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The hydration of nitriles catalyzed by water-soluble rhodium complexes

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Abstract

The water-soluble rhodium complex generated in situ from $[Rh(COD)Cl]_2$ and $P(m\text{-}C_6H_4SO_3Na)_3$ has been found to be a very effective catalyst for the hydration of nitriles, under basic conditions. © 2000 Elsevier Science Ltd. All rights reserved.

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The application of metal catalysts in aqueous systems that enables an easy recovery of the catalyst by decantation, has recently attracted attention.[1] Sulfonated phosphines are widely used as ligands in such processes. Triphenylphosphine trisulfonate (TPPTS), owing to its higher solubility in water, is generally the ligand of choice for carrying out commercial reactions in water and has been incorporated into several industrial processes, e.g. the hydroformylation of propylene by $RhCl(TPPTS)_3$,[2] the telomerization of dienes with $Pd(TPPTS)_4$[3] and the functionalization of dienes by *cis*-$PtCl_2(TPPTS)_2$.[4]

Carboxamides are classically prepared by the hydration of the corresponding nitriles in the presence of a strong base or strong acid. These processes, however, lead to the formation of carboxylic acids as side products.[5] Several attempts have been made to develop catalytic methods which can give the desired amides selectively.[6] To the best of our knowledge, only two water-soluble catalysts have been used for the hydration of nitriles and no attempts have been made to recycle the catalysts.[6a–c] The water-soluble catalysts $PdCl(OH)(bipy)(H_2O)$[6a,b] and $IrH(CO)(TPPTS)_3$[6c] gave low activities. In this paper we present our preliminary results concerning the hydration of nitriles, especially acetonitrile, catalyzed by the water-soluble $[Rh(COD)Cl]_2$/TPPTS system.

No reaction occurred when acetonitrile (10 mL) was treated with water (10 mL) at 90°C in the presence of TPPTS (0.3 mmol). When the reaction was conducted with $[Rh(COD)Cl]_2$ (0.01 mmol)/TPPTS (0.3 mmol), acetamide was selectively obtained with the turnover frequency of

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50.8 mol of acetamide per mol of Rh per hour. The activity of the catalytic system was found to be a function of the pH of the solution. Rates of catalysis were independent of the base concentration at a pH greater than ~11.7. At lower $[OH^-]$ a linear dependence of the catalytic rates was found (Fig. 1). From plots of $[OH^-]$ versus the rate of catalysis, the rate constant of 36.3 M^{-1} s^{-1} was determined for nucleophilic attack of OH^- on the coordinated nitrile. At a pH of ~11.7 the effectiveness of our system for the hydration of acetonitrile relative to the fastest known catalytic systems is given in Table 1. $[Rh(COD)Cl]_2$/TPPTS is ~3.4 times more reactive than the water-insoluble analog system $[Rh(COD)Cl]_2/PPh_3$ (Table 1, entries 1 and 3). Our system is the best water-soluble catalyst and the second best catalyst reported for the hydration of acetonitrile with an initial turnover frequency of 295.3 at 90°C and pH of ~11.7 (Table 1, entry 2). A maximum turnover number of 934.2 is reached after 24 h with the comcomitant decrease of the turnover frequency to 38.9 turnovers/h (Fig. 2).

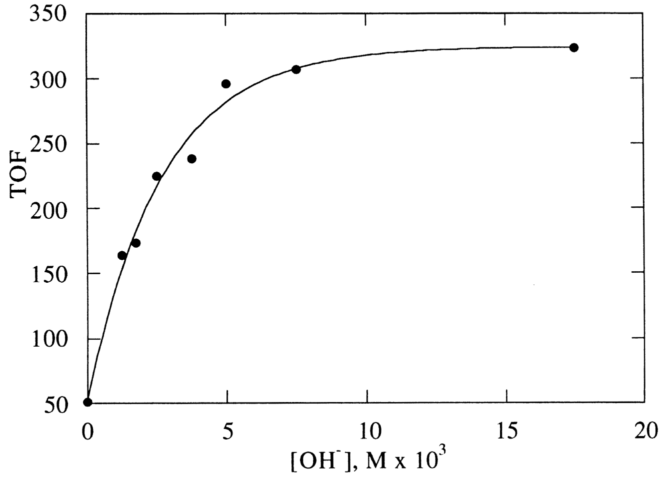

Figure 1. Dependence of the rate of acetonitrile hydration on hydroxide concentration at 90°C[7]

Table 1
Comparison of catalytic activities for hydrolysis of acetonitrile to acetamide at pH of ~11.7[7]

Run	Catalyst	Temp. (°C)	TOF[d]	Reference
1[a]	$[Rh(COD)Cl]_2$/TPPTS	80	207	this work
2[a]	$[Rh(COD)Cl]_2$/TPPTS	90	295.3	this work
3[b]	$[Rh(COD)Cl]_2/PPh_3$	80	60.5	this work
4[c]	$[Rh(COD)Cl]_2$	80	68.5	this work
5	$PdCl(OH)(bipy)(H_2O)$	76	29.4	6a
6	$IrH(CO)(TPPTS)_3$	100	5.7	6c
7	$[PtH(PMe_2OH)(PMe_2O)_2H]$	90	380	6d
8	$[PtH(H_2O)(PMe_3)_2][OH]$	78	178	6e
9	$[PtH(H_2O)(PEt_3)_2][OH]$	78	70	6e

a/ Acetonitrile (10 mL), water (10 mL), $[Rh(COD)Cl]_2$ (0.01 mmol), TPPTS (0.3 mmol) and NaOH (0.1 mmol).
b/ The hydration conditions are the same as in run 1 except that PPh_3 (0.3 mmol) was used in stead of TPPTS.
c/ Only $[Rh(COD)Cl]_2$ (0.01 mmol) was used as the catalytic system.
d/ TOF: turnover frequency (mol of acetamide/(mol of cat. hr).

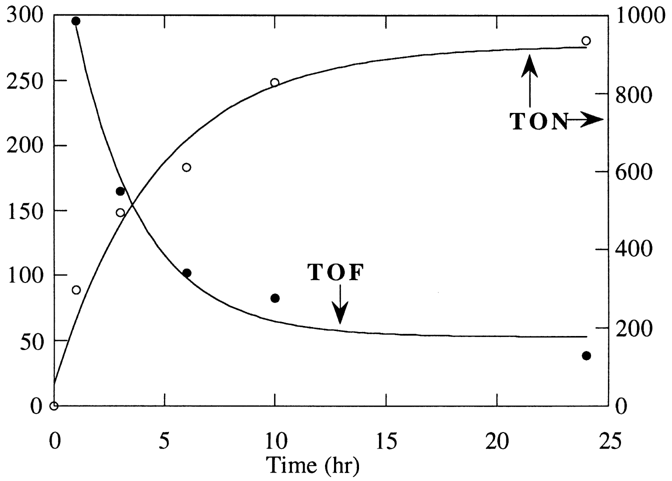

Figure 2. Time resolved-evolution of acetamide formation during the hydration of acetonitrile at 90°C and pH of ~11.7[7]

The rate of catalysis is temperature dependent (Table 2). $[Rh(COD)Cl]_2$/TPPTS was found to have superior reactivity at 25°C (31 turnovers/h) than the platinum system *trans*-$PtHCl(PMe_3)_2$/ NaOH.[6e] The activation enthalpie calculated from the Eyring plot (Fig. 3) was 8.58 kcal mol^{-1}.

An important aspect of the aqueous-phase catalysis is the possibility to separate the catalyst easily from the reaction medium and to recycle it in further experiments. Table 3 displays the results obtained for the hydration of acetonitrile after several consecutive runs with $[Rh(COD)Cl]_2$/TPPTS. A decrease in the catalytic activity was observed between each of the five recycling experiments. This decrease in activity is mainly attributed to the dissolution of rhodium complex in acetamide organic solutions which are slightly yellow. Indeed, we observed that $[Rh(COD)Cl]_2$/TPPTS is very soluble in molten acetamide. It is relevant to point out that no metallic rhodium formation was observed after the reactions and the aqueous phases remained as yellow solutions, indicating no decomposition of the catalyst. As has been previously demonstrated,[6g] the separation of acetamide from the catalyst by sublimation is expected to lead to the decomposition of the catalyst with a subsequent severe decrease of the catalytic activity during the catalyst recycling.

Table 2

Hydration of acetonitrile to acetamide catalyzed with $[Rh(COD)Cl]_2$/TPPTS at pH of ~11.7[7]

Temp. (°C)	25	60	70	80	90
TOF	31	93.4	157.5	207	295.3

The hydration mechanism is thought to involve an initial substitution of chloride by hydroxide on treatment of $[Rh(COD)Cl]_2$ with NaOH. Indeed, when $[Rh(COD)(OH)]_2$, prepared from $[Rh(COD)Cl]_2$ and KOH,[8] was used as a substitute for $[Rh(COD)Cl]_2$, identical catalytic activities were obtained.

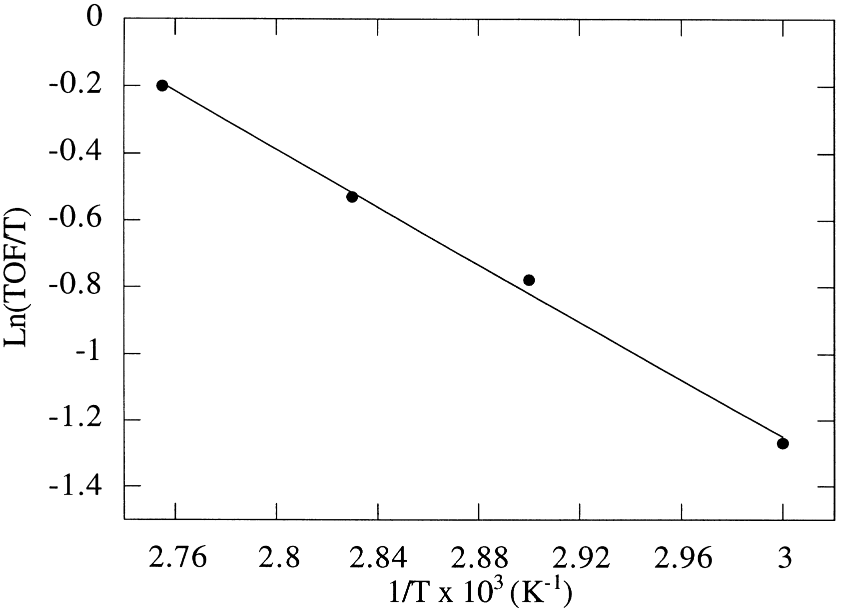

Figure 3. Eyring plot of temperature dependence of rate for the hydration of acetonitrile catalyzed by $[Rh(COD)Cl]_2$/ TPPTS

Table 3
Catalyst recycling for the hydration of acetonitrile to acetamide at 90°C and pH of ~11.7[a]

Cycle[b]	0	1	2	3	4	5
TOF	295.3	187	136	90	72	43

a/ Acetonitrile (10 mL), water (10 mL), $[Rh(COD)Cl]_2$ (0.01 mmol), TPPTS (0.3 mmol) and NaOH (0.1 mmol).[7]
b/ Number of catalyst recycles.

$[Rh(COD)Cl]_2$/TPPTS also catalyzes the hydration of water insoluble nitriles such as phenylacetonitrile and benzonitrile. Under the same catalytic conditions as for acetonitrile,[7] except that the amount of nitrile was reduced to 5 mmol, phenylacetonitrile and benzonitrile were completely converted to the corresponding amides after 24 h at 90°C and pH of ~11.7.

We are currently examining the scope of our catalytic system using various nitriles. Attempts to improve the catalytic activities and to study the hydration mechanism are in progress.

Acknowledgements

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7. Typical procedure for the hydration of acetonitrile: In a glass liner of a 45 mL autoclave and under an atmosphere of nitrogen, $[Rh(COD)Cl]_2$ (0.01 mmol) and TPPTS (0.3 mmol) were dissolved in 10 mL of degassed water containing the desired amount of NaOH, at room temperature. Then acetonitrile (10 mL) degassed with N_2 was introduced. The autoclave was flushed several times with 80 psi of N_2 then placed in an oil bath at the desired temperature for the required reaction time. The autoclave was cooled to room temperature then the mixture was evaporated to dryness. The residue afforded acetamide on extraction with acetone. Recycling experiments: The rhodium-containing residue obtained after removal of solvents and acetamide was re-used with a fresh charge of degassed acetonitrile (10 mL) and water (10 mL). In the case of benzonitrile and phenylacetonitrile, ethyl acetate was added to the reaction mixture. The organic phase was separated from the aqueous one, dried ($MgSO_4$), and then analyzed by ^1H NMR after the solvent was evaporated.
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