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Catalytic reduction of 4-nitrobenzoic acid by *cis*-[$Rh(CO)_2(amine)_2$](PF_6) complexes under water–gas shift reaction conditions: kinetics study

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Rhodium(I) complexes of the type, cis-[$Rh(CO)_2(amine)_2$](PF_6) where (amine = 3-picoline, 2-picoline, pyridine, 2,6-lutidina or 3,5-lutidine) dissolved in 80% aqueous amine solutions catalyzed the selective reduction of 4-nitrobenzoic acid to 4-aminobenzoic acid under CO atmosphere. The importance of these catalytic systems is their high chemo selectivity for the aromatic nitro group of the 4-nitrobenzoic acid with respect to the carboxylic group, allowing the production of the desired aromatic amine in high yields. The 4-aminobenzoic acid production depends on the nature of the coordinated amine. The Rh/3,5-lutidine system, the most active catalyst among tested, displays turnover frequencies for 4-aminobenzoic acid production of about 173 moles per mole Rh per day for $[Rh] = 1 \times 10^{-4}$ mol, $[\text{4-nitrobenzoic acid}] = 3.82 \times 10^{-3}$ mol, 10 mL of 80% aqueous 3,5-lutidine, $P(CO) = 0.9$ atm at 100 °C. Analyses of kinetic results for the Rh/3,5-lutidine system show a first order dependence on 4-nitrobenzoic acid concentration, a non-linear dependence on CO pressure, a segmented Arrhenius plot and dependence on the nature of the reducing gas agent. These data are discussed in terms of a possible mechanism.

KEY WORDS: 4-Nitrobenzoic acid; 4-aminobenzoic acid; catalytic reduction; rhodium complexes; carbon monoxide.

1. Introduction

The 4-nitrobenzoic acid is produced in large quantities for organic synthesis and as an intermediate in the manufacture of pesticides, dyes and industrial solvents. The toxicology and carcinogenesis studies of 4-nitrobenzoic acid were carried out for the National Toxicology Program of the US Department of Health and Human Services in which they conclude that there are evidences of carcinogenic activity and hematological toxicity of the 4-nitrobenzoic acid in rats and mice [1]. For the above reasons, our research group is interested in the reduction of 4-nitrobenzoic acid to 4-aminobenzoic acid, which is a non-toxic product and does not show any carcinogenic activity. The 4-aminobenzoic acid is widely found in the nature as a factor in vitamin B complex. Enhances the growth of various microorganisms and it is essential to the anaerobic metabolism of some bacteria. It is called bacterial vitamin H and its biosynthesis is blocked by sulfonamide drugs. Also is a hematopoietic vitamin. On the other hand, the 4-aminobenzoic acid is used principally in making pharmaceuticals. Other uses include perfumes manufacture, dyes and folic acid synthesis, and feed stock additives [2].

The reduction of nitroarenes catalyzed by transition metal complexes under CO/H_2O (equation 1) has been well documented [3–18].

$$R\text{-}NO_2 + 3CO + H_2O \longrightarrow R\text{-}NH_2 + 3CO_2 \qquad (1)$$

Earlier research in our group demonstrated the selective reduction of nitrobenzene to aniline (selectivity > 99%) by rhodium(I) complexes, cis-[$Rh(CO)_2(amine)_2$](PF_6) (amine = 4-picoline, 3-picoline, 2-picoline, pyridine, 3,5-lutidine or 2,6-lutidine) dissolved in 10 mL of 80% aqueous amine, $[Rh] = 1 \times 10^{-4}$ mol, $P(CO) = 0.9$ atm at 100 °C under the water gas shift reaction (WGSR, equation. 2) conditions [19]. Proposed mechanisms for these systems involve the formation of rhodium–nitrene species which can react with hydride intermediates (Rh-H), formed under the WGSR [20] conditions to give aniline [21].

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (2)$$

In the course of exploring the applicability of this system for the reduction of substituted nitroarenes it became a matter of interest to study the catalytic reduction of 4-nitrobenzoic acid to 4-aminobenzoic acid under CO/H_2O.

Described here is the activation, kinetics and mechanistic studies of the catalytic reduction of 4-nitrobenzoic acid by *cis*-[$Rh(CO)_2(amine)_2$](PF_6) complexes dissolved in 80% aqueous amine under WGSR conditions. This type of complexes is apt for studying the effects on the

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catalytic activity by changing the π electronic density or the steric environment of the heterocyclic amine, which act as a ligand as well as a solvent system.

2. Experimental

2.1. Materials

Pyridine (py), methyl pyridines (2-picoline (2-pic), 3-picoline (3-pic), and 4-picoline (4-pic)) and dimethyl pyridines (3,5-lutidine (3,5-lut) and 2,6-lutidine (2,6-lut)) were obtained from Aldrich and distilled over KOH. 4-Nitrobenzoic acid (4-NBA) was obtained from Aldrich and used as received. Water was doubly distilled. All gas mixtures He/H_2 (91.4%/8.6%, v/v), CO/CH_4 (95.8%/4.2%, v/v) and $CO/CH_4/CO_2/H_2$ (84.8%/5.1%/5.3%/4.8%, v/v) were purchased from BOC Gases and were used as received. The H_2 and CO gases were purchased from AGA. The rhodium complexes *cis*-$[Rh(CO)_2(amine)_2](PF_6)$ (amine = 3-picoline, 2-picoline, pyridine 2,6-lutidine, or 3,5-lutidine) were prepared as reported by Denise and Pannetier [22].

2.2. Instrumentation

Gas samples analyses from catalytic runs were performed as described in detail previously [19] on a Hewlett-Packard 5890 Series II programmable (ChemStation) gas chromatograph fitted with a thermal conductivity detector (TCD). The column used was Carbosieve-B (80–100) mesh obtained from Hewlett–Packard using a He/H_2 mixture as the carrier gas. Liquid samples analyses were done on a Varian 3800 programmable gas chromatograph fitted with a 5% biphenyl and 95% dimethyl-siloxane capillary column (30 m × 0.250 mm) and a flame ionization detector (FID). The column temperature was fixed at 175 °C with nitrogen carrier-gas flow rate of 0.5 mL/min. A Hewlett-Packard 6890 Series programmable gas chromatograph fitted with a 5% phenylmethyl siloxane capillary column (30.0 m × 250 μm × 0.25 μm) and a HP-5973 mass selective detector was used to confirm the identity of the reaction products at the end of each run. The pH determinations were performed on a Denver model Acumet Basic pH-meter.

2.3. Catalyst testing

Catalyst tests were performed under batch reaction conditions in two different ways due to the necessity to carry out the analyses of both gas and liquid phase separately. In one way, a given amount of the rhodium complexes (1×10^{-4} mol) dissolved in 10 mL 80% of aqueous amine, a given amount of 4-nitrobenzoic acid (typically, 5×10^{-4} mol) and naphthalene (internal standard) were added to a 100 mL glass reactor vessel (provided with a septum for sample withdrawing), then the solution was degassed by two freeze-pump-thaw cycles. The reaction vessel was charged with CO (typically, 0.7 atm) at 25 °C and then suspended in a circulating thermostated oil bath at a given temperature (typically, 100 °C) for 4 or 6 h. The specified temperature was maintained at ± 0.5 °C by continuously stirring of the oil bath as well as the reaction mixture which was provided with a Teflon-coated magnetic stirring bar. Liquid samples (10 μL) were removed and analyzed by the GC provided with a FID detector and by GC-MS at the end of the reaction time. The GC-MS of the only organic product formed (molecular ion peak at $m/e = 137$ and base peak at $m/e = 120$) is similar to a pure sample of 4-aminobenzoic acid. Naphthalene was used as internal standard, to allow calculation of absolute quantities of 4-nitrobenzoic acid consumed and 4-aminobenzoic acid produced. Calibration curves were generated for naphthalene, 4-nitrobenzoic acid and 4-aminobenzoic acid using 1.0 μL size aliquots. The CO high pressure studies (2.76–4.14 atm) were done using a glass-lined stainless steel autoclave (300 mL) from Parr instrument equipped with internal mechanism stirring, temperature control unit a sampling valve.

The second way was done in two steps; in the first step, a given amount of the rhodium complexes (1×10^{-4} mol) dissolved in 10 mL 80% of aqueous amine were added to a 100 mL glass reactor vessel fitted with a Teflon stopcock plus a ground-glass joint for attachment to a vacuum line equipped with a manometer and gas inlet, then the solution was degassed by two freeze-pump-thaw cycles. The reaction vessel was charged with the CO/CH_4 mixture (0.7 atm of CO at 25 °C) and then suspended in the circulating thermostated oil bath at 100 °C for 6 h. The temperature was maintained at ± 0.5 °C by continuously stirring of the oil bath as well as the reaction mixture which was provided with a Teflon-coated magnetic stirring bar. Gas samples (1.0 mL) were analyzed by the GC provided with a TCD detector, at the end of the reaction time. Methane was used as internal standard, to allow calculation of absolute quantities of CO consumed and CO_2 and H_2 produced, during a time interval with calibration curves being prepared periodically for H_2, CO, CH_4 and CO_2.

In the second step and after the above-described system reaches a constant WGSR activity [23], a given amount of 4-nitrobenzoic acid (5×10^{-4} mol) were added to the reaction vessel at room temperature. Subsequent to addition of the sample of 4-nitrobenzoic acid, the glass reactor vessel was charged with CO/CH_4 at a given CO pressure (typically 0.7 atm at 25 °C) and placed in the heated oil bath for 4 h at 100 °C, then gas samples (1.0 mL) were removed from the reactor vessel in a manner similar to describe in detail for the WGSR catalytic test [21] and analyzed by the GC provided with the TCD detector.

3. Results and discussion

3.1. Catalysis study of the 4-nitrobenzoic acid reduction

The rhodium(I), *cis*-[Rh(CO)$_2$(amine)$_2$](PF$_6$), complexes dissolved in 80% aqueous amine form systems which show catalytic activity in the selective reduction of 4-nitrobenzoic acid to 4-aminobenzoic acid (equation 3) under P(CO) = 0.9 atm at 100 °C. For such systems, formation of 4-aminobenzoic acid and CO$_2$ were observed in the initial gas samples taken soon after the reaction solution reached operation temperature. Also, the GC-MS and GC results shows that 4-aminobenzoic acid is obtained with selectivity over 99.9% at 6–96% conversion range in 4 h. The remarkable performance of these systems is the selective reduction of the aromatic nitro group without the reduction of carboxylic group of the 4-NBA. Furthermore, the well known chemo selectivity reduction towards the nitro group in the presence of another potential reduction groups, such as nitrile, olefin, alkyne and ketone using ruthenium complexes have been documented [13,17].

Table 1 summarizes the production of 4-aminobenzoic acid (TF(4-ABA) = mol of 4-aminobenzoic acid (mol Rh*day)$^{-1}$) by these Rh systems. For such systems, formation of 4-aminobenzoic acid (detected by analyzing the catalysis liquid phase) and CO$_2$ (detected by analyzing the catalysis gas phase) equaled stoichiometrically (3 : 1 CO$_2$/4-aminobenzoic acid molar ratio, within experimental uncertainties) as required by equation (3). For example, two parallel catalytic runs prepared from *cis*-[Rh(CO)$_2$(3,5-lut)$_2$](PF$_6$) (1×10^{-4} mol) plus 10 mL of 3,5-lutidine/H$_2$O (8/2, v/v), 4-nitrobenzoic acid (5×10^{-4} mol), under P(CO) = 0.9 atm at 100 °C, one using CH$_4$ and the other naphthalene as internal standards respectively, gave 1.23 ± 0.12 mmol of CO$_2$ and 0.40 ± 0.04 mmol of 4-aminobenzoic acid, which represents an average of approximately 3.08 : 1 CO$_2$/4-aminobenzoic molar ratio.

Table 1
Reduction of 4-nitrobenzoic acid by *cis*-[Rh(CO)$_2$(amine)$_2$](PF$_6$) complexes under CO/H$_2$O[a]

Amine (pK_a)[b]	Yield of CO$_2$ (mmol)[c]	TF (CO$_2$)[d]	Yield of 4-amino-benzoic acid (mmol)[c]	4-nitrobenzoic acid conversion (%)[c]	TF (4-amino-benzoic acid)[d]
Py (5.27)	1.04	64	0.35	71	21
3-Pic (5.52)	0.98	59	0.33	66	20
2-Pic (5.97)	0.37	23	0.21	42	8
3,5-Lut (6.23)	1.23	72	0.40	82	24
2,6-Lut (6.75)	0.03	2	0.01[e]	6	1

[a] 5×10^{-4} mol of 4-nitrobenzoic acid, [Rh] = 1×10^{-4} mol, 8 mL of amine, 2 mL of H$_2$O, 4-nitrobenzoic acid/Rh molar ratio = 5, P(CO) = 0.9 atm at 100 °C.

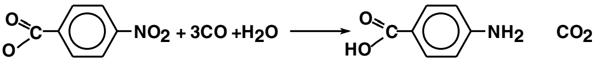
[b] From Ref. [24].

[c] After 4 h.

[d] TF(product) = mol of product(mol Rh*day)$^{-1}$). Experimental uncertainty ca.10%.

To estimate the significant difference between the values obtained by the two GC methods described above, 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% [25].

Further, the Rh/amine system exhibits no WGSR activity (i.e., molecular hydrogen is not formed) in the presence of 4-nitrobenzoic acid. Additionally, no activity toward the reduction of 4-nitrobenzoic acid was observed when a solution formed by 10 mL of 80% aqueous amine and 4-nitrobenzoic acid (5×10^{-4} mol) was tested under similar experimental conditions but in the absence of any of the *cis*-[Rh(CO)$_2$(amine)$_2$](PF$_6$) complexes. However, activity toward the WGSR was observed when the catalytic solutions were tested in the absence of 4-nitrobenzoic acid (table 2) as reported before [23].



The results show that TF(4-aminobenzoic acid) values depend on the nature of the coordinated amine and decrease in the following order: 3,5-lutidine > pyridine > 3-picoline > 2-picoline > 2,6-lutidine. A slight increase of the activity with the increment of amine pK_a in absence of steric effect is observed. However, some differences were observed for the pyridines substituted in the ortho position; for example the 4-nitrobenzoic acid reduction activity with the 2,6-lutidine ligand is the lowest among the substituted tested pyridines due to the steric effect of two methyl groups in the ortho position.

The active solutions have undergone some buffering owing to 4-aminobenzoic acid and CO$_2$ produced and the subsequent formation of carbonates. Further, the expected shift in effective basicity resulting from consumption of 4-nitrobenzoic acid (pK_a = 3.41) and the

Table 2
WGSR activities by *cis*-[Rh(CO)$_2$(amine)$_2$](PF$_6$) in aqueous pyridine and substituted pyridines[a]

Amine	TF(CO$_2$)[b]	TF(H$_2$)[b]
4-Picoline	80	80[c]
3-Picoline	13	14
2-Picoline	2	1
Pyridine	50	55[c]
2,6-Lutidine	2	2
3,5-Lutidine	24	22

[a] [Rh] = 1 x 10^{-4} mol, 8 mL of amine, 2 mL of H$_2$O, P(CO) = 0.9 atm at 100 °C.

[b] TF(gas) = mol of gas(mol Rh*day)$^{-1}$). Experimental uncertainty ca. 10%.

[c] From Ref. [23].

formation of 4-aminobenzoic ($pK_a = 4.92$) was probed by determining the resulting solution pH (table 3). In all cases an increment of ca. one pH unit was observed with the exception of the Rh/(2,6-lut) system due to its low conversion to products.

The Hg test is one of the *most* popular and easiest to use in order to determine the heterogeneous versus. homogenous nature of a catalytic system [26,27]. When a set of experiments was carried out under the Hg test, for each of the rhodium complexes, the catalytic reduction of the 4-NBA–4-ABA was not inhibited. These results imply that these Rh systems work homogenously.

For the most active Rh/(3,5-lut) system the effects of varying the 4-nitrobenzoic acid concentration [4-NBA], the carbon monoxide pressure P(CO) and the temperature (*T*) on the catalysis of the reduction of the 4-nitrobenzoic acid to 4-aminobenzoic acid were explored and these results are reported in table 4–6. The calculated kinetics activity defined as TF(4-ABA) was reproducible to within less than 10% for a series of experimental runs. In addition, the TF(4-ABA) for the kinetics runs were determined for short periods (4–6 h) where [H_2O] and P(CO) were essentially constant, diminishing by less than 15% overall. Hence, possible shifts in [H_2O] and P(CO) dependent equilibria among the catalyst component during a run were minimized owing to the near constancy of [H_2O] and P(CO).

On the other hand, these soluble amine–carbonyl rhodium complexes tend to decompose in water to metallic Rh when the carbon monoxide pressure dropped more than 40% at the working temperature. The decomposition of the catalysts is accompanied with a high decreased of the catalytic activity.

3.2. *Effect of 4-nitrobenzoic acid concentration*

The effect of varying the 4-nitrobenzoic acid concentration (0.21–3.82 mmol) for the Rh/3,5-lutidine catalytic system is summarized in table 4. The turnover frequency of 4-aminobenzoic acid formation (TF(4-ABA)) increased from 12 ([4-NBA] = 0.21 mmol) to 173 day^{-1} ([4-NBA] = 3.82 mmol). The plot of TF(4-ABA)/day

Table 3
Variations of pH during the reduction of 4-nitrobenzoic acid by *cis*-[$Rh(CO)_2(amine)_2$](PF_6) under CO/H_2O[a]

Amine	pH(initial)	pH(final)[b]
Pyridine	6.7	7.1
3-Picoline	7.2	8.2
2-Picoline	7.3	7.9
4-Picoline	7.8	8.4
3,5-Lutidine	7.8	8.4
2,6-Lutidine	7.8	7.6

[a] 5×10^{-4} mol of 4-nitrobenzoic acid, [Rh] = 1×10^{-4} mol, 8 mL of amine, 2 mL of H_2O, 4-nitrobenzoic acid/Rh molar ratio = 5.
[b] P(CO) = 0.9 atm at 100 °C.

Table 4
Substrate/Rh molar ratio effects on reduction of 4-nitrobenzoic acid catalysis by *cis*-[$Rh(CO)_2(3,5\text{-lut})_2$]($PF_6$) under CO/H_2O[a]

4-nitrobenzoic acid (mmol)	4-NBA /Rh molar ratio	Yield of 4-aminobenzoic acid (mmol)[b]	4-nitrobenzoic acid conversion (%)[b]	TF(4-aminobenzoic acid)[c]
0.21	2	0.21	99	12
0.50	5	0.40	82	24
1.00	10	0.95	95	56
1.50	15	1.28	86	77
1.91	19	1.65	83	99
2.91	29	2.19	75	131
3.82	38	2.89	76	173

[a] [Rh] = 1×10^{-4}mol, 8 mL of 3,5-lutidine, 2 mL of H_2O, P(CO) = 0.9 atm at 100 °C.
[b] After 4 h.
[c] TF(4-aminobenzoic acid) = mol of 4-aminobenzoic acid(mol Rh*day)$^{-1}$). Experimental uncertainty ca.10%.

Table 5
Carbon monoxide pressure effects on reduction of 4-nitrobenzoic acid catalyzed by *cis*-[$Rh(CO)_2(3,5\text{-lut})_2$]($PF_6$) under CO/H_2O[a]

4-aminobenzoic acid (mmol)	P(CO) (atm)	4-nitrobenzoic acid conversion (%)[b]	Yield of 4-aminobenzoic acid (mmol)[b]	TF(4-aminobenzoic acid)[c]
0.98	0.50	27	0.26	11
0.99	0.70	51	0.50	20
1.03	0.97	90	0.93	37
1.03	1.93	93	0.96	38
1.04	2.76	100	1.04	41
1.03	4.14	95	0.98	39

[a] [Rh] = 1×10^{-4} mol, *T* = 100 °C, 8 mL of 3,5-lutidine, 2 mL of H_2O, 4-nitrobenzoic acid/Rh molar ratio = 10.
[b] After 6 h.
[c] TF(4-aminobenzoic acid) = mol of 4-aminobenzoic acid (mol Rh*day)$^{-1}$). Experimental uncertainty ca. 10%.

Table 6
Temperature effects on reduction of 4-nitrobenzoic acid catalysis by *cis*-[$Rh(CO)_2(3,5\text{-lutidine})_2$]($PF_6$) under CO/H_2O[a]

T (° C)	Yield of 4-aminobenzoic acid (mmol)	TF(4-aminobenzoic acid)[b]	4-nitrobenzoic acid conversion (%)[c]
60	0.15	9.2	31
70	0.30	17.9	61
80	0.38	23.0	78
90	0.39	23.4	79
100	0.40	24.2	81

[a] 5×10^{-4} mol of 4-nitrobenzoic acid, [Rh] = 1×10^{-4} mol, 8 mL of 3,5-lutidine, 2 mL of H_2O, P(CO) = 0.9 atm, 4-nitrobenzoic acid/Rh molar ratio = 5.
[b] TF(4-aminobenzoic acid) = mol of 4-aminobenzoic acid(mol Rh*day)$^{-1}$) Experimental uncertainty ca.10%.
[c] After 4 h.

values versus. [4-NBA]/ Rh molar ratio under 0.9 atm of CO at 100 °C for 4 h shown in figure. 1, is linear. This behavior was also confirmed by plotting the log TF(4-ABA)/day versus. log [4-NBA]/Rh molar ratio in which a slope with a value of 0.9 ± 0.1 was observed indicating that the reaction is first order on 4-nitrobenzoic acid concentration under $P(CO) = 0.9$ atm at 100 °C in the 4-NBA/Rh molar ratio (2–38) range.

3.3. *Effect of carbon monoxide pressure*

Figure 2 is a plot of TF(4-ABA)/day versus. P(CO) for $[Rh] = 1 \times 10^{-4}$ mol at 100 °C (Table 5). A non-linear dependence of TF(4-ABA)/day on P(CO) variation in the range of the study (0–4.14 atm) was noted indicating that CO activation occurs *via* a pre-equilibrium formation of a carbonyl species followed by slower reaction to give the products, e.g.,

$$[\mathrm{RNO_2-Rh}]^+ + \mathrm{CO} \overset{K_1}{\rightleftarrows} [\mathrm{RNO_2-Rh-CO}]^+ \xrightarrow{k_1} [\mathrm{Rh}]^+ + \mathrm{products} \qquad (3)$$

The rate law ($r_{4\text{-ABA}}$) for such behavior would be:

$$r_{4-\mathrm{ABA}} = \left(\mathrm{k_1}K_1\mathrm{P_{CO}}[\mathrm{Rh}]_{\mathrm{tot}}\right)/(1 + K_1\mathrm{P_{CO}}) \qquad (4)$$

where $[Rh]_{tot} = [RNO_2\text{-}Rh]^+ + [RNO_2\text{-}Rh\text{-}CO]^+$ and K_1 includes $[RNO_2]$ and the solubility of CO in the medium. At high carbon monoxide pressure, $K_1P_{CO} >> 1$, then the above expression (equation 4 can be reduced to (Note that TF(4-ABA) would be the rate divided by $[Rh]_{tot}$):

$$\mathrm{TF(4-ABA)} = k_1 \qquad (5)$$

On the other hand, at low carbon monoxide pressure $K_1Pco << 1$, then equation. (4) is reduced to

$$\mathrm{TF(4-ABA)} = k_1K_1\mathrm{P_{CO}} \qquad (6)$$

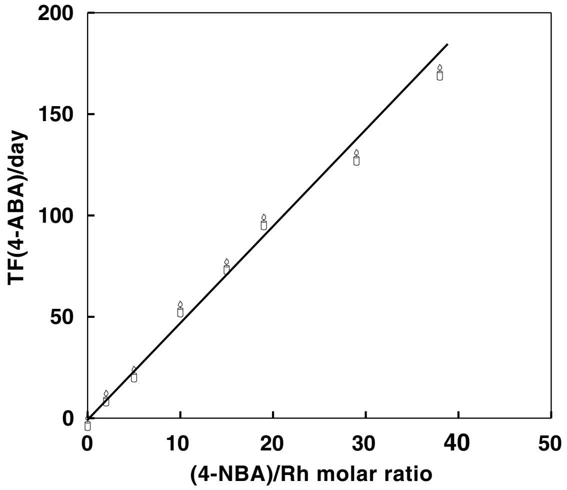


Figure 1. Plot of TF(4-ABA) versus. [4-NBA] for the Rh/(3,5-lut) system. Reaction conditions: $[Rh] = 0.1$ mmol, $P(CO) = 0.9$ atm at 100 °C and 10 mL of 80% of aqueous 3,5-lutidine. (Line drawn for illustrative purposes only).

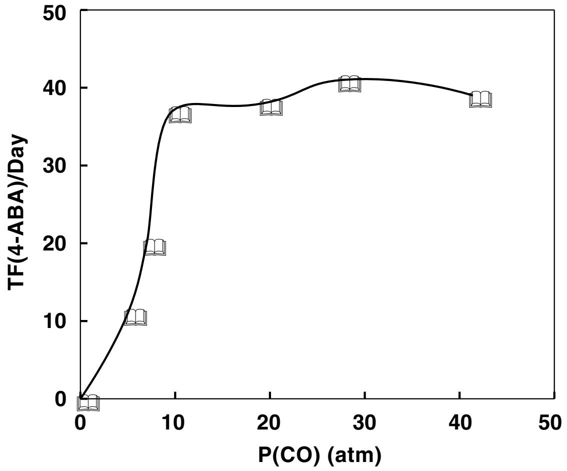


Figure 2. Plot of TF(4-ABA) versus. P(CO) for the Rh/3,5-lut system. Reaction conditions: $[Rh] = 0.10$ mmol, [4-nitrobenzoic acid] = 0.5 mmol, 4-nitrobenzoic acid/Rh molar = 5, 100 °C and 10 mL of 80% of aqueous 3,5-lutidine. (Line drawn for illustrative purposes only).

For this kinetics model, plots of TF(4-ABA)/day versus P(CO) at low carbon monoxide concentration should be linear with slopes of k_1K_1 and zero intercept. Indeed, the experimental plot is linear in the 0–0.97 atm range with nearly zero intercept value as predicted by equation (6).

3.4. *Effect of temperature*

To determine the activation parameters, TF(4-ABA)/day values for the Rh/(3,5-lut) system were measured at various temperatures in the 60–100 °C range (table 6). Over 100 °C occurs the decomposition of the catalyst, which leads to a drastic decrease of the catalytic activity. Figure 3 displays the Ln TF(4-ABA)/day values against 1/T plot for $[Rh] = 1 \times 10^{-4}$ mol, $[4\text{-NBA}] = 5 \times 10^{-4}$ mol and $P(CO) = 0.9$ atm. Arrhenius plot of Ln TF(4-ABA)/day values were non-linear in the 60–100 °C range, giving a convex curve. The apparent activation energies obtained from the slopes of the respective segments are 104.2 kJ/mol K at temperatures < 80 °C and 6.3 kJ/mol K at temperatures > 80 °C. Arrhenius plots, which are concave upwards, suggest a change in the rate-limiting step between two competitive reaction [28]. Other factor such as variation of nuclearity and/or oxidation state of the catalytic active species may be responsible for curvatures in the Arrhenius plot [29].

Non-linear Arrhenius plots similar to the one reported here have previously been observed by us [18] in the reduction of nitrobenzene to azoxybenzene catalyzed by $Rh_2(CO)_4Cl_2$ immobilized on poly(4-vinylpyridine) in contact with 80% aqueous 2-ethoxyethanol under WGSR conditions. The temperature dependence also followed a segmented Arrhenius type plot.

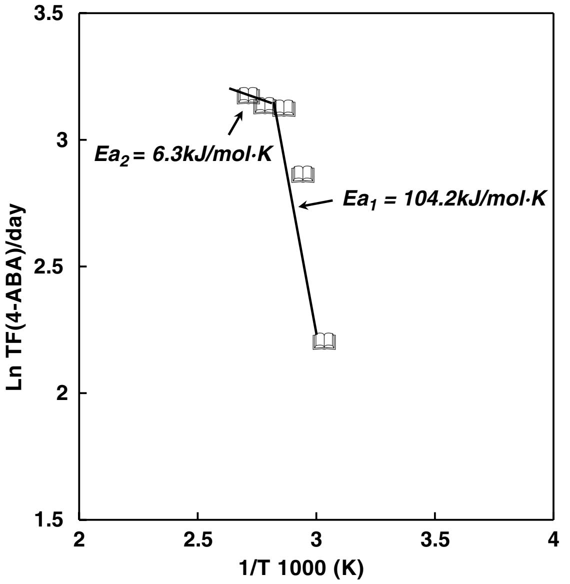


Figure 3. An Arrhenius-type plot from the data obtained for [Rh/3,5-lut] = 0.1 mmol, [4-nitrobenzoic acid] = 0.5 mmol, 4-nitrobenzoic acid/Rh molar ratio = 5, P(CO) = 0.9 atm, 10 mL of 80% of aqueous 3,5-lutidine.

Table 7
Reducing gas effects on reduction of 4-nitrobenzoic acid catalysis by *cis*-[Rh(CO)$_2$(3,5-lutidine)$_2$](PF$_6$)[a]

Reducing gas	Yield of 4-aminobenzoic acid (mmol)[b]	TF(4-amino-benzoic acid)[c]	4-nitrobenzoic acid conversion (%)[b]
CO/H_2	0.05	2	5
H_2	0.24	10	24
CO/H_2O	0.92	37	94

[a] 1 × 10^{-4} mol of 4-nitrobenzoic acid, [Rh] = 1 × 10^{-4} mol, 8 mL of 3,5-lutidine, 2 mL of H_2O, P(gas) = 0.9 atm at 90 °C, 4-nitrobenzoic acid/Rh molar ratio = 10.
[b] After 6 h.
[c] TF(4-aminobenzoic acid) = mol of 4-aminobenzoic acid(mol Rh*day)$^{-1}$). Experimental uncertainty ca. 10%.

3.5. Effect of the reducing gas agent

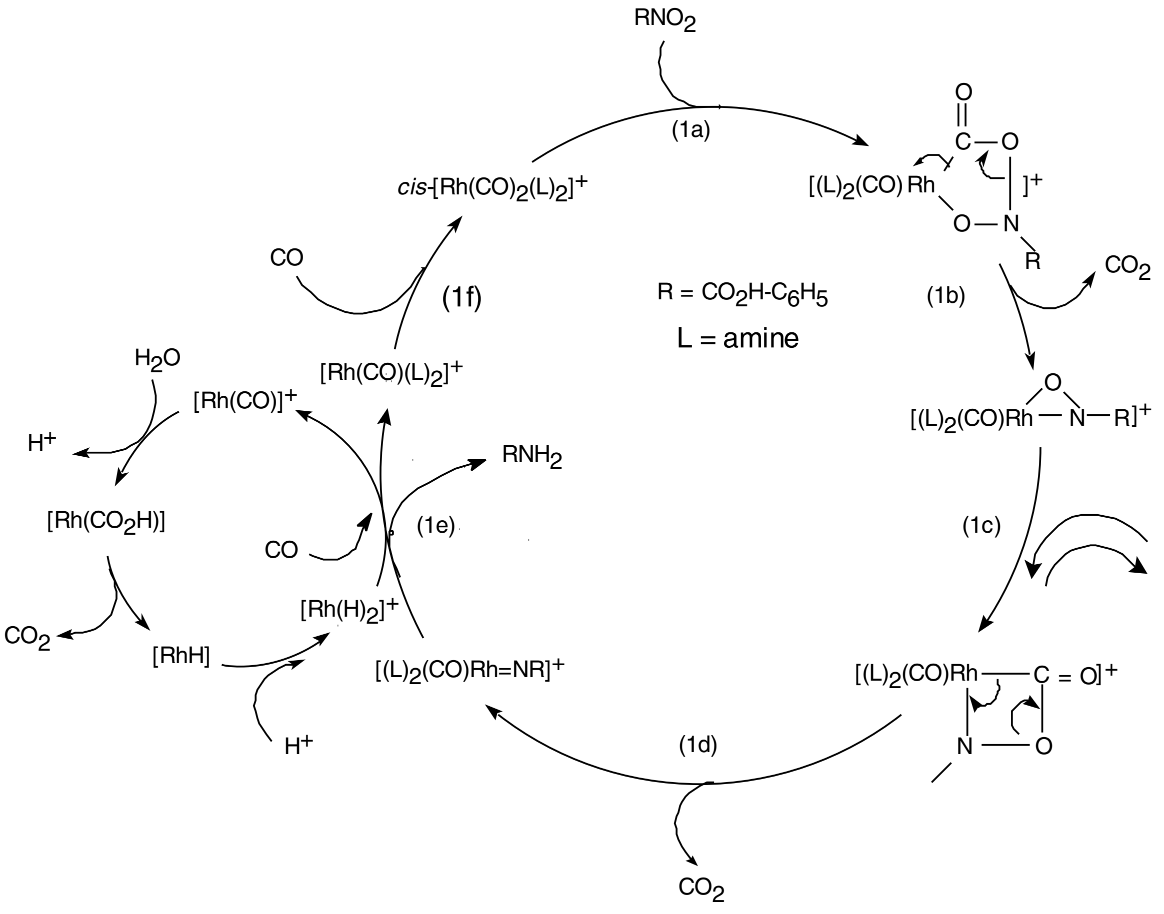
The effect of varying the reducing gas is summarized in Table 7. The catalytic activity follows the order CO/H_2O > H_2 > CO/H_2 for the Rh/3,5-lutidine system. Water and carbon monoxide serve as a hydrogen source for the formation of rhodium hydride intermediates (Rh–H). So, it should be possible to intercept this Rh–H species by reaction with 4-nitrobenzoic acid to generate rhodium 4-nitrobenzoic acid intermediates. Under WGSR conditions the latter would expect to react further to give 4-aminobenzoic acid.

3.6. Mechanistic considerations

The evaluation of the mechanism for 4-aminobenzoic acid formation by the catalytic system prepared from *cis*-[Rh(CO)$_2$(amine)$_2$](PF$_6$) dissolved in 80% aqueous amine and 4-nitrobenzoic acid in CO shows a few key features: First, 4-aminobenzoic acid was the only organic product detected. Second, the temperature studies suggest a mono-polynuclear equilibrium between active rhodium species, under 4-nitrobenzoic acid reduction conditions. Third, the early reported FT-IR and ^{13}C NMR in situ [23], X-ray [30], and other studies [31] suggested the presence of mononuclear cationic and polynuclear anionic carbonyl compounds as reaction intermediates which probably are formed in the present system. Fourth, catalytic schemes for the reduction of nitrobenzene to aniline have been proposed in which nitrobenzene cycloaddition to a metal carbonyl complex is an important first step [16,32]. Fifth, the CO_2 turnover frequency in the presence of 4-nitrobenzoic acid for the Rh/3,5-lut system (72 day^{-1}) is greater than the WGSR activity (24 day^{-1}) for the same system in the absence of 4-nitrobenzoic acid. Presumably in the former system a reactive intermediate prior to rate limiting H_2 formation is intercepted by catalytic species generated from the 4-nitrobenzoic acid additions to rhodium precursor. Given the above, the reaction mechanism depicted in scheme I is proposed for the reduction of 4-nitrobenzoic acid to 4-aminobenzoic acid catalyzed by mononuclear cationic Rh species.

In scheme 1, the cycloaddition (1a) of the nitro group to the Rh–CO bond followed by elimination of CO_2 leads to the formation of the nitrosobenzoic acid-rhodium [Rh(η^2-ONR)]$^+$ complex (1b) (the other ligands of the rhodium complex are omitted in the text for clarity). In this regard, Skoog et al. [33] carried out the characterization and the kinetic studies related to the reaction between nitroarenes (ArNO$_2$) and Ru(dppe)(CO)$_3$ where dppe = 1,2-bis(diphenylphosphino)ethane. Their kinetics results show a first order reaction in each reagent and an electron transfer process was proposed. Further, an intermediate, identified as Ru(dppe)(CO)$_2$(η^2-ONAr) was formed. The stability of this species is greatly enhanced by the presence of electron-withdrawing substituents on the nitroaromatic compound. A comparison between the velocity of the reduction of nitrobenzene [19] and 4-nitrobenzoic acid by the Rh(I) cis-[Rh(CO)$_2$(3,5-lut)$_2$](PF$_6$) complex dissolved in 10 mL of 80% aqueous 3,5-lutidine, [Rh] = 1 × 10^{-4} mol·, P(CO) = 0.9 atm at 100 °C under the water gas shift conditions shows that the catalytic activity is 1.5 times higher for the nitrobenzene substrate conversion as expected. The acid group of the 4-nitrobenzoic acid withdraws electron density from the nitro aromatic compound and stabilizes the [Rh(η^2-ONR)]$^+$ (1b) intermediate. Render this to react further more slowly.

Reversible insertion of one CO molecule to the Rh–O bond (1c) could form the [Rh(η^2-CO(O)NR)]$^+$ complex. Decarboxylation of the rhodium [Rh(η^2-CO(O)NR)]$^+$ (1d) may generate a rhodium–nitrene



Scheme 1. Proposed catalytic cycle for the reduction of 4-nitrobenzoic acid.

complex $[Rh=NR]^+$ and CO_2. Subsequent hydrogenation of this rhodium–nitrene specie via intermolecular hydride transfer [16] by the $[Rh\text{-}(H)_2]$ species (1e) formed under conditions similar to the WGSR [21] affords 4-aminobenzoic acid and the unsaturated $[Rh(CO)(amine)_2]^+$ specie. Carbonylation of the unsaturated $[Rh(CO)(amine)_2]^+$ specie should regenerate the catalytic precursor, cis-$[Rh(CO)_2(amine)_2]^+$ complex (1f) to get the reduction catalytic cycle closed.

We reported the catalyzed reduction of nitrobenzene by cis-$[Rh(CO)_2(amine)_2](PF_6)$ ($[Rh] = 1 \times 10^{-4}$ mol; amine = 4-picoline, 3-picoline, 2-picoline, pyridine, 3,5-lutidine or 2,6-lutidine) dissolved in 10 mL of 80% aqueous amine under CO (0.9 atm at 100 °C) [19]. Aniline was the only organic product formed (selectivity > 99%). The aniline formation (yield in mmol, 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. The Rh/2-picoline shows the higher catalytic activity ($TF(CO_2) = 125$ day^{-1}) in the nitrobenzene reduction than those found for the other ligands and solvent systems studied. However, in the reduction of 4-nitrobenzoic acid to 4-aminobenzoic acid the Rh/2-picoline ranges among the lower ($TF(CO_2) = 23$ day^{-1}).

As we can see in scheme 1, the rhodium-nitrene $[(L)_2(CO)Rh=NR]^+$ species formed in step (1d) can be hydrogenated probably by Rh–H species formed under conditions similar to the WGSR affording aniline from nitrobenzene [16]. This situation is favored when the Rh-nitrene specie has moderated bulky ligands as in the case of the $Rh(2\text{-pic})_2$ system. However, in the $Rh(2\text{-pic})_2$/4-nitrobenzoic acid systems formation of the bulky intermediate $[(2\text{-pic})_2(CO)Rh(\eta^2\text{-}C(O)ON(R)O)]^+$ in step (1a) should not be favorable due to the steric constrains induced not only by the bulky coordinated ortho-substituted 2-picoline or 2,6-lutidine but also by the carboxylic group of the organic substrate. In order to examined this hypothesis we carried out an experiment by using as a catalytic precursor the complex cis-$[Rh(CO)_2(4\text{-pic})_2](PF_6)$ (bearing a less crowed 4-picoline ligand and having similarly pK_a (6.00) to the 2-picoline (5.97) dissolved in 10 mL of 80% aqueous 4-picoline under CO (0.9 atm at 100 °C by 4 h). Under this reaction condition 4-aminobenzoic acid was the only organic product formed (selectivity > 99%; yield = 0.42 and 1.27 mmol/4 h of 4-ABA (TF(4-ABA) = 24 day^{-1}) and CO_2 (TF(CO_2) = 76 day^{-1}), respectively. It can be observed that the Rh(4-pic) system is 3.5 times more active than the Rh(2-pic) system. This result suggest a critical steric parameter, which can be view as the effect of competition for binding to the catalytic Rh center, which is more affected by steric constraint than by electronic effects.

4. CONCLUSIONS

The following conclusions can be drawn from the catalytic studies of the 4-nitrobenzoic acid reduction by cis-$[Rh(CO)_2(amine)_2](PF_6)$ complexes dissolved in 80% aqueous amine under CO.

These catalytic systems are very stable, active and chemo selective in the reduction of the nitro group of the 4-nitrobenzoic acid with respect to the carboxylic group, affording high yields of 4-aminobenzoic acid. Among the catalyst studied Rh(4-pic) and Rh(3,5-lut) systems were the most active.

The Rh/(3,5-lut) system shows a non-linear dependence of the rate on P(CO) and temperature. The former indicated that CO activation occurs *via* a pre-equilibrium formation of a carbonyl species and the latter suggested that the observed segmentation in the Arrhenius-type plot is the result of the 4-nitrobenzoic acid reduction catalyzed by rhodium complexes, with different energy pathways.

Finally, a single-step catalytic scheme for the reduction of 4-nitrobenzoic acid, in which formation of 4-aminobenzoic acid occurred in the coordination sphere of the Rh center, is proposed. Apparently the catalytic activity observed in these systems is the consequence of a fine balance between steric and electronic factors, so the control or modulation in the design of the ligands can provide a very effective tool to modify the catalytic behavior in these kinds of Rh/amine complexes.

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