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Homogeneous reduction of nitrobenzene to aniline under CO/H_2O, catalyzed by cis-$[Rh(CO)_2(amine)_2]PF_6$. The role of the amine effect

C. Linares, M. Mediavilla and A.J. Pardey*

Facultad de Ciencias, Escuela de Química, Universidad Central de Venezuela, Caracas, Venezuela

P. Baricelli*

Centro de Investigaciones Químicas, Facultad de Ingeniería, Universidad de Carabobo, Valencia, Venezuela

C. Longo-Pardey

Facultad de Farmacia, Universidad Central de Venezuela, Caracas, Venezuela

S.A. Moya

Departamento de Química Aplicada, Facultad de Química y Biología, Universidad de Santiago de Chile,
Santiago de Chile, Chile

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Homogeneous catalytic reduction of nitrobenzene to aniline by cis-$[Rh(CO)_2(amine)_2]PF_6$ (amine = 4-picoline, 3-picoline, 2-picoline, pyridine, 3,5-lutidine or 2,6-lutidine) in aqueous amine 2/8, v/v, $P(CO) = 0.9$ atm, $T = 100°C$, $[Rh] = 10$ mM under water–gas shift reaction conditions is described. The effect of various amines as additives was examined.

Keywords: water–gas shift reaction, rhodium catalyzed reduction, carbon monoxide, aniline

1. Introduction

The water–gas shift reaction (WGSR),

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (1)$$

is catalyzed by homogeneous metal complexes, which can work under mild conditions [1–5]. One application of the WGSR, which has drawn attention, is the reduction of nitrobenzene to aniline,

$$C_6H_5{-}NO_2 + 3CO + H_2O \rightarrow C_6H_5{-}NH_2 + 3CO_2 \qquad (2)$$

catalyzed by transition metal complexes of group VIII [6–19].

Ford and Pardey [2a] in 1989 described a homogeneous catalytic system for the WGSR based on the use of cis-$[Rh(CO)_2(amine)_2]PF_6$ (amine = 4-picoline, pyridine, 2-picoline or 2,6-lutidine) dissolved in aqueous amine 2/8, v/v, $P(CO) = 0.9$ atm, $T = 100°C$, and $[Rh] = 10$ mM. The catalytic activity was shown to be sensitive to the nature of amines. The H_2 turnover frequencies (TF = moles of H_2/(g-atom. wt. of Rh)/24 h) followed the order 4-picoline (80) > pyridine (55) > 2-picoline (3) > 2,6-lutidine (1). Both electronic and steric effects apparently influence this trend. The Rh/aqueous 4-picoline system ranks among the most active of those WGSR catalysts having long term stability, a crucial property for practical applications.

The present study examines the properties of catalysts based on cis-$[Rh(CO)_2(amine)_2]PF_6$ dissolved in pyridine or substituted pyridines. This type of complexes is apt for studying the effects of changes in the π electronic density or in the steric environment of the heterocyclic amine. The goal of this study is to evaluate the steric and electronic effect of various heterocyclic amines (pyridine or methyl or dimethyl pyridines), which act as a ligand as well as a solvent system, in the reduction of nitrobenzene to aniline under WGSR conditions.

2. Experimental

2.1. Materials

Pyridine, methyl pyridines (4-picoline and 2-picoline) and 2,6-lutidine were obtained from Aldrich and were distilled from KOH before use. $RhCl_3{\cdot}3H_2O$ was obtained from Aldrich. Nitrobenzene was distilled in H_2SO_4 (1 M) and redistilled in $CaCl_2$ prior to use. Water was doubly distilled. The gas mixture CO/CH_4 (94/6%) was purchased from BOC Gases.

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* To whom correspondence should be addressed.

The rhodium complexes, cis-$[Rh(CO)_2(amine)_2]PF_6$, were prepared as reported [20].

2.2. Batch reactor procedures

The batch reactor techniques used here parallel those described previously [2]. Except where noted, the catalysis solutions were prepared by dissolution of 250 mmol of nitrobenzene and 0.1 mmol of rhodium complex, cis-$[Rh(CO)_2(amine)_2]PF_6$, in 10 ml of amine/water, 8/2, v/v and placed in a reactor flask fitted with a Teflon stopcock plus a ground-glass joint for attachment to a vacuum line equipped with a manometer and gas inlet. The solution was degassed by three freeze–pump–thaw cycles. The flask was charged at the pressure of 0.9 atm with the CO/CH_4 (94/6%) mixture (CH_4 was present as an internal standard). The reactor vessel was stirred magnetically in a thermostated glycerin bath (100°C) for 3 h.

The progress of the reaction was followed by taking samples of the gas phase with Sample-Lok series A-2 gas syringes (Dynatech Precision Sampling Corporation), which can be inserted into a small T-tube section of the vacuum line capped with a rubber septum, and analyzing for CO, CH_4 and CO_2 by GC technique.

2.3. Instrumentation

Gas sample analyses from catalytic runs were performed on a Hewlett-Packard 5890 series II programmable gas chromatograph fitted with Carbosieve-B (mesh 80–100) column and thermal conductivity detector. Analyses of liquid phase reaction product were done on a Hewlett-Packard 5890 series II programmable gas chromatograph fitted with 3% OV-10N Supelcoport (mesh 80–100) column and flame ionization detector using ortho-xylene as an internal standard, and identified by co-injection on a Hewlett-Packard 5890 series II programmable gas chromatograph-mass spectrometer fitted with Pona capillary column (50 m).

3. Results and discussion

The catalytic activity on the reduction of nitrobenzene to aniline by cis-$[Rh(CO)_2(amine)_2]PF_6$ (amine = 4-picoline, pyridine, 2-picoline, or 2,6-lutidine) in aqueous amine solution was examined in our laboratories based on the previous report that such system is an efficient catalyst for the WGSR [2a].

The reactivity of several amines (pyridine and substituted pyridines) as additives for the reduction of nitrobenzene to aniline was evaluated. In these reactions the only organic product observed was aniline. In table 1 are reported the data obtained from these studies.

Table 1
Reduction of nitrobenzene with CO/H_2O in the presence of cis-$[Rh(CO)_2(amine)_2]PF_6$ in aqueous amine as catalyst precursors [a]

Amine	pK_a [b]	$TF(CO_2)$/day [c]	Aniline [d] (mmol)
pyridine	5.27	20	0.08
3-picoline	5.52	85	0.35
2-picoline	5.97	125	0.52
4-picoline	6.00	31	0.13
3,5-lutidine	6.23	107	0.44
2,6-lutidine	6.75	110	0.46

[a] [Rh] = 10 mM, [substrate]/[Rh] = 2500, 8 ml of amine, 2 ml of H_2O, $P(CO) = 0.9$ atm and $T = 100°C$.
[b] Ref. [21].
[c] Experimental uncertainty ±10%.
[d] Selectivity > 99%. Conversion = 0.02%. Based on CO_2 formed after 3 h.

For such systems, formation of aniline (detected by analyzing the catalysis liquid phase) and CO_2 (detected by analyzing the catalysis gas phase) equalled stoichiometrically (within experimental uncertainties) as required by eq. (2). For example, a catalysis run was carried out by preparing a solution from cis-$[Rh(CO)_2(2\text{-picoline})_2]PF_6$ (0.1 mmol) plus 10 ml of 2-picoline/water (8/2, v/v), nitrobenzene (0.25 mmol) and *o*-xylene as an internal standard. Heating the solution under CO (0.9 atm) at 100°C in the batch reactor described above led to the formation of an active catalyst solution which converts nitrobenzene to aniline (17%). The average of three replicates values of aniline formation determined by analyses of the gas (based on CO_2 formed) and liquid phases were 0.43 ± 0.03 and 0.38 ± 0.03 mmol respectively.

To estimate the significant difference between the values obtained by the two GC methods described above, a Student *t*-test was applied. The results show that there is no statistically significant difference between both GC methods for a confidence level of 95% [22] and point to the feasibility of using the production of CO_2 to estimate the aniline production. The advantage of this method includes simplicity of the procedure and shorter time required for analysis.

The aniline formation (mmol, based on CO_2 formed after 3 h) followed the order: 2-picoline (0.517) > 2,6-lutidine (0.455) > 3,5-lutidine (0.444) > 3-picoline (0.353) > 4-picoline (0.128) > pyridine (0.082). The aniline production values for these rhodium/amine catalysts proved to be strongly dependent on the nature of the amine ligand. Modest differences were observed for those pyridines methylated or dimethylated in ortho position with 2-picoline system displaying the highest activity. In contrast to the reactivity pattern observed in the homogeneous catalysis of the WGSR by cis-$[Rh(CO)_2(amine)_2]PF_6$/aqueous amine systems, the sterically hindered 2-picoline and 2,6-lutidine, which are poor additives for the WGSR, are the most effective additives for reduction of nitrobenzene among the amines tested. The positive influence of methyl group on reactivity of these amino carbonyl complexes is noted

Table 2
Effect of variation [substrate]/[Rh] ratio on reduction of nitrobenzene with CO/H_2O in the presence of cis-$[Rh(CO)_2(2\text{-picoline})_2]PF_6$ in aqueous 2-picoline as catalyst precursor [a]

[substrate]/[Rh]	$TF(CO_2)$/day [b]	Aniline [c] (mmol)	Aniline conversion (%)
2500	125	0.52	0.2
250	112	0.47	2
25	105	0.43	17

[a] [Rh] = 10 mM, 8 ml of 2-picoline, 2 ml of H_2O, $P(CO) = 0.9$ atm and $T = 100°C$.
[b] Experimental uncertainty ±10%.
[c] Based on CO_2 formed after 3 h.

comparing the activity of the pyridine complex, which displayed the lowest activity. The relative ineffectiveness of pyridine as an additive in the reduction of aromatic nitro compounds catalyzed by $Rh_6(CO)_{16}$/nitrogen-containing ligands has been noted before [19].

Further study was carried out to the system cis-$[Rh(CO)_2(2\text{-picoline})_2]PF_6$/aqueous 2-picoline which displayed the highest activity. The effect of varying the ratio [nitrobenzene]/[Rh] was examined in the 2500 to 25 range at $P(CO) = 0.9$ atm and $T = 100°C$, and it is summarized in table 2. It is notable that the reaction rate is almost independent of the initial concentration of nitrobenzene within this range. Studies related to variation of other reaction parameters are now in progress.

4. Conclusions

It has been demonstrated that active nitrobenzene reduction catalysts are generated on dissolving cis-$[Rh(CO)_2(\text{amine})_2]PF_6$ in aqueous amine solution under WGSR conditions. Among the catalyst studied cis-$[Rh(CO)_2(2\text{-picoline})_2]PF_6$ was the most active. Aniline was the principal product observed (> 99% selectivity).

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