vs. the C 1s signal) showed in the 300 eV binding energy region two discrete Rh $3d_{5/2}$ lines at 309 (s) and 307.7 (w) eV, indicating the presence of Rh(III) and Rh(I) species [18]. The absence of a line at 307 eV indicates, that within the accuracy of the XPS measurements, the recovered catalyst did not contain metallic rhodium [18].

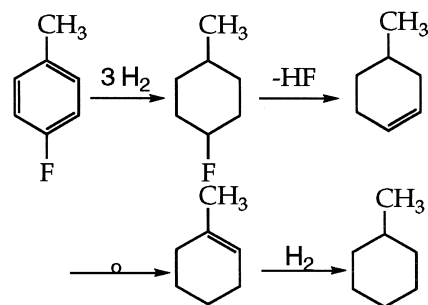
The heterogenized ion pair SG-1 was found to promote the conversion of many aryl chlorides and fluorides into halogen-free hydroaromatics (Table 1) just as the non-entrapped catalyst does [9,10]. However, in contrast to the latter, SG-1 was found not to catalyze the dehalogenation and hydrogenation of aryl bromides under such conditions (vide infra). The catalyst used in the reactions listed in Table 1 could be recycled, in most cases, for at least 4–6 times. Metal leaching, if at all, was below the detection limit of 1 ppm. Nevertheless, the catalytic activity decreased after each run probably due to blocking of some of the pores leading to the entrapped catalyst. Reopening of the pores by sonication in boiling CH_2Cl_2 followed by washing with boiling water (or dilute base) regenerated most of the original activity (cf. Ref. [19]). Typical yields of 4-methylcyclohexane obtained in the dehalogenation–hydrogenation of 4-chlorotoluene under the conditions of Table 1 were 32%, 32%, 28%, 26%, 22% and 22%, respectively, in the first six runs. Since, however, the washing of the used catalyst with a dilute base, or even with water, cleaves some Si–O bonds [20] slow deterioration of the silica backbone was found to take place until at one of the advanced runs the catalyst underwent complete destruction and lost its activity. In general, the ceramic catalyst used in the transformations of aryl chlorides lasted longer than in the hydro-

genation of aryl fluorides that form HF during the process.

Although chloro- and fluorobenzenes yield the same cyclohexane derivatives upon hydrogenation these substrates were shown to follow different pathways. While the chloro compounds are first dehalogenated to give halogen-free benzenes that undergo hydrogenation in the second step (Scheme 1), fluorobenzenes are first converted into thermally labile fluorocyclohexanes that eliminate HF at the reaction temperature (in a non-catalytic process) to give cyclohexenes, followed by catalytic addition of H_2 . These sequences of reactions have been verified by 1H NMR spectrometry. The elimination of HF yields substituted cyclohexenes that often isomerize in the present of SG-1 [13] prior to their hydrogenation. For example, 4-fluorotoluene follows the sequence of reactions outlined in Scheme 2. The overall rate of transformation of aryl fluorides is usually faster than that of the corresponding chlorides (Table 1). The reactions of both halides are influenced by steric effects (2-substituted halides react slower than the 3- and 4-substituted analogs), as well as by electronic factors (electron attracting substituents enhance the catalyses and vice versa electron releasing groups). In several cases, e.g., in the reaction of 1-chloronaphthalene and 9-chloroanthracene, SG-1 was capable of completely removing the chlorine, whereas the non-entrapped catalyst failed to do so. This, however, may be attributed to the higher temperature and pressures employed for the heterogenized catalyst, i.e., $50^\circ C$ and > 10 atmospheres of H_2 vs. $30^\circ C$ and atmospheric pressure of H_2 used with the non-entrapped catalyst [9,10]. In general, no chlorinated products could ever be detected with the entrapped catalyst.



Scheme 1. Dehalogenation and hydrogenation of chlorobenzene.



Scheme 2. Hydrogenation and dehalogenation of 4-fluorotoluene.

Differences in the required conditions in the two systems seems to be responsible also for the fact that the heterogenized catalyst promotes partial or even complete hydrogenolysis of methoxyl moieties (see e.g., Table 1, experiments 4–6 and 13, 14).

Except for benzyl chloride, that gave under the conditions of Table 1 quantitative yield of methylcyclohexane, chlorine atoms bound to non-aromatic carbon atoms were found to be resistant to hydrogenolysis. Thus, e.g., 3-chloropropylbenzene afforded exclusively the hydroaromatic compound 3-chloropropylcyclohexane (25% conversion under the conditions of Table 1). Hydrogenation of chloronitrobenzenes in the presence of SG-1 was found to take place preferentially at the nitro group to give the respective chloroanilines.

Many trials to convert aryl bromides and iodides into halogen-free hydroaromatics under the conditions of Table 1 were, at first, unsuccessful. Thus, in the best experiments bromo- and iodobenzene as well as 4-bromotoluene and 1- and 2-bromonaphthalene gave only traces ($< 0.5\%$) of the expected cyclohexanes, and the recovered ceramic material proved completely inactive as hydrogenation catalyst (even when in the second run aryl chlorides, alkenes, alkynes and unsubstituted aromatics were used as substrates). In fact even bromine atoms in non-aromatic systems, except that in benzyl bromide were found to poison the catalyst. Benzyl bromide reacted under 35 atm. H_2 to give quantitative yield of toluene free of any methylcyclohexane after 18 h at $80^\circ C$ (cf. the reaction of

benzyl chloride described above). In 4-bromochlorobenzene neither of the halogen atoms nor the aromatic C–C bonds were affected. Unlike 3-chloropropylbenzene the bromo-analog proved completely refractory to SG-1. Also, the addition of traces of bromine as well as of many non-reducible bromine containing substances, such as HBr, Et₂NH₂Br, Et₃NBr and LiBr were found to stall the catalysis. However, no destruction of the catalyst was noted when the bromine atom had been incorporated in the quaternary ammonium-rhodate ion pair. For example, the sol-gel entrapped [(C₈H₁₇)₃-NMe]⁺[RhBrCl₃.nH₂O]⁻, SG-2 (formed by replacement of the Aliquat 336 by the corresponding methyltrioctylammonium bromide) was shown to promote the conversion of 4-chlorotoluene to methylcyclohexane, under the conditions of Table 1 to an extent of 10%. The immobilized ion pair, obtained from RhCl₃.3H₂O and tetraheptylammonium bromide (SG-3) yielded under these conditions as much as 68% of halogen-free products: 39% of toluene and 29% of methylcyclohexane. The recovered catalyst from the latter two processes was not deactivated and could be reused in advanced runs as well as in catalytic dehalogenation-hydrogenation of chlorobenzene.

In search for the reason for the catalyst poisoning we have first assumed that the lowering of the pH by small amounts of HBr which may have been formed from the bromo-compounds during the initial step of the process is responsible for the effect. We found however, that neutralization of the reaction mixture by either triethylamine or NaOMe did not revive the activity of the catalyst. In fact, the addition of gaseous HCl hardly affected the reaction rate. Replacement of half of the dichloroethane by acetic acid in the standard experiment with 4-chlorotoluene even enhanced the process. The yield of methylcyclohexane rose after 18 h from 32% to 54% in the first run. Thus, any connection between the pH and catalyst deactivation could be ruled out. The actual reason for the phenomenon was found to be the formation of

free radicals that readily reduce the acting Rh(I) species to inactive *entrapped* metallic rhodium. Whenever catalyst poisoning took place the orange color of SG-1 (that usually did not change even upon recycling) turned black. The same change in color occurred also when a free radical initiator (e.g., benzoyl peroxide) was added to the reaction mixtures of some of the aryl chlorides listed in Table 1. Therefore, we added to the reaction mixture of bromobenzene, the free radical scavenger, hydroquinone (twice the molar amount of the rhodium in the SG-1) and observed immediate conversion of the substrate into cyclohexane. However, as the hydroquinone itself underwent hydrogenation the process stopped after most of the additive had been consumed. The catalyst darkened and could not be reused. Substitution of this radical scavenger by 2,5-di-*tert*-butylhydroquinone which is not hydrogenated under our reaction conditions, prevented completely the destruction of the catalyst and enabled its recycling in a second run. The catalytic dehalogenation-hydrogenation of aryl bromides in the presence of 2,5-di-*tert*-butylhydroquinone proved to be substantially slower than the reaction of aryl chlorides in the absence of this additive. For example, under the conditions of Table 1 (molar ratio substrate:additive 10:1) bromobenzene yielded 6% of benzene and 7% of cyclohexane, and 4-chlorobromobenzene formed 2% of benzene and 12% of cyclohexane (free of any monohalobenzene).

4. Conclusion

It should be recalled that the non-entrapped RhCl₃-Aliquat 336 catalyst promotes equally well the dehalogenation-hydrogenation of both aryl chlorides and aryl bromides provided that the halogen atoms are bound to an aromatic ring that is being reduced in the process [9,10]. It seems to us that the different behavior between the sol-gel entrapped and non-entrapped catalysts, in respect to their activation of aryl bromides, is associated with either of the following

two facts. (a) Oxygen adsorbed on silica surfaces is highly reactive [21] and may assist the generation of a bromine radical from HBr [22]. (b) The *homogeneous* RhCl₃–Aliquat 336 ion pair may ultimately be converted under H₂ into catalytically active nanoclusters that are not affected by free radicals. Because of Finke's observation that only minute quantities of nanoclusters of rhodium are needed for catalyzing the hydrogenation of benzene [12], we cannot say for sure that small quantities of such particles, that are not detectable by XPS measurements, are not involved also in our catalyses. In any event it is advisable to apply 2,5-di-*tert*-butylhydroquinone or similar compounds in dehalogenation and hydrogenation of aryl bromides whenever the formation of free radicals is possible.

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