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### Authors

Trabuco, Elizeu  
Ford, Peter C

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# Hydrodechlorination of 1,2-dichloroethane by rhodium catalysts under water gas shift reaction conditions

Elizeu Trabuco<sup>a,b</sup>, Peter C. Ford<sup>b,\*</sup>

<sup>a</sup> Departamento de Química e Geociências-IBILCE, UNESP, São José do Rio Preto, SP, Brazil

<sup>b</sup> Department of Chemistry, University of California, Santa Barbara, CA, 93106, USA

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## Abstract

Homogeneous catalysts prepared from rhodium trichloride in aqueous aromatic amines have been shown to reduce C–Cl bonds under mild water gas shift conditions ( $T = 100^\circ\text{C}$ ,  $P_{\text{CO}} = 1.0 \text{ atm}$ ). In a 4-picoline/water solvent mixture, 1,2-dichloroethane is reduced to ethylene and ethane in yields compatible with the consumption of the reducing agent CO and with the formation of  $\text{CO}_2$ . Variation of the catalyst solutions by using different substituted pyridines shows a pattern of catalytic activity parallel to that reported previously for  $\text{H}_2$  production from the shift reaction. There is a moderate dependence of activity on the basicity of the aromatic amine, but a methyl group at the  $\alpha$ -position exercises a strong negative steric effect. Long term studies show decrease of the activity with the time perhaps due to the build up of chloride in the medium. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Hydrodechlorination; 1,2-dichloroethane; Rhodium catalysts

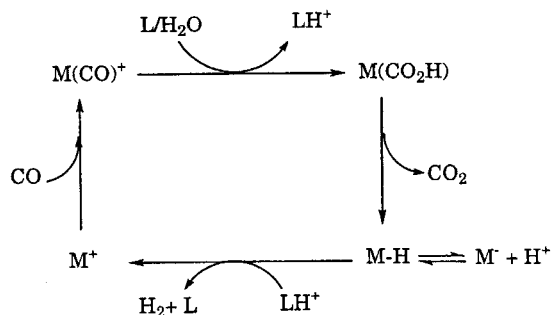
## 1. Introduction

Chlorocarbon compounds are abundant and toxic by-products of several large-scale industrial processes [1] and are persistent pollutants in the environment [2]. For these reasons it is attractive to develop new catalysts for activating C–Cl bonds and reducing chlorocarbons to hydrocarbons or other less toxic and/or more easily degraded materials. Group VIII metals have been widely used as heterogeneous catalysts for hydrodehalogenation (HDH) of aryl and alkyl halides in heterogeneous systems us-

ing  $\text{H}_2$  as the reductant [3–5]. Homogeneous catalysis of halocarbon HDH has also been reported for several systems including reductions of haloaromatic compounds with palladium phosphine complexes in alkaline alcohol [6] and by  $\text{NaBH}_4$  [7,8]. The present study was initiated to see if similar HDH of chlorocarbons could be achieved in aqueous media using carbon monoxide as the reductant under relatively mild homogeneous water gas shift reaction (WGS) conditions [9–11].

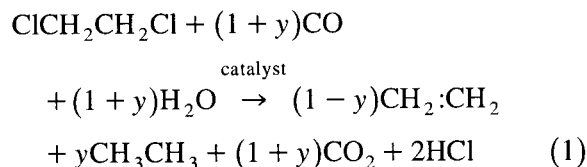
Among the most active homogeneous WGS catalysts under mild conditions is that prepared from the rhodium precursor  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  in aqueous aromatic amine solutions [12–16]. In addition to its high catalytic activity, this system

\* Corresponding author. Tel.: +1-805-893-2443; Fax: +1-805-893-4120; E-mail: ford@chem.ucsb.edu



Scheme 1. Proposed cycle for the water gas shift catalysts by rhodium-aqueous aromatic amine(L) solutions ( $\text{M}^+ = \text{Rh}_z\text{L}_y(\text{CO})_x^+$ , where  $z$  is 1 or 2) (see Ref. [14]).

has been shown to display long term stability, a key point in considering practical application. The general mechanism proposed for the homogeneous catalysis of the WGSR by metal complexes involves the nucleophilic activation of coordinated CO to give reactive intermediates such as metal hydrides or low valent metal centers which subsequently react with water to produce dihydrogen (Scheme 1) [9–11]. However, these reactive species can instead be intercepted by other substrates, and such reactions are likely to be the key steps in the Reppe type hydrogenation and hydroformylation of olefins as well as the reduction of nitrobenzenes demonstrated to be homogeneously catalyzed by various metal complexes [10,16–21]. An analogous mechanism appears to be valid for the WGSR catalyzed by the  $\text{RhCl}_3$ -aqueous aromatic amine solutions [14], and it is notable that this system is also effective in olefin hydrogenation and hydroformylation [22] as well as nitrobenzene reduction [23]. Here we report that this catalyst is also effective for the hydrodechlorination of 1,2-dichloroethane (DCE) to ethylene and ethane under WGSR conditions (Eq. (1)).



## 2. Experimental

### 2.1. Materials

All solvents (Aldrich) as well as the  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  (Johnson–Matthey) were used as received. Gases and gas mixtures, including  $\text{CO}/\text{CH}_4$  (94%/6%),  $\text{CO}/\text{CH}_4/\text{H}_2/\text{CO}_2$  (85/5/5/5), ethylene and ethane, were prepurified grade from Linde. Water was doubly distilled.

### 2.2. Instrumentation

Gas samples from catalysis runs were analyzed on a Hewlett-Packard 5830 A gas chromatograph equipped with a thermal conductivity detector and Carbosieve-B (mesh 80–100) columns. The oven temperature was programmed from 35 to 175°C with a ramp rate 20°C  $\text{min}^{-1}$ . The carrier gas was He at a flow rate of 30  $\text{ml s}^{-1}$ . A gas mixture  $\text{CO}/\text{CH}_4/\text{H}_2/\text{CO}_2$  (85/5/5/5), pure ethylene and pure ethane were used to generate calibration curves. In catalysis runs  $\text{CH}_4$  was used as an internal standard.

### 2.3. Catalytic test procedures

Catalytic activity and kinetics runs were conducted using the batch reactions techniques in a glass reactor flask fitted with a Teflon stopcock and a glass joint for attachment to the vacuum line equipped with gas inlets and manometer.

In a typical catalysis experiment, rhodium trichloride (100  $\mu\text{mol}$ ) was dissolved in the solvent mixture (9.0 ml aromatic amine/water, 7/2 v/v) in a reactor vessel containing a Teflon coated stirring bar. The 1,2-dichloroethane substrate (1.0 ml) was added and then the solution was degassed by two freeze–pump–thaw (f–p–t) cycles, using dry ice/acetone as coolant. The reactor was charged with a  $\text{CO}/\text{CH}_4$  (94/6) gas mixture such that the internal partial pressure of CO reached 1.0 atm at the reaction

temperature (100°C). The reactor was then immersed in a stirred thermostatic silicone oil bath.

Periodically, gas samples (0.5 ml) were withdrawn and analyzed by gas chromatography. This method allowed calculation of quantities of CO consumed and H<sub>2</sub>, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> produced during the run. In some cases, after the gas analysis, the reaction vessel was cooled to –77°C, then flushed to remove the gas phase previously generated. The reactor was then recharged with the CO/CH<sub>4</sub> (94/6) mixture and the flask was returned to the oil bath until the next reading.

### 3. Results and discussion

Earlier studies have shown that homogeneous systems prepared from RhCl<sub>3</sub> in aqueous aromatic amines demonstrate good catalytic activity for the water gas shift reaction in batch reactors [13] as well as in a continuous-flow

stirred reactor [14]. Attempts to prepare rhodium-based WGSR catalysts in various mixed organic solvent/water media consistently have shown the aromatic amines such as pyridine and various *meta*- and *para*-substituted pyridines to give the more active systems, with the turnover frequency for hydrogen production, Tf(H<sub>2</sub>), being as much as an order of magnitude higher than in the other solvents employed (turnover frequency being defined as moles of product formed or reactant consumed per mole of rhodium per day). Of these, RhCl<sub>3</sub> in 4-picoline/water (8/2, v/v) solution proved to be the most active catalyst [13], and there appeared to be a modest correlation of catalytic activity to the basicity of the aromatic amine. However, solutions prepared from the *ortho*-substituted pyridines, such as 2-picoline and 2,6-lutidine were more than an order of magnitude less active for the shift reaction, and this result was interpreted in terms of steric effects upon pre-equilibria necessary to generate the active catalyst.

Table 1

Activities of catalysts prepared from RhCl<sub>3</sub> in different aqueous aromatic amine solutions toward the hydrodechlorination of 1,2-dichloroethane under CO (RhCl<sub>3</sub> · 3H<sub>2</sub>O = 11 mmol, T = 100°C, P<sub>CO</sub> = 1.0 atm)

Run	Aromatic amine <sup>a</sup>	pK <sub>a</sub> <sup>f</sup>	Turnover frequency*		Percent conversion
			CH <sub>2</sub> =CH <sub>2</sub>	CH <sub>3</sub> -CH <sub>3</sub>	
A <sup>b</sup>	4-pic	6.00	7.3	32	34
B1 <sup>c</sup>			24	69	30
B2 <sup>d</sup>			37	18	11
B3 <sup>e</sup>			15	36	41
C <sup>b</sup>	3-pic	5.52	12.5	28	34
D <sup>c</sup>			15	59	20
E <sup>c</sup>	py	5.27	8.4	2.5	7.5
F <sup>b</sup>	2-pic	5.97	2.1	2.0	2.8
G <sup>b</sup>	2,6-lut	6.75	–	–	–
H <sup>b</sup>	2,4,6-TMP	7.5	0.15	–	0.12

<sup>a</sup>pic = Picoline, lut = lutidine, TMP = 2,4,6-trimethylpyridine.

<sup>b</sup>Reaction time = 22.5 h.

<sup>c</sup>Reaction time = 5 h.

<sup>d</sup>After a 5 h-period by the catalytic activation.

<sup>e</sup>Four 5-h cycles.

<sup>f</sup>Ref. [24].

\* Turnover frequency = moles product/mole catalyst/day.

\*\* The conversion was calculated by the sum of the moles of ethylene plus the moles of ethane found, divided by the moles initial of DCE, multiplied by 100.

In the present investigation, the  $\text{RhCl}_3$ -aqueous aromatic amine systems were tested for WGS activity before examining the reaction with DCE and the catalytic properties reproduced those described in the earlier studies [12,13]. For example, a typical WGS catalyst solution prepared from 100  $\mu\text{mol}$   $\text{RhCl}_3$  in 10 ml of 8/2 4-picoline/water gave a turnover frequency for  $\text{CO}_2$  formation,  $\text{Tf}(\text{CO}_2)$ , of  $113 \pm 12 \text{ d}^{-1}$  with  $P_{\text{CO}} = 1.0 \text{ atm}$  at  $100^\circ\text{C}$ . For comparison,  $\text{Tf}(\text{CO}_2)$  values reported for previous studies in this laboratory are  $101 \pm 9$  [12] and  $100 \pm 15 \text{ d}^{-1}$  [13] under analogous conditions. In such experiments turnover frequencies for  $\text{H}_2$  formation and for  $\text{CO}$  consumption,  $\text{Tf}(\text{CO})$ , were comparable to the more reliably measured  $\text{Tf}(\text{CO}_2)$  values consistent with the stoichiometry of the water gas shift ( $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ ).

When 1,2-dichloroethane was added as substrate to the same or similar catalyst, the  $\text{H}_2$

production decreased but  $\text{Tf}(\text{CO})$  and  $\text{Tf}(\text{CO}_2)$  values remained high, indeed in some cases were as much as 40% higher than in absence of this substrate. In addition, GC analysis clearly identified the formation of ethylene and ethane, products of the reductive dechlorination of the DCE. Table 1 summarizes the results of a number of runs probing the effect of the aromatic amine solvent on the activity. From these data it is clear that the pattern of HDH reactivity toward DCE parallels the water gas shift activities of the same solvent systems. There is a moderate effect of basicity enhancing the systemic reactivity for methyl groups in the *meta*- and *para*- sites on the pyridine, but methyl groups in the *ortho*-positions strongly inhibit the reactivity. In each case  $\text{CO}$  consumption and  $\text{CO}_2$  production are about equal, while net  $\text{H}_2$  production is largely suppressed. In other words, the reducing equivalents generated by the conversion of  $\text{CO}$  to  $\text{CO}_2$  are largely consumed by

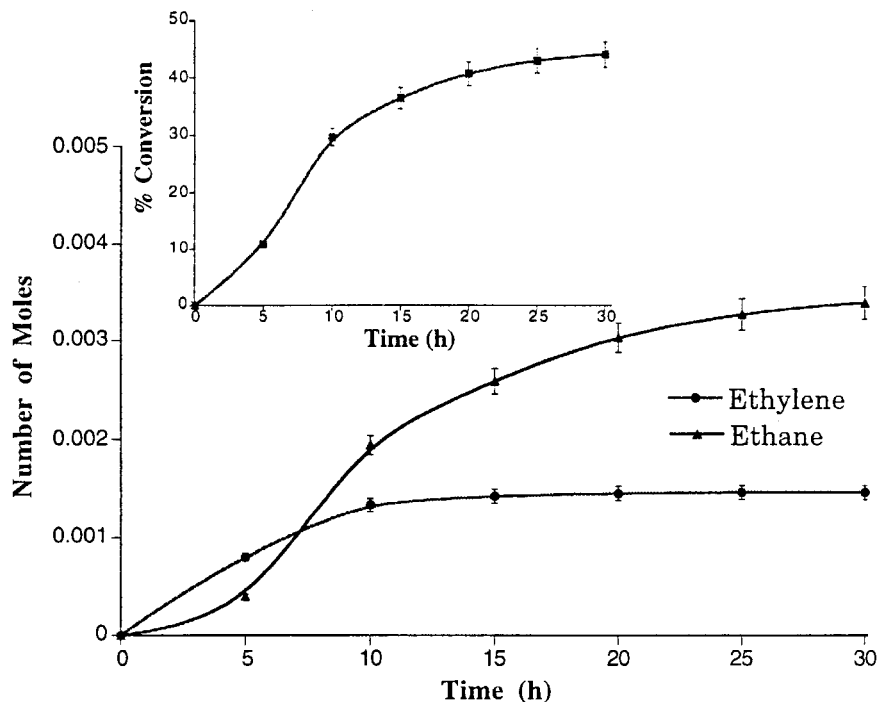


Fig. 1. Temporal formation of ethylene and ethane production and for the total conversion of DCE into those two products. The inset plots percent conversion of DCE as a function of time for the same system. The catalysis solution was based on the  $\text{RhCl}_3$  precursor in a solution of 4-picoline/ $\text{H}_2\text{O}$ /DCE (7/2/1 v/v/v) and  $P_{\text{CO}} = 1.0 \text{ atm}$ ,  $T = 100^\circ\text{C}$ . The initial quantity of DCE was 0.0011 moles. Lines are drawn for illustrative purposes only.

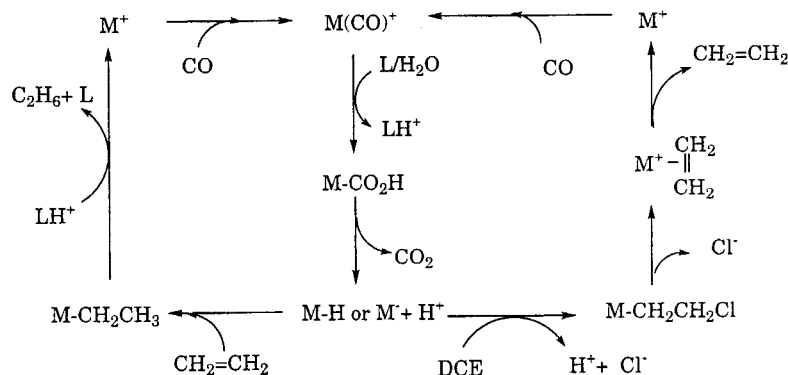
the reduction of DCE to ethylene and ethane. It might be noted that such systems were active toward DCE reduction regardless of whether or not the system was allowed to mature by allowing the water gas shift reaction to function prior to adding the DCE. However, greater initial activity was found if this were done, consistent with WGSR studies which demonstrated that working catalysts based on the  $\text{RhCl}_3$  precursor require several hours to reach maximum activity [13–15].

The current data is insufficient to demonstrate a probable HDH mechanism; however, it is likely that this reaction shares common steps with the WGSR catalysis by the same species. This argument draws support from the manner in which HDH activity tracks WGSR activities in response to changing the aromatic amines. This suggests that the principal CO activation steps remain the same and proceed with comparable rates in the two catalytic mechanisms. According to the earlier studies of the WGSR mechanism [13,14], this is likely to be the general base catalyzed reaction of  $\text{H}_2\text{O}$  with a rhodium coordinated CO to form a rhodium hydride or reduced metal complex (Scheme 1). Presumably it is one of the latter species that is responsible for reducing the DCE.

An additional qualitative observation is that the ethylene/ethane ratio decreases as a catalysis run matures. This is demonstrated in Fig. 1

for a catalysis system initiated directly from  $\text{RhCl}_3$ . Initially, ethylene production exceeds that of ethane, but the  $\text{Tf}(\text{ethylene})/\text{Tf}(\text{ethane})$  ratio decreases as the reaction proceeds. Total conversion is shown to level off at  $\sim 50\%$  (Fig. 1, see below). Since  $\text{Tf}(\text{ethylene})$  is initially higher than  $\text{Tf}(\text{ethane})$  but later falls to a much lower value, it appears reasonable to suggest that ethylene is the first product of the HDH mechanism, and that this product undergoes further catalyzed reduction to ethane. Parallel tests made with only ethylene as substrate confirm that under analogous conditions, ethylene is readily hydrogenated to ethane in a 1:1 stoichiometry, as would be expected from earlier studies regarding the hydrogenation of 1-hexene [22]. Ethylene was not reduced to ethane when the reaction was run without the rhodium salt.

An additional complication in the analysis was the observation of an unrelated side reaction involving the DCE in the reaction medium. At the end of some runs in aqueous 4-picoline, a precipitate was observed after cooling the system. This solid was characterized spectroscopically and by X-ray crystallography to be the 1,2-bis(4-methyl-*N*-pyridinium)ethane dichloride dihydrate salt ( $[\text{BPE}]\text{Cl}_2$ ). Since this also occurs in rhodium-free solutions  $\text{BPE}^{2+}$  is apparently produced by the uncatalyzed reaction of 4-picoline with 1,2-dichloroethane [25]. The formation of this salt is an alternative pathway



Scheme 2. Proposed cycle for the reductive dechlorination of 1,2-dichloroethane by  $\text{H}_2\text{O}/\text{CO}$  catalyzed by rhodium-aqueous aromatic amine(L) solutions ( $\text{M}^+ = \text{Rh}_z\text{L}_y(\text{CO})_x^+$ , where  $z$  is 1 or 2).

for loss of DCE, and is the likely reason that total conversion to ethylene and ethane appears to be limited to  $\sim 50\%$ . However, one must be concerned whether  $\text{BPE}^{2+}$  formation is somehow involved in the HDH mechanism. In order to examine this question, a parallel experiment was initiated by adding  $[\text{BPE}]\text{Cl}_2$  in quantities comparable to the DCE concentrations used above to a working rhodium–aqueous 4-picoline WGSR catalyst solution. Neither ethylene nor ethane was detected among the reaction products, thus,  $[\text{BPE}]\text{Cl}_2$  formation is not a precursor to the formation of those two products. However, the WGSR activity was noted to decrease, an effect that may be attributable to the report of modest inhibition of rhodium based shift reaction catalysis by the presence of chloride [16].

Scheme 2 is a speculative proposal regarding the mechanism of the HDH seen here. Since HDH turnover frequencies follow a pattern with regard to the steric and electronic properties of the amines similar to that seen for the WGSR catalysis, it appears that HDH catalysis is similarly constrained by the rate of CO activation to give  $\text{CO}_2$  plus low valent rhodium or rhodium hydride complexes. The latter are suggested to reduce the DCE to give intermediates which undergo HCl elimination to give ethylene. Although, further reduction to ethane without initial formation of free ethylene may play a role, the shift in the relative magnitudes of Tf(ethylene) and Tf(ethane) as an individual run proceeds, suggests that at a substantial fraction of the ethane is formed by the  $\text{CO}/\text{H}_2\text{O}$  hydrogenation of ethylene.

In summary, the  $\text{RhCl}_3$ –aqueous aromatic amine system which had previously been reported [13–15,22,23] to be active for water gas shift reaction catalysis, for Reppe type hydroformylation of alkenes, and for the  $\text{CO}/\text{H}_2\text{O}$  hydrogenation of alkenes and nitrobenzene is also effective for the hydrodechlorination of 1,2-dichloroethane to ethylene and ethane. Ongoing studies are concerned with testing the generality of these catalytic properties with other

halocarbon compounds and with schemes to ‘heterogenize’ such HDH catalysts for applications in flow reactors.

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