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# Catalytic activity of $[Rh(CO)_2(bBzlH_2py)]Cl.1.5H_2O$ and $[CoCl(bBzlH_2py)_2]Cl.2H_2O$

**Stanislaus Alexander, Virupaiah Gayathri* and Nadur Muddanna Nanjegowda**

*Department of Chemistry, Central College Campus, Bangalore University, Bangalore 560001, India*

The complex $[Rh(CO)_2(bBzlH_2py)]Cl.1.5H_2O$ [$bBzlH_2py$ = 2,6-bis(benzimidazolyl)pyridine] reversibly binds CO and in alcoholic solvents loses CO to form yellow $[RhCl(bBzlH_2py)(OH_2)].H_2O$. When NO or $O_2$ gas was passed through a 2-methoxy ethanolic solution of $[Rh(CO)_2(bBzlH_2py)]Cl$, formation of $CO_2$ was observed. Hence the possible catalytic activity of the complex towards the reactions NO + CO, CO + $O_2$, and NO + $O_2$ was studied and the NO + CO system is quite promising. The complexes $[Rh(CO)_2(bBzlH_2py)]Cl.1.5H_2O$ and $[CoCl(bBzlH_2py)_2]Cl.2H_2O$ were tested for their possible catalytic activity towards oxidation of alcohols using $O_2$ and $H_2O_2/O_2$ as oxidants. These complexes in the presence of $H_2O_2$ at refluxing temperature convert alcohols to aldehydes/ketones/acids.

**Keywords:** oxidation, alcohols, CO, NO, cobalt and rhodium complexes

Transition metal complexes are used as catalysts because of their bonding ability, variety of ligands, variability of oxidation states and coordination number. For catalytic oxidations, because of the limited thermal stability of most organic molecules, conditions are largely confined to the liquid phase and moderate temperatures. Within these constraints either homogeneous or heterogeneous catalysts may be employed although low activity may be a problem with the latter. Since the molecules concerned often contain various functional groups, chemo-, regio- and stereo-selectivity are also important considerations. There are, however, a range of oxidants which in combination with a variety of metal catalysts, appear to have broad scope in organic synthesis. $H_2O_2$ is particularly significant since the coproduct is water. On the other hand, the coproduct of oxidation of TBHP or $R_3NO$ can be readily recycled. One of the most common reactions in organic synthesis is the oxidation of alcohols to the corresponding carbonyl compounds. Molecular oxygen, N-bromosuccinic acid, lead acetate, selenium oxide, oxyacids like peracetic acid, perbenzoic acid, periodic acid, t-BuOOH, N-methylmorpholine oxide, N-hydroxyphthalimides, iodysyl-benzene, sodium bromate and 2-methylpropanol/$O_2$ are some of the oxidants that have been used for the oxidation of alcohols to aldehydes/acids, secondary alcohols to ketones and 1,2-glycols to carbonyl compounds.[1-3]

$[RhCl(PPh_3)_3]$ and $[Rh(diphos)]^+$ in the presence of TBHP catalyse the oxidation of 1-phenyl ethanol, $\alpha$-tetralol, 2-octanol and benzyl alcohol.[4] In some cases, when alcohols are used as the solvents in oxidation reactions along with the substrate they also get oxidised. $[Rh(LL)_2]^+$ and $[Rh(LL)(diene)]^+$ (LL = $PhSCH_2CH_2SPh$, diene = 1,5-cyclooctadiene and norbornadiene) are effective as catalysts for the oxidation of terminal olefins to methyl ketones in presence of dioxygen as the oxidant, wherein the solvent (primary or secondary alcohol) is oxidised to the corresponding acetal or ketone.[5] Cobalt(II) Schiff base complexes are found to be good catalysts for oxidation and epoxidation reactions.[6] $[Co(bipy)_2]^{2+}$ activates $H_2O_2$ for the selective ketonisation of methylenic carbons, oxidation of alcohols and aldehydes and the dioxygenation of aryl olefins and acetylenes.[7]

Amongst the primary contributors to global air pollution are CO, oxides of nitrogen, hydrocarbons, sulfur oxides and particulates. In recent years, oxidation of CO and reduction of NO are also of environmental importance as they are found in exhaust gases. CO oxidation, NO decomposition and NO + CO reduction over perovskite-like oxides have been studied by several workers.[8,9] The prevention of pollution demands the conversion of CO and NO into less harmful entities. The compound $[Rh_6(CO)_{16}]$ is an effective catalyst for the oxidation of CO to $CO_2$ with $O_2$ at temperatures of 80°C or greater when a stoichiometric ratio of CO and $O_2$ is present at a pressure of 15–20 atmospheres.[10] Some transition metal complexes are found to catalyse the oxidation of CO and reduction of NO.[11-21] With this in view, herein we have investigated the catalytic activity of cobalt and rhodium complexes towards oxidation of alcohols and a rhodium complex towards NO + CO, NO, and CO + $O_2$ reactions.

## Experimental

*Reagents*

Rhodium trichloride was purchased from Arora Matthey Ltd.; cobalt chloride from BDH. $[Rh(CO)_2(bBzlH_2py)]Cl.1.5H_2O$ and $[CoCl(bBzlH_2py)_2]Cl.2H_2O$ were prepared by literature methods.[22,23] All the solvents and alcohols were purified and distilled before use. The NO, CO and $O_2$ gases were passed through purifying traps before passing through the system.

*Measurements*

IR spectra (nujol mulls) were recorded on a Nicolet 400D FT-IR spectrometer. Electronic spectra of the solutions were recorded on a Hitachi-520 spectrophotometer. The $^1H$ NMR spectra were recorded on a Bruker 400 MHz FT NMR spectrometer with TMS as the internal reference. GC of the products were recorded on a Varian model gas chromatograph using a column of 10% carbowax supported on chromosorb W.

*Procedure*

*Catalytic conversion of NO/CO/$O_2$*

The reactions were carried out in a fume cupboard. A known amount of 2-methoxy ethanol and the catalyst were taken in a flask which was connected to traps containing 75 ml of $Ba(OH)_2$ of known concentration. The reaction flask was heated to 100°C and the NO/$O_2$ or a combination of CO + $O_2$ or NO + CO was passed through the system and the outgoing gases were passed through the $Ba(OH)_2$ solution to absorb $CO_2$ produced during the reaction to form $BaCO_3$. The reactions were carried out for 10 h and the remaining $Ba(OH)_2$ solution was estimated and the amount of $CO_2$ formed was calculated.

*Oxidation of alcohols*

The flask containing the reaction mixture maintained at 100°C was connected to a water condenser, which in turn was connected to a trap containing 4% 2,4-dinitrophenyl hydrazine solution. Typically $3\times10^{-5}$ M of the complex and 11.3 ml of 30% $H_2O_2$ were taken in a flask and stirred at 100°C under $O_2/N_2$ atmosphere for about 1·5 h. Then the substrate was added and the outgoing gases were passed through 2,4-dinitrophenyl hydrazine solution. The reaction was continued for 10 h. The 2,4-dinitrophenyl hydrazine derivatives were filtered, recrystallised and the melting points were compared with those given in the literature.[24] For quantitative measurements, a gas chromatograph was used.

## Results and discussion

The complexes $[Rh(CO)_2(bBzlH_2py)]Cl.1.5H_2O$ and $[CoCl(bBzlH_2py)_2]Cl.2H_2O$ are five coordinate and the former reversibly

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* Correspondent. E-mail: gayathritvr@yahoo.co.in

binds CO.[22,23] TGA measurements of these complexes confirm the presence of 1.5 and 2 molecules of water of hydration respectively. The green complex $[Rh(CO)_2(bBzlH_2py)]Cl$ is insoluble in nitrobenzene, chloroform but soluble in $CH_3OH$, $C_2H_5OH$ and DMF in which it loses CO to give yellow solid of the formula $[RhCl(bBzlH_2py)(OH_2)].1H_2O$. This yellow complex behaves as a non-electrolyte in DMF and the TGA of the complex has revealed that one of the water molecules is coordinated. The yellow complex is capable of absorbing CO to give back the parent complex.

$$[RhCl(bBzlH_2py)(OH_2)].1H_2O \xrightleftharpoons[\text{-2CO}]{\text{+2CO, S}} [Rh(CO)_2(bBzlH_2py)]Cl.1.5H_2O$$

S = ethanol, methanol, 2-methoxy ethanol, 2-ethoxy ethanol or DMF

When NO or $O_2$ gas was passed through 2-methoxy or 2-ethoxy ethanol solution of $[Rh(CO)_2(bBzlH_2py)]^+$ formation of $CO_2$ was observed. Hence the possible catalytic activity of the complex towards NO, $O_2$, CO + $O_2$ and NO + CO reactions were studied.

In a typical reaction, NO or $O_2$, NO + CO or CO + $O_2$ gases were passed through $[Rh(CO)_2(bBzlH_2py)]^+$ ($3.8 \times 10^{-5}$ M) in 2-methoxy ethanol solution (25 ml) at 110°C. The reactions produced $CO_2$. A blank reaction was carried out without the complex and $CO_2$ formation was not observed. After 10 hours of the reaction, the complex was isolated and the IR spectrum of the solid did not have peaks corresponding to νNO, νCO or $\nu O_2$, but was similar to that of $[Rh(bBzlH_2py)(OH_2)]^+$ which was formed on attempted recrystallisation of $[Rh(CO)_2(bBzlH_2py)]Cl.1.5H_2O$ in alcohol. The results are given in Table 1.

From the data, it was observed that when NO or $O_2$ gas was passed through a 2-methoxy ethanol solution containing the complex, $CO_2$ was produced. Several workers have reported that when primary and secondary alcohols undergo dehydrogenation, they produce aldehydes and ketones respectively. When $O_2$ gas was passed through $[Rh(CO)_2(bBzlH_2py)]^+$ in solvents like $CH_3CN$, pyridine, aniline, ethanol, DMF, 2-ethoxy ethanol or 2-methoxy ethanol, $CO_2$ formation was observed only in 2-methoxy ethanol and 2-ethoxy ethanol. When the reactions were carried out in these two solvents, the formation of $CO_2$ occurred even after 32 hours.

The mechanism of formation of hydrides, carbonyls and hydridocarbonyls when transition metal halides are allowed to react with group 15 ligands (example $PPh_3$) in alcohols and related solvents has been visualised as follows.[25,26] Initially, the solvent ($RCH_2OH$; R = Me, $MeOCH_2$, $EtOCH_2$ or $MeCH_2$) would decompose to produce an aldehyde in the case of primary alcohol (or a ketone from a secondary alcohol).

$$RCH_2OH \rightarrow RCHO + H^+ + H^-$$

The aldehyde formed would undergo oxidative addition across the CH bond to form a metal(III) hydride or an acyl-metal(III) hydride intermediate. For the formation of a carbonyl, the intermediate would then undergo an acyl-alkyl rearrangement, followed by hydrogen transfer to the alkyl group, which results in a hydrocarbon. The mechanism of formation of $CO_2$ by the passage of $O_2$ or NO through the solution of $[Rh(CO)_2(bBzlH_2py)]^+$ in 2-methoxy ethanol in the present investigation proceeds through the activation of coordinated CO. Here 2-methoxy ethanol forms 2-methoxy acetaldehyde which decomposes to give dimethyl ether and $CO_2$. Hence in the NO system, the products are expected to be dimethyl ether, $N_2$ and $CO_2$. In the $O_2$ system, the products are dimethyl ether and $CO_2$. The following mechanism may be proposed for the catalytic reduction of NO or $O_2$ by the complex in 2-methoxy ethanol (Scheme1).

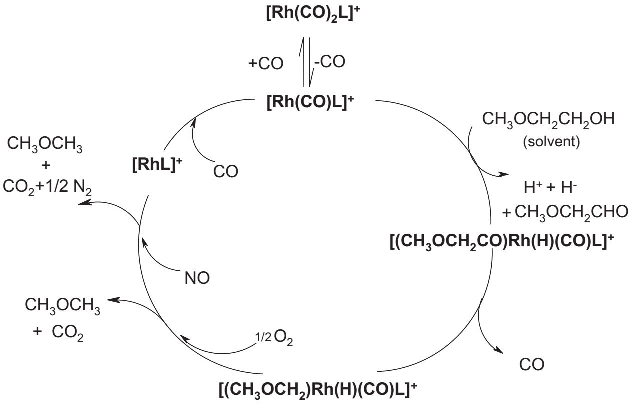
The GC analysis of the reaction systems indicated the presence of 2-methoxy acetaldehyde. The electronic spectra of these systems exhibited peaks due to the d-d transitions of Rh(III) species. $[Rh(CO)_2(bBzlH_2py)]^+$ is an Rh(I) complex and during the reaction it gets oxidised to rhodium(III) and the latter is found to be active.

When a mixture of NO + CO or CO + $O_2$ gases were passed through $[Rh(CO)_2(bBzlH_2py)]^+$ in 2-methoxy ethanol at 110°C, the formation of $CO_2$ was observed. A comparison of the results of CO + $O_2$ with those of the $O_2$ (Table 1) system reveals that TN for the latter is more than the former, implying that CO gas may hinder the catalytic oxidation reactions. The TN for the NO + CO system is more (Table 1) when compared to that of the NO system, indicating that NO reacts with both the CO gas passed through the system and the CO produced from decomposition of 2-methoxy ethanol. Preliminary reactions suggest that when compared to CO + $O_2$, the NO + CO reaction system is quite promising.

**Table 1** Reactions of NO, $O_2$, NO + CO and CO + $O_2$ in 2-methoxy ethanol with $[Rh(CO)_2(bBzlH_2py)]Cl.1.5H_2O$ as catalyst

| Temp: 100°C | Time: 10 h [catalyst] = $3.8 \times 10^{-5}$ M | |
|---|---|---|
| System complex + 2-methoxy ethanol | Amount of $CO_2$ (mmol) × $10^{-2}$ | TN/h |
| NO | 82 | 1.45 |
| NO + CO | 99 | 2.61 |
| $O_2$ | 126 | 3.34 |
| $O_2$ + CO | 99 | 2.61 |

Turn over number TN = (No. of moles of product)/(No. of moles of catalyst × No. of hours)



**Scheme 1** Catalytic cycle for the reduction of NO/$O_2$ with $[Rh(CO)_2(bBzlH_2py)]^+$ in 2-methoxy ethanol

*Oxidation of alcohols*

When $O_2$ gas was passed through $[CoCl(bBzlH_2py)_2]^+$ and $[Rh(CO)_2(bBzlH_2py)]^+$ in alcohol at room temperature and at higher temperature, the formation of aldehyde/ketone was not observed. But on adding $H_2O_2$ to the system at refluxing temperature the formation of aldehyde/ketone was observed. Hence these two complexes were examined for their catalytic activity towards the oxidation of alcohols like methanol, ethanol, n/i-propanol, n/i-butanol and benzyl alcohol using $O_2$ and $H_2O_2$ as oxidants. In a blank reaction without the complex, the formation of aldehyde or ketone was not observed.

When the outgoing gases from the cobalt and rhodium reaction system was passed through 2,4-dinitrophenyl hydrazine solution, the corresponding derivatives of aldehydes or ketones were obtained. These were isolated and their melting points were compared with the literature m.p.s. These derivatives were also characterised by $^1H$ NMR studies. It was noticed that methanol and *t*-butanol failed to give the carbonyl derivatives. Since the α-carbon of the latter is not associated with protons, it does not undergo oxidation to produce the carbonyl compound. In the case of methanol, the formaldehyde formed may further get oxidised to acid; hence the formation of aldehyde is not observed. The reactions were carried out in various solvents like THF, $CH_3CN$, DMF and *t*-BuOH by using $H_2O_2$ as the oxidant. Oxidation of alcohol occurred only with *t*-BuOH as solvent. When $O_2$ gas was passed through a mixture of *t*-BuOH and $CH_3CN$ taken in different ratios in the presence of $H_2O_2$ at 100°C, the induction period and the time required for the aldehyde/ketone formation increased with increase in the amount of $CH_3CN$. This may be due to the π-donor nature of $CH_3CN$, which may hinder the reaction.[27]

The complexes $[CoCl(bBzlH_2py)_2]^+$ and $[Rh(CO)_2(bBzlH_2py)]^+$ are soluble in 30% $H_2O_2$ to give homogeneous solutions. Passage of $O_2$ gas through these solutions maintained at 100°C for a few hours (4 to 5 h for the cobalt system and 2 h for rhodium system), followed by addition of alcohols, produced the corresponding aldehydes or ketones. Blank reactions were carried out without $H_2O_2$ and also without the complexes. In these cases, the reactions were carried out by taking these complexes in 0.12 mole of 30% $H_2O_2$ at 100°C with a complex to substrate ratio of 1:1250 for the cobalt system and 1:2500 for the rhodium system for 10 h in $O_2$ atmosphere and the results are tabulated in Table 2.

From the above data, it may be noted that when methanol was used as the substrate, in both the cases aldehyde was not formed

**Table 2** Products of oxidation of alcohols with cobalt and rhodium complexes at 100°C with $H_2O_2$ as the oxidant [Catalyst] = $3.8 \times 10^{-5}$ M

| Substrate | $[Rh(CO)_2(bBzlH_2py)]Cl.1.5H_2O$ | | | $[CoCl(bBzlH_2py)_2]Cl.2H_2O$ | | |
|---|---|---|---|---|---|---|
| | Aldehyde/Ketone TN/h | Acid TN/h | Total TN/h | Aldehyde/Ketone TN/h | Acid TN/h | Total TN/h |
| Methanol | – | 29.4 | 29.4 | – | 6.8 | 6.8 |
| n-propanol | 0.2 | – | 0.2 | 0.2 | 15.8 | 16 |
| Isopropanol | 0.8 | – | 0.8 | 0.3 | 8.7 | 9 |
| n-butanol | 1.7 | – | 1.7 | 0.8 | 3.1 | 3.9 |

but acid formation was observed. In the case of other alcohols in the cobalt systems, both acid and aldehyde/ketone was formed but in the rhodium system only aldehyde/ketone was observed. In the cobalt system, decomposition of the complex occurred and precipitation of heterocycle was noticed. Since rhodium systems were found to be homogeneous and selective, the rhodium system was used for further investigations. The reactions were carried out both in $O_2$ and $N_2$ atmospheres in the presence of $H_2O_2$ and the TN of the products were nearly the same, indicating that $O_2$ does not participate in the reaction and $H_2O_2$ was the only oxidant.

For the oxidation of benzyl alcohol using the rhodium complex, since benzyl alcohol and 30% $H_2O_2$ were found to be immiscible, 10 ml of $CH_3CN$ was added to make the system homogeneous and reactions were carried out in the presence of both $O_2$ and $N_2$. Since the TN was the same in both $O_2$ and $N_2$ atmospheres, further investigations were carried out only in an $N_2$ atmosphere. It was found that as the concentration of the complex increased, there was a slight increase in the yield but the TN decreased (Catalyst: $2.7 \times 10^{-5}$ M, TN 24.1; catalyst $9.6 \times 10^{-5}$ M, TN 7.6). A plot of product yield at different intervals of time (Fig. 1) indicated that as the time progresses, the amount of benzaldehyde formed increases up to 10 h and in the subsequent period it starts decreasing, indicating further oxidation of benzaldehyde to benzoic acid.

The electronic spectra of the resultant solution of the rhodium system after the oxidation of alcohols showed very weak peaks in the range 400–500 nm due to d–d transitions, indicating the presence of Rh(III). After the reaction, the catalyst was isolated but its IR spectrum did not show any peaks due to oxo- or peroxo- species. When $H_2O_2$ was treated with $[Rh(CO)_2(bBzlH_2py)]Cl$, a yellow compound was formed and its IR spectrum also did not indicate the presence of oxo- or peroxo- species. In both cases, the resulting spectra were similar to the complex $[RhCl(bBzlH_2py)(OH_2)].H_2O$ indicating the unstable intermediate. Hence the following scheme is suggested for the rhodium system (Scheme 2). One possible first step may be the oxidation of the rhodium species by $H_2O_2$ to form a rhodium-oxo-complex with an increased oxidation state of rhodium(I) to rhodium(III). Addition of the alcohol then yields the aldehyde with the generation of the $[RhL]^+$ system which then adds on $H_2O_2$ to complete the cycle.

Tung and Sawyer[7] have suggested an oxene intermediate $[(bipy)_2CoO^{\cdot}]$ which oxidises benzyl alcohol and cyclohexanol to benzaldehyde and cyclohexanone respectively when $[Co(bipy)_2]^+$ is used as the catalyst. The electronic spectrum of the $[CoCl(bBzH_2py)_2]^+$ system indicated the presence of cobalt(II). When $H_2O_2$ was refluxed with $[CoCl(bBzlH_2py)_2]Cl$, heterocycle separated out on prolonged heating and acid formation was observed, indicating that the aldehyde formed undergoes further oxidation to form acid. The following mechanism is suggested for the oxidation of alcohols by $[CoCl(bBzH_2py)_2]^+$ (Scheme 3).

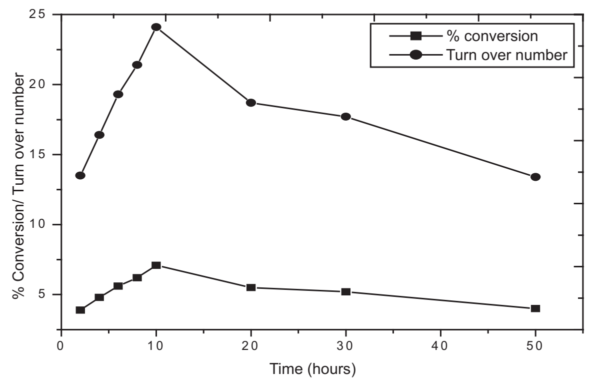
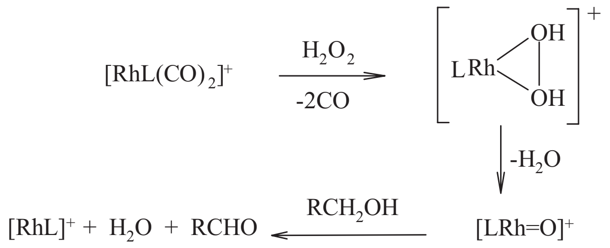
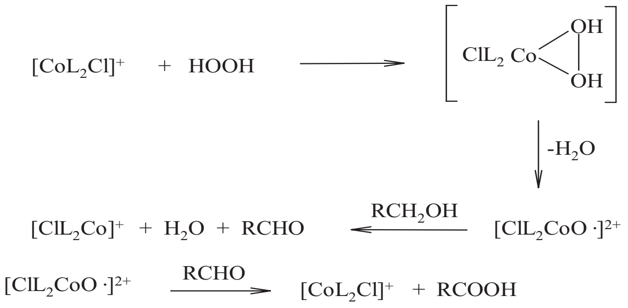


**Fig. 1** Plot of % conversion of benzyl alcohol or TN at different intervals of time using $2.7 \times 10^{-5}$ M of $[Rh(CO)_2(bBzlH_2py)]^+$ at 100°C in presence of $H_2O_2$.
Catalyst: Substrate 1:2500. Substrate: $H_2O_2$ 1: 3.



**Scheme 2** (L = $bBzH_2py$)



**Scheme 3** L = $bBzlH_2py$

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