Hydrogen-transfer hydrodehalogenation of aromatic halides with alcohols in the presence of noble metal catalysts

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Abstract

Catalytic hydrodehalogenation of aromatic halides was carried out in an alcohol solution containing base compounds in the presence of carbon-supported noble metal catalysts. It was found that dechlorination of 1,2,4-trichlorobenzene to benzene effectively occurred in a 2-propanol solution of a base compound such as NaOH or KOH in the presence of Rh/C or Pd/C at temperatures below 65°C. When deuterium-labeled 2-propanol, $CD_3CD(OD)CD_3$, was used as a solvent, 1,2,4-trichlorobenzene was dechlorinated to give benzene containing D atoms with high yield, indicating that the hydrodechlorination reaction includes hydrogen-transfer from 2-propanol to chlorobenzenes. Iodo-, bromo- and fluoro-benzenes were also readily dehalogenated in the catalytic system. © 1997 Elsevier Science B.V.

Keywords: Hydrodehalogenation; Aromatic halides; Hydrogen-transfer; 2-propanol; Base compound; Noble metal catalyst
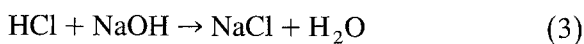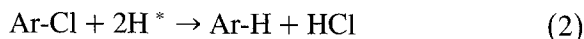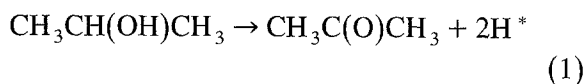
1. Introduction

The development of effective procedures for dehalogenation of organic halides is a current issue in protecting ourselves from pollution by industrial halogen-containing organic wastes. There has been reported a number of catalytic dehalogenation methods for organic halides. In conventional procedures, molecular hydrogen has been widely employed for the catalytic hydrodehalogenation of organic halides [1], in which high hydrogen pressure (about 50 atm) is

often necessary [2,3]. In recent years, facile methods have been developed including transfer hydrogenation by using hydrogen donors such as metal hydrides [4,5], formic acid and its salts [6–9] and alcohols [10–13]. The hydrogen-transfer usually proceeds under relatively mild conditions in the presence of noble metal or transition metal catalysts.
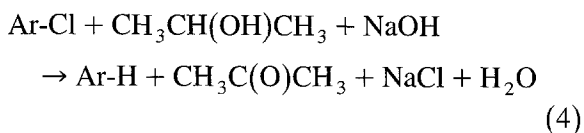
We have found that polychlorinated biphenyls (PCBs) can be completely dechlorinated to biphenyl and phenylcyclohexane using a 2-propanol solution of sodium hydroxide in the presence of carbon-supported noble metal catalysts at temperatures below 82°C [14]. The following reaction scheme has been postulated including hydrogen-transfer from 2-propanol to organic chlorides, where aryl chloride (Ar-Cl) is em-

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ployed as an example of a substrate and a hydrogen-transfer species is denoted as H^*.

$$CH_3CH(OH)CH_3 \rightarrow CH_3C(O)CH_3 + 2H^* \tag{1}$$

$$Ar\text{-}Cl + 2H^* \rightarrow Ar\text{-}H + HCl \tag{2}$$

$$HCl + NaOH \rightarrow NaCl + H_2O \tag{3}$$

$(1) + (2) + (3)$

$$Ar\text{-}Cl + CH_3CH(OH)CH_3 + NaOH$$
$$\rightarrow Ar\text{-}H + CH_3C(O)CH_3 + NaCl + H_2O \tag{4}$$

However, there has been little experimental evidence for this scheme except that dehydrogenation of 2-propanol takes place on noble metal catalysts [15].

In this study, we wish to demonstrate that 2-propanol functions as a hydrogen-donor in the present system with 1,2,4-trichlorobenzene as a substrate, and discuss the hydrogen-transfer scheme. Systematic experiments were done to examine the advantages of the proposed system by using four carbon-supported noble metal catalysts (Rh/C, Pd/C, Ru/C and Pt/C), five base compounds (NaOH, KOH, Ca(OH)$_2$, Na$_2$CO$_3$ and (C$_2$H$_5$)$_3$N) and four solvents (2-propanol, 1-propanol, ethanol and 2-butanol). Finally, the present system was applied to dehalogenation of iodobenzene, bromobenzene and fluorobenzene as well as chlorobenzene.

2. Experimental

2.1. Materials

Four carbon-supported noble metal catalysts (Pd/C, Rh/C, Ru/C and Pt/C) used in this study were purchased from N.E. Chemcat (powder; mean particle size, ca. 30 μm). The concentration of noble metal was 5 wt% in all catalysts. The catalysts were pre-dried in a vacuum for 30 min at 200°C and kept in a desiccator. Deuterium-labeled 2-propanol,

CD$_3$CD(OD)CD$_3$ (99 atom % D) and CH$_3$CH(OD)CH$_3$ (98 atom % D) were obtained from Aldrich. Other chemicals employed here were purchased from Wako Pure Chemicals.

2.2. General procedure

In a typical example, a solution of 1,2,4-trichlorobenzene and NaOH in alcohol (60 ml) was added to a 200 ml three-necked flask joined to a thermometer, a condenser and a nitrogen cylinder. After the air in the flask was completely replaced by nitrogen, a catalytic amount of carbon-supported noble catalyst was added. The reaction mixture was stirred vigorously with a magnetic stirrer and was kept at a desired temperature (40–82°C) using a thermostated water bath. During the reaction, an aliquot of the reaction mixture was taken and diluted by a suitable solvent for analysis. The dechlorination reaction using deuterium-labeled 2-propanol was carried out with 5 ml of solution in a test tube.

2.3. Analysis

The concentration of aromatic halides, benzene and acetone was determined using capillary GC (HP 6890) equipped with an FID and a column of HP-5 (25 m $\times$ 0.32 mm, 0.52 μm film thickness) or DB-Wax (30 m $\times$ 0.32 mm, 0.5 μm film thickness). n-dodecane was used as the internal standard. The products in the reaction with deuterium-labeled 2-propanol were analyzed by GC/MS (GC: HP 5890, MS: HP 5971A) with a column of HP-5MS (30 m $\times$ 0.25 mm, 0.25 μm film thickness).

3. Results

3.1. Catalytic activity of noble metal catalysts for hydrodechlorination of 1,2,4-trichlorobenzene

Fig. 1 shows a typical example of the concentration change of tri-, di- and mono-chlorobe-

nzene and benzene during the hydrodechlorina-
tion reaction of 1,2,4-trichlorobenzene. The re-
action was carried out using 2-propanol as a
solvent and NaOH as a base compound in the
presence of Pd/C at 64°C. The initial concen-
tration of the substrate was 20 mM and that of
NaOH was 90 mM, i.e., the 1.5 molar equiva-
lent to the Cl atoms contained in the initial
amount of trichlorobenzene. As the concentra-
tion of trichlorobenzene decreased, the concen-
tration of di- and mono-chlorobenzene gradually
increased to the maximum value, followed by a
decrease in the concentration down to disap-
pearance. The concentration of benzene in-
creased without loss of material balance. These
results indicate that trichlorobenzene was
dechlorinated stepwise to yield the chlorine-free
product.

The catalytic activities of four carbon-sup-
ported noble metal catalysts (Rh/C, Pd/C,
Pt/C and Ru/C) were examined in the hydro-
dechlorination reaction of 1,2,4-trichlorobe-
nzene at 42°C. The time course of benzene yield
is shown in Fig. 2. It can be seen that Rh/C
was the most active, followed by Pd/C, Pt/C
and Ru/C.

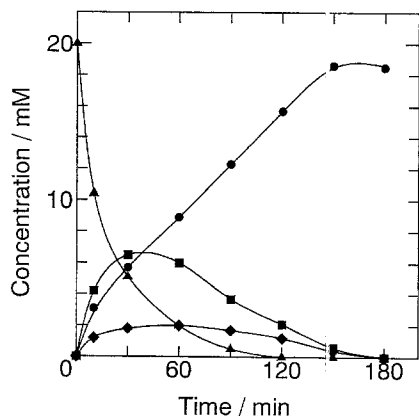When the initial concentration of 1,2,4-tri-

Fig. 2. Time course of the yield of benzene in the catalytic
hydrodechlorination of 1,2,4- trichlorobenzene. (●) Rh/C, (■)
Pd/C, (♦) Pt/C, (▲) Ru/C, Reaction conditions: 1,2,4-trichlo-
robenzene, 1.2 mmol; 2-propanol, 60 ml; NaOH, 5.4 mmol;
temperature, 42°C; catalyst, 150 mg.

chlorobenzne was increased to 200 mM (4.4%
solution), complete dechlorination was also
achieved by using Rh/C or Pd/C, in which
NaOH was suspended because the amount of
NaOH required was too large to be dissolved
completely. The reaction time could be readily
reduced by increasing the amount of catalyst
and elevating the reaction temperature to 82°C
(boiling and reflux condition). Indeed, the hy-
drodechlorination reaction was completed within
0.5 h using Rh/C (300 mg) at 82°C.

Of the two active catalysts (Pd/C and Rh/C),
Pd/C was adopted for the following experi-
ments, since it is moderately active to follow
the reaction process and is more economical for
practical use than Rh catalysts.

3.2. Dependence of the initial concentration of base compound on the dechlorination level of 1,2,4-trichlorobenzene

In order to elucidate the influence of base
compound on the hydrodechlorination reaction,
the reaction was performed at different initial
amounts of sodium hydroxide. Fig. 3 shows the
time dependence of the dechlorination level,
which represents the molar ratio between re-
leased Cl atoms, estimated from the change in

Fig. 1. Time course of the concentration of chlorobenzenes and
benzene during the catalytic hydrodechlorination of 1,2,4-trichlo-
robenzene. (▲) tri-chlorobenzene, (■) di-chlorobenzene, (♦)
mono-chlorobenzene, (●) benzene. Reaction conditions: 1,2,4-tri-
chlorobenzene, 1.2 mmol; 2-propanol, 60 ml; NaOH, 5.4 mmol;
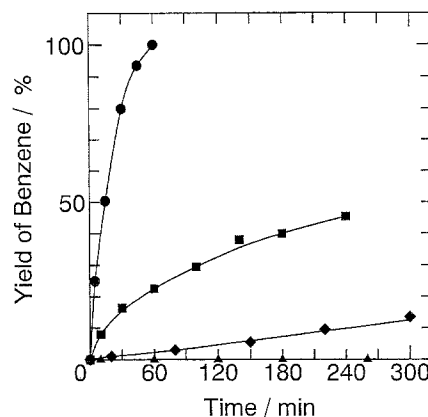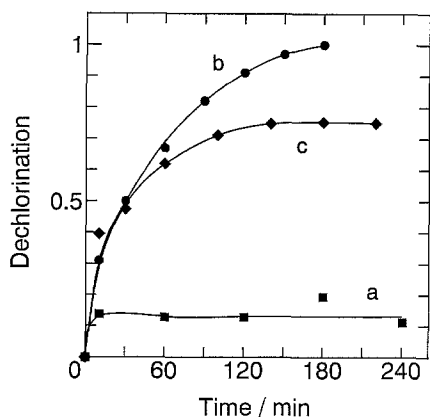5%Pd/C, 150 mg; temperature, 64°C.

Fig. 3. Effect of sodium hydroxide on the catalytic hydrodechlorination of 1,2,4-trichlorobenzene. Molar ratio of NaOH to Cl atoms contained in the initial amount of 1,2,4-trichlorobenzene: (●) 1.5, (♦) 0.69, (■) 0, Reaction conditions: 1,2,4-trichlorobenzene, 1.2 mmol; 2-propanol, 60 ml; 5%Pd/C, 150 mg temperature, 64°C.

the concentration of chlorobenzenes, and total Cl atoms initially contained in 1,2,4-trichlorobenzene. In the absence of sodium hydroxide, the hydrodechlorination reaction of 1,2,4-trichlorobenzene hardly occurred (curve a). When an excess molar amount of sodium hydroxide to Cl atoms contained in the initial amount of substrate was added, dechlorination was completed within 3 h (curve b). The addition of a smaller amount of sodium hydroxide led to incomplete dechlorination (curve c), in which the level of dechlorination (0.75) was in good agreement with molar ratio of NaOH to Cl atoms contained in the initial amount of 1,2,4-trichlorobenzene (0.69). This is because sodium hydroxide was consumed to neutralize HCl formed during the reaction (Eq. (3)). Thus, an excess molar amount of base compound (base/Cl > 1) is required to achieve complete hydrodechlorination.

3.3. Effect of various base compounds and solvents in hydrodechlorination reaction of 1,2,4-trichlorobenzene

Table 1 summarizes the conversion of 1,2,4-trichlorobenzene and the yield of (mono-, di-) chlorobenzenes and benzene when various solvents and base compounds were used. It was

found that NaOH and KOH are effective base compounds; the reaction was completed within 3 h by using 2-propanol as a solvent. In comparison, Na_2CO_3, $Ca(OH)_2$ and $(C_2H_5)_3N$ were less active for the reaction, where Na_2CO_3 and $Ca(OH)_2$ are insoluble to 2-propanol.

When primary alcohols such as 1-propanol and ethanol were used as a solvent, the conversion of 1,2,4-trichlorobenzene and the yield of benzene were very low. On the other hand, secondary alcohols such as 2-butanol and 2-propanol led to a high yield of benzene, although the yield with 2-propanol was incomparably high. This indicates that the secondary alcohol, 2-propanol, is undoubtedly a suitable solvent for the hydrodechlorination reaction.

3.4. Experimental evidence of hydrogen-transfer during hydrodechlorination reaction of 1,2,4-trichlorobenzene

The hydrodechlorination reaction of 1,2,4-trichlorobenzene was carried out using deuterium-labeled 2-propanol as a solvent, which could be distinguished from other sources of hydrogen such as trace amounts of water contained in the solvent and OH^- from sodium hydroxide. It was expected that benzene containing D atoms would be produced, if hydrogen-transfer from 2-propanol to chlorobenzenes took place in the reaction.

Table 1
Hydrodechlorination of 1,2,4-trichlorobenzene with Pd/C [a]

Solvent	Base	Time (h)	Convn. (%)	Yield (%)		
				benzene	1-Cl	2-Cl
2-propanol	NaOH	3.0	100	93	0	0
2-propanol	KOH	2.0	100	82	0	0
2-propanol	Na_2CO_3	3.0	14	0	0	3
2-propanol	$Ca(OH)_2$	3.0	12	0	0	1
2-propanol	$(C_2H_5)_3N$	3.0	9	0	0	0
Ethanol	NaOH	3.0	24	2	0	11
1-propanol	NaOH	3.0	39	5	0	36
2-butanol	NaOH	3.0	42	19	4	20

[a] Reaction conditions: 1,2,4-trichlorobenzene, 1.2 mmol; solvent, 60 ml; 5% Pd/C, 150 mg; base compound, 5.4 mmol; temperature, 64°C.
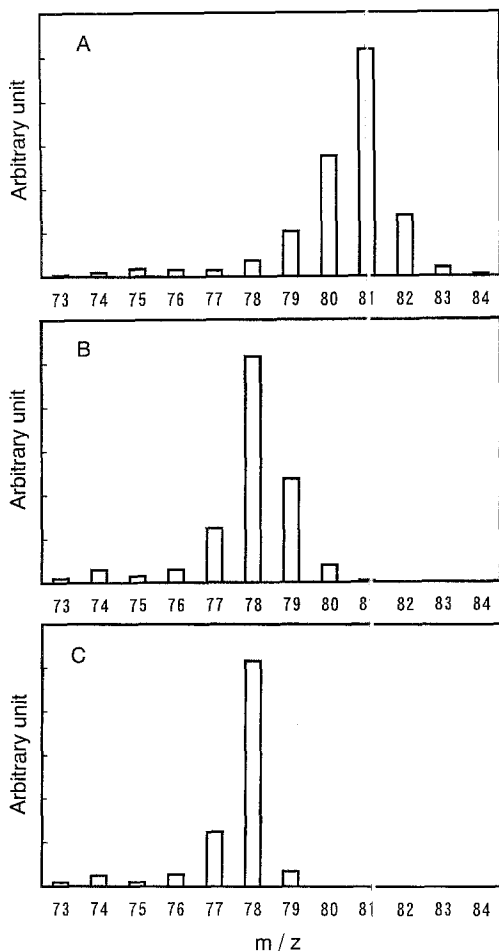
Fig. 4. Mass spectra of benzene produced in the hydrodechlorination of 1,2,4-trichlorobenzene using (A) deuterium-labeled 2-propanol, $CD_3CD(OD)CD_3$, (B) $CH_3CH(OD)CH_3$, (C) non-labeled 2-propanol, $CH_3CH(OH)CH_3$. Reaction conditions: 1,2,4-trichlorobenzene, 0.1 mmol; solvent, 6 ml; NaOH, 0.5 mmol; 5%Pd/C, 20 mg; temperature, 64°C; time, 3 h.

Fig. 4A, B and C show the mass spectral pattern ($m/z = 73$–84) of benzene produced in the experiment using $CD_3CD(OD)CD_3$,

$CH_3CH(OD)CH_3$ and $CH_3CH(OH)CH_3$, respectively. The peaks with mass numbers (m/z) of 81, 80, 79, 78 correspond to the parent peaks of $C_6H_3D_3$, $C_6H_4D_2$, C_6H_5D and C_6H_6, respectively. As seen in Fig. 4A, an intense parent peak of $C_6H_3D_3$ ($m/z = 81$) was observed, indicating that D-containing benzene was preferentially produced with high yield. Taking account of mass fragmentation, the actual content of D atoms in benzene could be roughly estimated to be $> 90\%$ of the theoretical content. In contrast, almost no D-containing products were observed in the reaction with $CH_3CH(OD)CH_3$ just like the non-labeled experiment (see Fig. 4B and C). Therefore, it was concluded that 2-propanol functions as a hydrogen-donor and α-hydrogen of 2-propanol is likely to be transferred to the substrate in the hydrodechlorination reaction.

3.5. Efficiency of hydrogen-transfer during hydrodechlorination reaction of 1,2,4-trichlorobenzene

During the hydrodechlorination of 1,2,4-trichlorobenzene, the amount of acetone increases as a result of hydrogen transfer (see Eq. (4)) and the concurrent dehydrogenation of 2-propanol with formation of H_2. Since the dechlorination of one Cl atom leads to the formation of one acetone molecule, the efficiency of hydrogen-transfer can be estimated from the following equation: (molar amount of released chlorine)/(molar amount of produced acetone).

Table 2 indicates the amount of released chlorine estimated from change in concentration

Table 2
Efficiency of hydrogen-transfer during catalytic dechlorination of 1,2,4-trchlorobenzene in 2-propanol solution [a]

Catalyst	Reaction time (h)	Released Cl (mmol)	Produced acetone (mmol)	H-transfer [b] (%)
5% Rh/C	0.2	3.5	5.6	63
5% Pd/C	3.0	2.8	9.5	29
5% Pt/C	3.0	1.8	9.7	19
5% Ru/C	3.0	0	2.7	0

[a] Reaction conditions: 2-propanol, 60 ml; 1,2,4-trichlorobenzene, 1.2 mmol; NaOH, 5.4 mmol; Temperature, 55°C; catalyst, 150 mg.
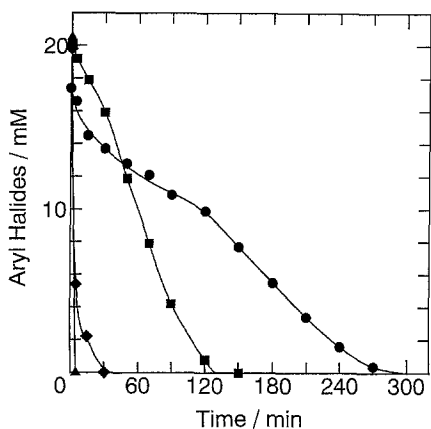[b] $100 \times$ (released Cl)/(produced acetone).

Fig. 5. Catalytic dehalogenation of a mixture containing equivalent molar amounts of C_6H_5F, C_6H_5Cl, C_6H_5Br and C_6H_5I. (▲) C_6H_5I, (◆) C_6H_5Br, (■) C_6H_5Cl, (●) C_6H_5F, Reaction conditions: 2-propanol, 60 ml; NaOH, 6.8 mmol; 5%Pd/C, 150 mg; temperature, 82°C.

of chlorobenzenes, the amount of produced acetone and the efficiency of hydrogen-transfer with four noble metal catalysts. A large amount of acetone was produced in all catalytic systems, exceeding the amount of released chlorine. From the estimated efficiency of hydrogen-transfer, it was found that Rh/C was the most efficient for hydrogen-transfer reaction, followed by Pd/C, Pt/C and Ru/C. This order is in agreement with that of the catalytic activity of dechlorination (see Fig. 2). Therefore, it can be concluded that the higher dechlorination activities of Rh/C and Pd/C arise from their high efficiency of hydrogen-transfer.

3.6. Application to dehalogenation of various aromatic halides

Fig. 5 shows the time course of a catalytic dehalogenation reaction of a mixture containing equivalent molar amounts of C_6H_5F, C_6H_5Cl, C_6H_5Br and C_6H_5I. It can be seen that C_6H_5I was preferentially dehalogenated within 5 min, and then dehalogenation of C_6H_5Br and C_6H_5Cl was completed, followed by dehalogenation of C_6H_5F after prolonged reaction (5 h). In previous papers, it has been reported that the dehalogenation rate of aryl halides follows

the order of $C_6H_5I > C_6H_5Br > C_6H_5Cl$ in the hydrodehalogenation reaction with hydrogen-donors [6,10,11] and H_2 [16], although C_6H_5F does not react in most catalytic systems. The difficulty of reductive dehalogenation may arise from its large bond dissociation energy [1]: C–F (453.6 kJ/mol), C–Cl (340.2 kJ/mol), C–Br (281.4 kJ/mol) and C–I (222.6 kJ/mol).

It can be seen that the dehalogenation rate of C_6H_5F accelerated after other aryl halides were dehalogenated ($t = 120$ in Fig. 5). This implies that the adsorption of aryl halides is rather selective and the adsorbed molecule is activated on the catalyst surface. In fact, the affinity of aryl halides to the catalyst (Pd/C) has been determined to be in the decreasing order: $C_6H_5I > C_6H_5Br > C_6H_5Cl > C_6H_5F$ [7].

4. Discussion

On the basis of the above experimental results, it was concluded that 2-propanol functions as a hydrogen-donor as well as a solvent in the catalytic hydrodehalogenation of aromatic halides. It has been reported that 2-propanol is widely used as hydrogen donors in homogeneous and heterogeneous catalytic transfer hydrogenation of organic compounds such as alkenes, ketones and aldehydes [17]. A reaction mechanism including hydride species as hydrogen transfer species has been proposed in the homogeneous system catalyzed by metal complexes [17]. The presence of hydride species has also been suggested in the dehydrogenation of 2-propanol with rhodium chloride, in which molecular hydrogen is formed by the reaction of a rhodium hydride intermediate with protons from the solvent [20]. Assuming that hydrogen of alcohols is likely to be transferred as a hydride species, it is reasonable to conclude that secondary alcohols are the best hydrogen donors among alcohols; an α-hydrogen of a primary alcohol is less likely to react as a hydride species because of the smaller electron-releasing inductive effect of the alkyl group and tertiary

alcohols have no α-hydrogen. Indeed, the D-labeled experiment in the present study has revealed that α-hydrogen of 2-propanol is exclusively transferred to the substrate. Furthermore, the presence of hydride species on the solid catalysts was assumed in the gas-phase hydrodechlorination of chlorobenzene with H_2 [18,19]. On the basis of these results, it is probable that the hydrogen-transfer species in our system consisting of 2-propanol, base compound and noble metal catalyst was a hydride species, although there is less information on the heterogeneous catalytic transfer hydrogenation than on the homogeneous system.

The key step in the overall reaction should be the hydrogen-transfer process on the catalyst surface, since high efficiency of hydrogen transfer leads to high dechlorination activity. In heterogeneous transfer hydrogenation with solid catalysts, the hydrogen donors can often be decomposed to evolve molecular hydrogen even in the absence of hydrogen acceptors. Therefore, it is likely that the acceptor adsorbs on the contiguous site of the donor to transfer hydrogen. In the homogeneous transfer hydrogenation, on the other hand, a single site mechanism including simultaneous coordination of the donor and the acceptor on the central metal of the catalyst has been often proposed [17].

It is interesting to note that selected base compounds such as NaOH and KOH are effective for the hydrodechlorination reaction. This implies that the role of base compounds is not limited to neutralization of HCl (Eq. (3)). It has been suggested that base compounds facilitate the catalytic dehalogenation of organic halides in some way [21,22]. Indeed, we found that NaOH promotes dehydrogenation of 2-propanol (Eq. (1)) with noble metal catalysts [23].

Finally, it should be noted that fluorobenzene, which is too stable to decompose in most catalytic systems with a hydrogen-donor, can be readily dehalogenated in our system. In a previous paper [14], we reported that our system is effective for dechlorination of polychlorinated biphenyls (PCBs). Thus, the present system is so powerful that it can be expected to decompose other toxic organic halides under mild conditions.

5. Conclusions

In the catalytic hydrodehalogenation system for aromatic halides consisting of a noble metal catalyst (Pd/C or Rh/C), a base compound (NaOH or KOH) and 2-propanol, the catalyst catalyzes dehydrogenation of 2-propanol and consecutive hydrogen-transfer to aromatic halides. High efficiency of hydrogen-transfer catalyzed by Rh/C and Pd/C leads to rapid hydrodehalogenation of aromatic halides. The addition of base compound is indispensable to remove the released halogen as its salt and is likely to promote dehydrogenation of 2-propanol.

Acknowledgements

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