

Transfer hydrodehalogenation of organic halides catalyzed by water soluble ruthenium(II) phosphine complexes

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Abstract

C–X bonds in carbon tetrachloride, chloroform and 1-hexyl halogenides were transformed into C–H bonds in a transfer hydrodehalogenation reaction catalyzed by water soluble ruthenium(II) phosphine complexes. A turnover frequency of up to 1000 h⁻¹ can be achieved when an aqueous solution of sodium formate is the hydrogen donor and RuCl₂(TPPMS)₂ (**1**) the catalyst (TPPMS = *m*-sulfophenyl diphenylphosphine sodium salt).

Keywords: Hydrodehalogenation; Hydrogen transfer reaction; Sodium formate; Ruthenium; Water soluble phosphines

1. Introduction

Hydrogenolysis of the carbon–chlorine bond is a very important reaction from preparative [1,2] and environmental point of view. Among environmental concerns, reaction of CFCs and PCBs has high priority either to transform them into useful derivatives (e.g. HCFs or HCFCs) or for safe destruction of existing CFC and PCB stocks. However, in spite of the high reactivity of the carbon–chlorine bond complete decomposition of these materials under mild conditions is still a challenging problem. Principally,

two routes are possible: oxidative or reductive decomposition. Biological methods have special importance in degradation of alkyl and aryl halogenides [3,4] i.e. in decontamination of PCB containing soil. Several heterogeneous catalytic methods were also developed for these reactions. If the oxidative route is used [5] usually one should handle corrosive gasses of high temperature (HCl, Cl₂, CO_x, H₂O). An interesting way to overcome the problem can be the decomposition of CFCs by ultrasonic irradiation [6] or in plasmas [7]. However, in this latter system only tiny amounts of CFCs can be disposed of. Electrochemical methods are also available to decompose carbon–chlorine bonds [8]. Some reductive methods apply high temperature [9–11], too.

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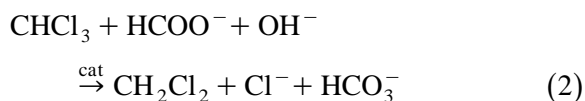
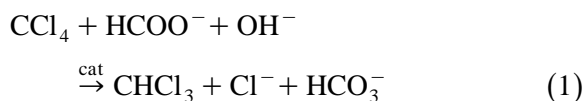
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Activation of the carbon–chlorine bond is well documented especially in the case of aryl chlorides [12]. Homogeneous catalytic methods for the hydrogenolysis of the highly inert C–F bond are also known [13,14]. Radical scission of the carbon–halogen bond is possible in the presence of nickel catalysts and sodium borohydride [15], AIBN ($\alpha\alpha'$ -azoisobutyronitrile) initiator and hypophosphorous acid [16] or tri-*n*-butyltin hydride [17] in water solution and in two phase systems. Sodium metal dechlorinates polychlorobiphenyls [18] in the presence of polymethylhydrosiloxane and various sodium compounds are also known to dehalogenate polychlorobenzenes [19,20] in the presence of transition metal catalysts.

Application of transfer hydrogenation for hydrogenolysis of the C–X bond has been reviewed [21–23]. Palladium on carbon in the presence of hypophosphite, aqueous alkali and phase transfer agent [24], formate salts [25] or polymer anchored palladium with atmospheric hydrogen and base [26–30] dehalogenate aromatic halides. The carbon–chlorine bond in carbon tetrachloride can be split in the presence of organic soluble ruthenium(II) catalysts and hydrogen [31] while benzyl chloride can be transformed into toluene in the presence of lithium formate as hydrogen donor and various organic soluble ruthenium or rhodium complexes [32] as catalysts.

Environmental concerns are becoming more and more important and catalytic research in biphasic or homogeneous aqueous systems has been intensified in the last few years [33–36]. During our studies of aldehyde reduction with aqueous sodium formate [37–39] catalyzed by **1** we observed a facile reaction of CCl_4 and CHCl_3 to yield CH_2Cl_2 under mild conditions (Eqs. (1) and (2)). Another water soluble ruthenium(II) complex, $\text{Ru}(\text{H}_2\text{O})_3(\text{PTA})_3(\text{tos})_2$ (**2**, PTA = 1,3,5-triaza-7-phosphaadamantane) also proved useful. Since the activity of these catalyst systems exceeds that of the organosoluble analogs [31,32] with the added advantage of not being oxygen sensitive, a more detailed investi-

gation was undertaken, the results of which are presented here.



2. Experimental

Reagents from commercial sources (Aldrich, Reanal) were used. Sodium formate (Reanal) was recrystallized from water, carbon tetrachloride and chloroform were distilled prior to use. Other compounds were used as received. TPPMS [40,41], PTA [42], $\text{RuCl}_2(\text{TPPMS})_2$ [41,43] and $[\text{Ru}(\text{H}_2\text{O})_6](\text{tos})_2$ [44] were synthesized according to published procedures. NMR spectra were recorded on a Bruker WP 200 SY spectrometer. GLC analysis was performed with a CHROM 5 gas chromatograph equipped with a 2.4 m long glass column packed with 10% Carbowax 20M on Chromosorb W (Carlo Erba, 80–100 mesh) and FID. Data were analyzed with a ZXA computing integrator. Percentages of peak areas were considered as GC yields as calibration shows no difference in detector sensitivity for CCl_4 , CHCl_3 and CH_2Cl_2 in the applied concentration range.

2.1. Preparation of $\text{Ru}(\text{H}_2\text{O})_3(\text{PTA})_3(\text{tos})_2$

PTA (85 mg, 0.55 mmol) was dissolved in 225 μl doubly distilled water under argon in a 5 ml Schlenk tube. 100 mg $\text{Ru}(\text{H}_2\text{O})_6(\text{tos})_2$ (0.18 mmol) was added with continuous stirring, the reaction mixture was heated to 50°C for 30 min and subsequently pumped to dryness. The product was washed with methanol and then with diethyl ether. Yield: 121 mg (70%). $\text{Ru}(\text{H}_2\text{O})_3(\text{PTA})_3(\text{tos})_2$ was characterized by ^{31}P NMR and FT-IR spectroscopy. ^{31}P NMR (H_2O , RT, ext. H_3PO_4), $\{^1\text{H}\}$, $\delta = -53.5$ ppm, $^2\text{J}(\text{PP})$

= 28 Hz, $\delta = -47$ ppm, $^2J(\text{PP}) = 32$ Hz, the compound is a mixture of facial and meridional isomers.

2.2. Catalytic transfer hydrodehalogenation of carbon tetrachloride

A thick walled glass reactor with a total volume of 60 ml, equipped with a manometer and Teflon coated stirring bar, was charged with 1.7 g (25 mmol) sodium formate, 15 ml doubly distilled water, 0.8 ml (8 mmol) carbon tetrachloride, 20 mg (0.05 mmol) TPPMS and 10 mg (0.011 mmol) $\text{RuCl}_2(\text{TPPMS})_2$. The reactor was closed and then immersed into an oil bath thermostated to $80 \pm 0.5^\circ\text{C}$. The yellow color of the aqueous phase indicates the formation of the catalytically active species, presumably $\text{HRu}(\text{HCOO})(\text{TPPMS})_3$ [21]. The pressure increased to 1.5–2 atm after reaching the thermal equilibrium and remained constant during the reaction. After 3 h reaction time the system was cooled in ice water, the remaining pressure was released and the organic and/or gas phase was directly subjected to GLC. The reaction was reproducible within the experimental error of the GC measurement ($\pm 3\%$). Because of the high tension of the substrates and products lower yields were observed when the reaction mixture was cooled only to room temperature instead of to 0°C . Analysis of the gas phase of the reaction mixture on 4 Å molecular sieve with TCD detector shows formation of hydrogen, but no methane or other hydrocarbons were detected and contrary to the observations in the analogous system [31] we had excellent reproducibility.

Caution! In the presence of certain hydrogen donors (for example sodium hypophosphite) the pressure in the system can rise up to 10 bar. All necessary precautions should be observed.

3. Results and discussion

Carbon tetrachloride can be transformed into chloroform and dichloromethane in a catalytic

Table 1

Turnover numbers (mol converted substrate/mol catalyst) in hydrodehalogenation of various halogenides

No.	Substrate (TPPMS) ₂ ^a	Catalyst		
		RuCl_2 - (PTA) ₃ (tos) ₂ ^b	$\text{Ru}(\text{H}_2\text{O})_3$ - (PPh ₃) ₃	RuCl_2 - (PPh ₃) ₃
1	CCl_4	478	88	64 ^c
2	CHCl_3	80	6	
3	$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$	291	n.d.	26 ^d
4	1-Cl-hexane	3	46	
5	1-Br-hexane	10	56	
6	1-I-hexane	68	86	
7	1-Cl-cyclohexane	2	5	
8	1-Br-cyclohexane	16	10	
9	$\text{C}_6\text{H}_5\text{Cl}$	0	0	

^a 25 mmol HCOONa , 15 ml H_2O , 0.011 mmol $\text{RuCl}_2(\text{TPPMS})_2$, 0.05 mmol TPPMS, 8 mmol substrate, 80°C , 3 h, GC yields.

^b 25 mmol HCOONa , 5 ml H_2O , 0.005 mmol $\text{Ru}(\text{H}_2\text{O})_3(\text{PTA})_3(\text{tos})_2$, 8 mmol substrate, 80°C , 3 h, GC yields.

^c 1.1 atm H_2 , 10 ml xylene-EtOH (1:1), 0.1 mmol $\text{RuCl}_2(\text{PPh}_3)_3$, 50 mmol CCl_4 , 25°C , 5 days [31].

^d 6 mmol HCOOLi , 10 ml dioxane, 0.05 mmol $\text{RuCl}_2(\text{PPh}_3)_3$, 2 mmol substrate, reflux, 6 h [32].

transfer hydrodehalogenation reaction in a closed system at 80°C using an aqueous solution of sodium formate as hydrogen donor and water soluble ruthenium (II) complexes as catalysts. There is no reaction in the absence of either sodium formate or ruthenium complex. Compared to other [31,32] ruthenium complexes, **1** turned out to be the most active one (Table 1, entries 1 and 3) The initial activity of this catalyst (turnover frequency; mol converted substrate/mol catalyst/h) is as high as 1000 h^{-1} and the yield of chloroform is more than 50% in 3 h, which is a remarkable difference to the earlier system where turnover numbers of around 60 could be reached in 5–14 days [31].

No dehalogenation of chlorobenzene was observed under these conditions (Table 1, entry 9). Although it is known [45], that under more forcing conditions triphenylphosphine can remove bromine or iodine from phenol derivatives, the water soluble triphenylphosphine analog TPPMS did not react with the substrates in our system.

Several other hydrogen sources were screened (see Table 2) aqueous HCOONH_4 and HCOONa

Table 2

Hydrodehalogenation of CCl_4 in the presence of **1** and various hydrogen donors ^a

No.	Hydrogen donor	Yield(%)	
		CHCl_3	CH_2Cl_2
1	HCOONa	54.9	5.5
2	HCOONH_4	57.3	1
3	$\text{HCOOH} + \text{HCOONa}$	27.5	0
4	HCOOH	3.5	0
5	Na_2HPO_2	31.0	0
6	H_2 ^b	1.8	0
7	<i>i</i> -PrOH ^c	2.8	0

^a 25 mmol hydrogen donor, 15 ml H_2O , 0.011 mmol **1**, 0.05 mmol TPPMS, 8 mmol CCl_4 , 80°C, 3 h, GC yields.

^b 5 atm H_2 at rt (ca. 12 mmol hydrogen)

^c 5 ml *i*-PrOH (65 mmol), 0.35 mmol KOH, 0.011 mmol **1**, 8 mmol CCl_4 , 80°C, 3 h, GC yields.

giving the best results. In more acidic medium (e.g. with $\text{HCOOH} + \text{HCOONa}$) decomposition of the hydrogen donor becomes the principal reaction [21] instead of a catalytic hydrogen transfer reaction, hydrogenolysis or reduction of the substrate. In the presence of HCOOH or NaH_2PO_2 the pressure rises up to 10 bar. Similar to literature results, molecular hydrogen is a very poor reducing agent in this system (Table 2, entry 6). The reason for that can be physical, e.g. low solubility of hydrogen in the liquid phase or chemical, as according to our earlier observation $\text{HRu}(\text{HCOO})(\text{TPPMS})_3$ is a more active catalyst for aldehyde reduction [37,38], too, than HRuClP_3 ($\text{P} = \text{PPh}_3$ or TPPMS). It should be noted, that both **1** and **2** are salted out from aqueous solution when the concentration of sodium formate is higher than 5 M.

As shown in Fig. 1, the catalyst is highly active at the beginning of the reaction, however there is only a slight increase in conversion after 30 min. As a standard, we applied 3 h reaction time.

It is evident that loss of activity in time is not a result of product inhibition, as the reaction takes place in the presence of CHCl_3 , larger amounts of CCl_4 , or high excess of chloride (Table 3, entry 3) and slight change in the pH during the reaction has no effect either. It is also

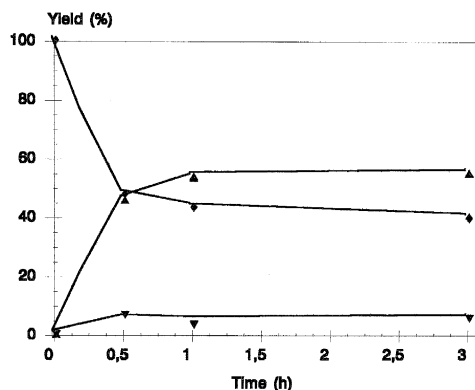


Fig. 1. Yield of chloroform and dichloromethane in the hydrodehalogenation of carbon tetrachloride in the presence of **1** and sodium formate. Conditions: 25 mmol HCOONa , 15 ml H_2O , 0.011 mmol $\text{RuCl}_2(\text{TPPMS})_2$, 0.05 mmol TPPMS, 8 mmol CCl_4 , 80°C, 3 h; GC yields, \blacklozenge : CCl_4 , \blacktriangle : CHCl_3 , \blacktriangledown : CH_2Cl_2 .

clear, that under the applied conditions (80°C) most if not all CHCl_3 and CH_2Cl_2 is in the gas phase. Increasing the catalyst concentration somewhat increased the yield of CHCl_3 and CH_2Cl_2 (Fig. 2). However, using the same catalytic system in a three phase flow reactor with continuous feed of substrate and discharge of products an alternative method for the safe and effective decomposition of aliphatic halogenides could be developed. Addition of a radical initiator AIBN decreased the yield of CHCl_3 (Table 3, entries 4 and 5) and resulted in a brownish precipitate.

Table 3

Effect of additives and amount of substrate on the transfer hydrodehalogenation of CCl_4 catalyzed by **1** ^a

No.	Additive	[Additive]:[Ru]	Yield(%)	
			CHCl_3	CH_2Cl_2
1	none	—	54.9	5.5
2	none ^b	—	61.9	14.3
3	none ^c	—	30.8	0.4
4	NaCl	270:1	49.9	0.9
5	AIBN	0.4:1	22.0	tr.
6	AIBN	2:1	19.3	tr.

^a Conditions: 25 mmol HCOONa , 15 ml H_2O , 0.011 mmol $\text{RuCl}_2(\text{TPPMS})_2$, 0.05 mmol TPPMS, 8 mmol CCl_4 , additive, 80°C, 3 h, GC yields.

^b 4 mmol CCl_4 .

^c 25 mmol CCl_4 .

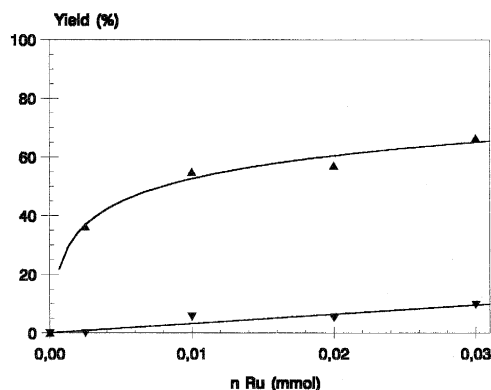


Fig. 2. Effect of catalyst concentration on the hydrodehalogenation of carbon tetrachloride. Conditions: see Fig. 1, [TPPMS]:[RuCl₂(TPPMS)₂] = 5:1.

Excess phosphine has practically no influence on the yield of CHCl₃, CH₂Cl₂ or on the turnover frequency (up to 14 times excess TPPMS was applied!), which suggests, that (i) phosphine dissociation is not a prerequisite to the formation of the catalytically active species and (ii) it is against a radical mechanism as triphenylphosphine (and TPPMS) can also work as a radical trap.

Transfer hydrogenolysis of other liquid halogenides was studied (Table 1). While benzyl chloride can be transformed into toluene cleanly, other alkyl halogenides gave low yields for both water soluble ruthenium complexes. For open chain C₆ halogenides **2** can be the catalyst of choice. The reactivity of the substrates corresponds to the expected I > Br > Cl order while sterically more demanding cyclohexyl halogenides gave similar results than the open chain analogues. Further hydrodehalogenation of dichloromethane was not observed under our conditions. Effect of the amount of CCl₄ shows, that at low substrate concentration the yield of CH₂Cl₂ is somewhat higher, so it is conceivable, that under such conditions it was formed from chloroform remaining coordinated after the first hydrogenolysis cycle. At this stage of research it is considered too early to speculate on the detailed catalytic cycle of the reaction. Our results are strongly against a radical mecha-

nism, however, the nature of substrate coordination and activation in this system remains to be determined.

4. Conclusion

A C–X bond in aliphatic or benzylic halides can be transformed into a C–H bond in a transfer hydrodehalogenation reaction in the presence of sodium formate as hydrogen donor and water soluble ruthenium complex **1** or **2** as catalyst. The activity of the system is considerably higher than that of published for analogous systems applying PPh₃ complexes of ruthenium.

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